# TREATING CONTAMINATED WATER: PREDICTING REACTIVITIES OF AQUEOUS ORGANIC CONTAMINANTS WITH HYDRATED ELECTRONS, AND DEVELOPMENT OF A BIOGARDEN TO MANAGE GREYWATER DISCHARGE IN MONTEVERDE, COSTA RICA 

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TREATING CONTAMINATED WATER: PREDICTING REACTIVITIES OF AQUEOUS ORGANIC CONTAMINANTS WITH HYDRATED ELECTRONS, AND DEVELOPMENT OF A BIOGARDEN TO MANAGE GREYWATER DISCHARGE IN MONTEVERDE, COSTA RICA

By<br>Rose C. Daily

## A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

In Environmental Engineering

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This dissertation has been approved in partial fulfillment of the requirements for the Degree of DOCTOR OF PHILOSOPHY in Environmental Engineering.

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## Author Contribution Statement

Chapter 2: Reactivities of Hydrated Electrons with Organic Compounds in Aqueous-Phase Advanced Reduction Processes is published in Environmental Science: Water Research \& Technology. The complete citation is listed below. The first author carried out all of the density functional theory calculations and analysis, developed all LFERs, conducted the Taft constant validation, and conducted the PFAS reactivity predictions. The second author developed the unsteady state kinetic model. Both authors worked on mechanism elucidation. Both authors contributed to the writing and review of the manuscript.

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## List of Abbreviations

| AOP | Advanced oxidation process |
| :---: | :---: |
| AORP | Advanced oxidation reduction process |
| ARP | Advanced reduction process |
| BOD | Biological oxygen demand |
| CEC | Centro Educacion Creativa |
| CMFR | Completely mixed flow reactor |
| COD | Chemical oxygen demand |
| DFT | Density functional theory |
| DO | Dissolved oxygen |
| $\mathrm{e}^{-}{ }_{\text {aq }}$ | Solvated electron |
| $E^{\circ}{ }_{\text {red,aq }}$ | One electron reduction potential |
| FASA | Perfluoroalkane sulfonamides |
| FOGs | Fats, oils, grease |
| FTAC | Fluorotelomer acrylates |
| FTCA | Fluorotelomer carboxylates |
| FTOH | Fluorotelomer alcohols |
| GCM | Group contribution method |
| GCMe | Group contribution method for the solvated electron |
| HDPE | High density polyethylene |
| HSSF | Horizontal sub-surface flow |
| LFER | Linear free energy relationship |
| LUMO | Lowest unoccupied molecular orbital |
| MVI | Monteverde Institute |
| OF | Objective function |


| PASC | Perfluoroalkane sulfonyl chlorides |
| :--- | :--- |
| PFAS | Per- and polyfluoroalkyl substances |
| PFCA | Polyfluorocarboxylate |
| PFECA | Perfluoroalkyl ether carboxylates |
| PFPA | Perfluoroalkyl phosphonic acid |
| PFPeA | Perfluoropentanoic acid |
| PFPiA | Perfluoroalkyl phosphinates |
| PFR | Plug flow reactor |
| PFSA | Perfluoroalkane sulfonates |
| QSAR | Quantitative structure activity relationship |
| SD | Sample deviation |
| SDG | Sustainable development goal |
| SFAene | Semifluorinated alkenes |
| SHE | Standard hydrogen electrode |
| SMD | Solvation model density |
| SOMO | Singly occupied molecular orbital |
| TDS | Total dissolved solids |
| TSS | Total suspended solids |
| UCR | University of Costa Rica |
| UN | United Nations |
| United States Environmental Protection Agency |  |


#### Abstract

Advanced reduction processes (ARPs) that generate highly reactive solvated electrons ( $\mathrm{e}^{-}$ aq) are a promising method for the destruction of conventional and emerging aqueous organic contaminants. While there is a large database of contaminant reactivity with $\mathrm{e}^{-}{ }_{\text {aq }}$ in the literature, there is little information on the detailed elementary mechanisms for reduction of multifunctional group compounds and the impact of those functional groups on reactivity. As it is difficult to determine specific mechanisms through experiments and time consuming to measure reactivity, the development of computational approaches to elucidate mechanisms and predict reactivity is becoming increasingly important. In chapter 2, I use density functional theory to calculate the aqueous-phase one electron reduction potential ( $E_{\text {red,aq }}^{\circ}$ ) of 251 diverse conventional organic compounds. I then use $E_{\text {red,aq }}^{\circ}$ to investigate the occurrence of three possible reduction mechanisms (association, concerted cleavage, stepwise cleavage) at all reactive sites and develop linear free energy relationships (LFERs) between $E_{\text {red,aq }}^{\circ}$ and the experimentally measured rate constant. Using the LFERs, I predict the reactivity of the Environmental Protection Agency per- and polyfluoroalkyl substance (PFAS) priority subset (EPA-75). In chapter 3, I develop group contribution methods (GCMes) for each reduction mechanism for 262 aliphatic and aromatic organic contaminants. The GCMes effectively predict compound reactivity through chemical structure fragmentation. The LFER and GCMe tools can be used to screen thousands of organic contaminants for degradability by homogeneous and heterogeneous ARPs, along with prioritizing them for further study.

Although Costa Rica has established water discharge laws, a lack of enforcement and resources has resulted in greater than $95 \%$ of all greywater discharged to the environment untreated, leading to eutrophication and an increased risk to public health. The Monteverde Zone, located at the top of the Guacimal watershed, is a key player in this issue, as greywater discharged in this zone flows downstream, impacting a large number of communities. While centralized water treatment is currently not feasible in this developing country, biogardens are an affordable, decentralized, nature-based solution to Costa Rica's greywater problem that utilize filtration techniques, plant uptake, and microbial degradation to effectively treat greywater. In chapter 4, I design and construct a horizontal sub-surface flow biogarden system for the Centro Educacion Creativa K-12 school, located in the Monteverde Zone, that effectively treats the campus' greywater to compliance levels. In addition to engineering a natural and effective treatment system, I use the biogarden as a local pilot project to educate the Monteverde community on the greywater issue and biogarden development.


## 1 Global Water Challenges

### 1.1 Understanding Water Treatment Challenges in Developed vs. Developing Countries and Exploring Approaches for Solutions

Water. The source of all life on planet earth. The most essential liquid found in our global ecosystem. Without water, life as we know it could not be sustained. Water is distributed throughout the world by ocean currents, the flow of river, precipitation, and transpiration, and is continuously replenished through the hydrological cycle ${ }^{1,2}$. For centuries, humans have successfully harnessed water resources for hydration, hygiene, cooking, agriculture, energy generation, and manufacturing. While the total amount of freshwater available on Earth's surface has remained relatively static throughout history, human use of freshwater has dramatically increased. Specifically, over the past century, human water use has increased six-fold as a result of exponential population growth, increased agriculture and animal farming, and expanded industrialization ${ }^{3,4}$. This intensification of water use globally has been accompanied by a surge in wastewater production ${ }^{3,5}$. Although we live in a modernized world, a significant amount of this wastewater receives little to no treatment, leading to pollution of drinking water supplies, eutrophication, human health issues, and the accumulation of contaminants in our environment ${ }^{6-8}$. Freshwater is a basic need for life, yet approximately one-third of our global population does not have access to safe drinking water and two-thirds lack access to safely managed water sanitation facilities ${ }^{9}$.

Water touches all corners of our earth through the hydrologic cycle; however, its distribution is uneven, causing an abundance of issues beyond water treatment. Water challenges can be broadly broken down into the following four categories: quality, quantity, distribution, and scarcity ${ }^{3,10,11}$. Collectively overcoming these challenges will be one of the biggest tests of this century. In 2015, at the United Nation's (UN) Summit, world leaders adopted the UN's 17 Sustainable Development Goals (SDGs) which are a universal call to action to improve the health and livelihood of all humans everywhere and the global environment ${ }^{12}$. SDG goal 6 specifically addresses the global water challenge (i.e. clean water and sanitation for all), however, water is woven into all 17 goals and plays an essential role in their achievement. Variations in natural fresh water supply due to geographical location and climate has resulted in water challenges looking different from one region to another, and thus a one-size fits all solution is not appropriate. Water-related barriers among regions will come in all forms, from lack of political will and funding, to insufficient resources, limited support, and disordered priorities.

Developed, wealthy nations located in water-rich norther regions, such as the United States and Canada, have conquered wastewater collection and treatment by implementing centralized water treatment plants that utilize various technologies to destroy contaminants, extensive sewer systems, and storm water management ${ }^{3,13,14}$. In addition, effective water distribution, redirection, and plumbing systems have allowed these countries to nearly eliminate drinking water scarcity issues. However, even with these promising systems in place, these nations are struggling to manage the reality of emerging contaminants that
threaten the quality of ground and surface water supplies ${ }^{13,15-17}$. Sourced from advancements in chemical-based pharmaceuticals, surfactants, manufacturing, pesticides, cleaners, flame retardants, and personal care products, the list of emerging contaminants grows daily and includes endocrine disrupting chemicals, carcinogens, and neuro-, eco-, and cyto-toxins ${ }^{18}$. Many of these contaminants have the ability to travel through water supplies, accumulate in the environment, and negatively impact the health of people, flora, and fauna ${ }^{15,19}$. Existing water treatment systems in these nations have proven to be ineffective at destroying the majority of emerging contaminants ${ }^{20}$, and thus time, money, and resources are currently being spent on scientists and researchers who are racing to find new and novel approaches for emerging contaminant destruction.

Meanwhile, a handful of developing countries, such as those in Central and South America, have successfully harnessed their geography, climates, and water supplies to produce an abundance of clean, green hydropower ${ }^{21-25}$. However, these countries struggle to provide basic drinking water supplies and sanitation services to their growing populations ${ }^{3,26}$. Centralized water treatment and sewer systems are essentially nonexistent in these countries, which often results in the unavoidable mixing of drinking water sources with discharged wastewater, leading to human health decline and environmental issues. Another major challenge faced by these regions is water scarcity. Latin America possesses approximately $30 \%{ }^{26}$ of the earth's freshwater supply, yet over a quarter of this region's population reside in areas classified as water scarce ${ }^{27}$. Leaders of these nations are working tirelessly to improve water sharing and distribution, but are often met with barriers related to financial support and a lack of resources.

Addressing this abundance of widespread and diverse water issues requires cooperation and a variety of carefully calculated approaches at different levels. A regional approach to emerging contaminants should be taken in developed countries because of the many stakeholders at play in this issue, including policy makers, chemical manufacturers, consumers, and municipalities ${ }^{3}$. An end-of-pipe approach is necessary to control, manage, and treat emerging contaminants that have already made their way into the environment, while a process-integrated approach should be taken to prevent the creation and discharge of new contaminants ${ }^{3}$. It is vital that all stakeholders across the region cooperate in these efforts because of the general mobility and toxicity of emerging contaminants. In developing countries that suffer from a lack of access to safe drinking water and sanitation facilities, a regional approach is less than ideal: quick action is needed yet is not possible because governmental action is hindered by non-accessible resources and funds that are necessary for large scale water treatment projects ${ }^{28,29}$. Rather, a local approach should be taken by developing countries to manage wastewater discharge within individual communities in a decentralized way that is effective, affordable, accessible to anyone, and can be integrated into the natural environment ${ }^{3}$. An additional and important component of the local approach in developing countries is education. Providing communities with a deeper knowledge of their water issue, how it impacts them and their neighbors, and best practices for management, will inspire and empower them to take action locally. Studies have demonstrated the importance of local pilot projects to serve as model educational examples and, when successful, can lead to an influx of funding and technical expertise ${ }^{30}$. A final, valuable component of the local approach, especially in developing countries, is
to develop solutions through a forward-facing lens. These nations can learn from the mistakes of their developed counterparts and understand in advance the implications of industrialization. Solutions to water scarcity and quality can be applied in a way that anticipates and prepares for future water challenges, such as widespread emerging contaminants, so these nations can be ready to take action long before remediation is necessary.

This dissertation explores and develops two different solutions that each address a select water challenge - one faced by a developed country and one faced by a developing country. One sub challenge to the expanding emerging contaminant issue in developed countries is determining whether novel treatment technologies will effectively degrade the vast number of structurally diverse compounds belonging to the emerging contaminant class. Investigating chemical reactivity is a promising means to determine the successful application of a technology, however, traditional reactivity investigations are too slow and costly to keep up with the ever-growing list of contaminants. Thus, a national approach is taken to overcome this sub-challenge and ensure emerging contaminants can quickly and accurately be screened for treatment via a selected treatment technology. The advanced reduction process (ARP) was selected as the novel treatment technology of interest (more details in section 1.2). Two tools, created with the user in mind and grounded in molecular chemistry, are developed that can predict reactivity of an aqueous organic contaminant in ARP using thermodynamic parameters and structural fragmentation, respectively. The tools can be used by policy makers and chemical manufacturers alike to regulate the production and discharge of contaminants, and to manufacture new chemicals with a fate less detrimental to the earth. For the developing country, a local approach is taken within a small town to manage their unchecked wastewater discharge and improve the health of the community. An affordable, decentralized, nature-based system is designed and constructed to effectively treat a portion of the community's wastewater and is accompanied by comprehensive community education and strategies for effective knowledge sharing.

### 1.2 Advanced Reduction Process

Advanced oxidation and reduction processes (AORPs) are a set of powerful treatment technologies that are advantageous relative to removal technologies because of their ability to fully break down a wide variety of aqueous organic contaminants. Unlike traditional oxidation and reduction, which occurs when a chemical species loses or gains an electron, respectively, AORP generates highly reactive and non-selective aqueous species, typically radicals, that effectively degrade complex organic contaminants into non-harmful byproducts ${ }^{31}$. Advanced oxidation processes (AOPs), a type of specialized oxidation process that fall under the AORP umbrella, have successfully been utilized to destroy many conventional emerging contaminants through the generation of highly reactive oxidants such as the hydroxyl radical $\left(\mathrm{HO}^{\circ}, \mathrm{E}^{\circ}=2.74 \mathrm{~V}^{32}\right)$ and sulfate radical $\left(\mathrm{SO}_{4}^{-\bullet}, \mathrm{E}^{\circ}=2.6 \mathrm{~V}^{33}\right)$. Similarly, ARPs that generate strong reductants, such as the solvated electron $\left(\mathrm{e}^{-}{ }_{\mathrm{aq}}, \mathrm{E}^{\circ}=-\right.$ $2.9 \mathrm{~V})^{32,34,35}$, carboxyl anion radical $\left(\mathrm{CO}_{2}{ }^{\bullet-}\right)^{36}$, and the hydrogen atom $\left(\mathrm{H}^{\bullet}\right)^{37}$, have successfully been applied to the destruction of perchlorate, alkyl halides, and the emerging class of contaminants known as per- and polyfluoroalkyl substances (PFASs) ${ }^{38}$.

The radicals mentioned in the previous paragraph and many others that are generated in AORP technology naturally occur in the environment, making this treatment technology a re-creation of a natural degradation process that is manipulated in an engineered setting for the destruction of aqueous pollutants and contaminants. Radicals are generated in environmental waters through many natural processes, including photolysis of water molecules via solar radiation (particularly prevalent near water surfaces) ${ }^{39}$, enzymatic reactions ${ }^{39}$, redox cycling of certain molecules ${ }^{40}$, and transition metal catalysis ${ }^{40}$. Concentrations of radicals in the environment are typically extremely low and depend on the environmental conditions, such as water pH , temperature, amount of sunlight available, and constituents present ${ }^{40}$.

Along with low concentrations, the lifetime of radicals in water is quite short, mainly due to their high reactivity. For example, $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ has a lifetime in the range of only microseconds to milliseconds ${ }^{41}$. However, the lifetime of a given species will vary in response to factors, such as reactivity, concentration, temperature, solvent properties, and presence of scavengers. The reaction kinetics of radicals with aqueous species and their respective concentrations govern the lifetime of this reactive species ${ }^{42}$. Low concentrations of reactants accompanied by slow kinetics leads to an extended radical lifetime, while the opposite scenario shortens the lifetime. The range of water temperatures observed in environmental settings can significantly impact kinetics. Higher water temperatures generally increase reaction rates, leading to a shorter radical lifetime ${ }^{43}$. However, water temperature also impacts solubility, liquid density, mobility, and partitioning processes, suggesting that impacts due to temperature can be far more complex. Depending on the water setting, scavengers, which are species that quickly react with radicals, effectively consuming them, are often the biggest dictator of radical lifetime ${ }^{44}$. Common scavengers of radicals in natural waters include oxygen $\left(\mathrm{O}_{2}\right)$, carbon dioxide $\left(\mathrm{CO}_{2}\right)$, nitrogen compounds $\left(\mathrm{NO}_{3}^{-}, \mathrm{NO}_{2}^{-}\right)$, metal ions, and some organic compounds ${ }^{45}$.

Within an engineered setting, the aforementioned factors still play a significant role in radical lifetime, however, they can more easily be controlled and manipulated to create an ideal oxidation or reduction environment. AORP engineered systems can be employed in a homogeneous ${ }^{46}$ setting, in which the reactive species are uniformly distributed throughout the liquid phase, or a heterogeneous ${ }^{45}$ setting, in which the reaction occurs at the interface of two phases (i.e. a solid and a liquid phase). A common homogeneous application is the use of a UV photoreactor to photolyze a chemical reagent, such as hydrogen peroxide $\left(\mathrm{H}_{2} \mathrm{O}_{2}\right)$ or persulfate $\left(\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right)$, to generate radicals, such as $\mathrm{HO}^{*}$ or $\mathrm{SO}_{4}{ }^{-}$ , respectively ${ }^{47}$. Electrochemical cells are a common heterogeneous application that facilitates the generation of radicals through electrochemical reactions that are catalyzed by metal oxide-based electrodes. The selection of a homogeneous or heterogeneous application and the desirable radical(s) to be generated depends on many factors such as the properties of the contaminant, treatment objective, and engineering considerations (cost, energy usage, etc.).

Radical species selection is often based on reactivity with the contaminants, which can be determined through experiments and, more recently, predictive tools. Reactivities of reactive radical species in AOPs have been actively studied and some predictive
approaches ${ }^{48}$ have been reported in the literature, however, the same is not true for solvated-electron-based ARPs. Few studies have holistically focused on the reactivities of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ in ARPs and the specific mechanisms of reduction. We have chosen to focus our efforts on solvated-electron-based ARPs to develop structure-dependent reactivity investigations in $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ ARP systems. In this study, we develop two computer-based tools that can estimate the reactivities of $\mathrm{e}^{-}$aq with aliphatic and aromatic organic contaminants in aqueous-based ARP.

### 1.3 Overview of Dissertation Chapters

Beginning first with the regional approach to the emerging contaminant issues faced by developed countries, chapters 2 and 3 work to address the question: can computational tools be used in place of experimental approaches to accurately predict the reactivity of conventional and emerging aqueous organic contaminants with solvated electrons? We begin to explore this question in chapter 2 by compiling a foundational dataset of structurally diverse aliphatic compounds, including a subset from the emerging class of per- and polyfluoroalkyl substances (PFAS) contaminants. Using the density functional theory (DFT) computational approach, we calculate the one electron reduction potential, $E^{\circ}{ }_{\text {red,aq }}$, for each compound in our dataset at all possible attacking sites and for all possible reduction mechanisms (i.e. association, concerted cleavage, stepwise cleavage). This vital step allowed us to build a large, representative database containing greater than 1,400 data entries that describe the reducibility of every single site of a large and diverse group of compounds. Upon this foundation, we elucidate the reduction mechanisms for all compounds, develop our linear free energy relationships (LFERs) based on the relationship between a kinetic parameter, second-order reactivity, and a thermodynamic parameter, one electron reduction potential, and validate the scientific meaning of our computed $E^{\circ}$ red,aq values using correlations with the Taft constants. Using our LFERs, we predict the reactivity of a representative group of emerging PFAS contaminants with solvated electrons ( $\mathrm{e}^{-} \mathrm{aq}$ ).

One limitation of our proposed LFERs is that $E^{\circ}{ }_{\text {red,aq }}$ must be known (either measured experimentally or calculated via DFT) in order to predict reactivity of a compound with $\mathrm{e}^{-}$ aq and elucidate reduction mechanisms. While there is readily available $E^{\circ}{ }_{\text {red,aq }}$ data in the literature for conventional compounds, this data is often lacking for emerging contaminants. Thus, we are eager to develop a second computational tool that can accurately predict reactivity of contaminants with $\mathrm{e}^{-}$aq in the absence of thermodynamic and molecular descriptor data. In chapter 3, we build upon the foundation we developed in chapter 2 to generate group contribution methods (GCMs) that predict reactivity based solely on chemical structure fragmentation. With no chemical or molecular descriptors necessary, GCMs are highly attractive tools that quickly and accurately predict reactivity based on chemical structure and the relationship between reactive sites and neighboring functional groups. Note that in both chapters 2 and 3, we predict second-order rate constants between organic contaminants and $\mathrm{e}^{-}$aq which actually represent estimates of reactivity with their associated uncertainties attributed to the limitations of the tools we developed.

The results of chapters 2 and 3 make three important contributions. First, the investigation of various single electron transfer mechanisms via $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ sheds light on the relative contributions to overall second-order reaction rates of conventional organic contaminants in an engineered aqueous ARP environment (here an engineered environment refers to one in which the temperature, ionic strength, pH , and concentrations of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ are controlled). This newfound chemical reaction information paves the way for further research into this topic, such as investigation of full reduction pathways of organic contaminants in ARP, reduction byproduct formation, and the impact of real water solutions (i.e. multiple unique species present) on reactivity.

Additionally, the LFER and GCMe tools allow for the estimation of compound reactivity (i.e. second-order rate constants) with $\mathrm{e}^{-}{ }_{\text {aq }}$ without the need for costly and time-consuming experiments. This is especially useful for screening large groups of aqueous organic contaminant for treatment via ARP. Screening results can then be used to prioritize contaminants for treatment by various processes and for further study. Note that the reactivity estimates generated by these tools are only as accurate as the data with which they were built. Pulse-radiolysis, the standard method to measure experimental secondorder rate constants, is associated with uncertainty between a factor of 2 and 5. In addition, each computational tool has its own associated uncertainty, such as the GCMe considering steric hinderance and solvation effects only implicitly (rather than explicitly) through the consideration of the Arrhenius frequency factors and activation energy. Further details on this and the degree of uncertainty associated with these tools can be found in the proceeding chapters.

Lastly, those outside of the scientific community, specifically policy makers and chemical manufacturers, will find value in these tools. Policy makers can use the prioritization and screening results to regulate the production and discharge of new and existing contaminants. For example, the Environmental Protection Agency (EPA), the national environmentally focused governing body of the United States, is responsible for protecting public health through the regulation of the nation's drinking water supply via the Safe Drinking Water Act. When the EPA sets a maximum contaminant level (MCL, enforceable) or health advisory level (HAL, non-enforceable) for an aqueous contaminant, they also need to provide a treatment technique (TT) or guidance on treatment methods for municipalities, respectively. With the use of the screening tools, the EPA can confidently recommend (or not recommend) ARP as an effective TT. This treatment guidance is then passed on to state governments and municipalities who will play an active role in regulating, removing, and treating the aqueous contaminants of concern within their jurisdiction. Furthermore, U.S. chemical manufacturers, such as DuPont and DOW, can use the tools to direct their efforts of manufacturing new chemicals with a fate less detrimental to the environment and humans. The GCMe tool will be especially useful for chemical manufacturers as the reactivity of a compound can be estimated solely by its chemical structure, thus making it appropriate for use in the early stages of chemical development. When a new chemical is being developed, future contamination issues can be avoided if the chemical is designed with an effective treatment method in mind. AORP is becoming increasingly popular in contaminant degradation efforts and thus it is important for chemical manufacturers to consider reducibility via $\mathrm{e}^{-}$aq when creating new
chemicals. Regarding distribution of this information, both computational tools developed as part of this dissertation are published in an open-access format online and are available to all. It is our hope that the research sectors of political institutions and chemical manufacturers find and utilize our tools and the other predictive tools available online for other treatment processes.

In Chapter 4, we move away from investigating molecules, bonds, and chemical reactions, and expand our view of water treatment to include people, cultures, and communities. We shift our focus to viewing water treatment challenges in developing countries through a local lens and ask ourselves: How can we effectively manage greywater discharge in Costa Rica in a way that prioritizes the environment and involves community education? This final chapter explores nature-based engineering solutions for decentralized greywater treatment in a developing community in Costa Rica. Similar to water treatment at the chemical level, there are many factors at play in community-level water treatment: government and policy, cultural perceptions, values, and norms, the state of the economy, available resources, the environment, and climate change. We begin by investigating each of these factors individually in order to understand the full picture of the greywater discharge issue faced by Costa Rica. Once we have an understanding of the full picture, we move into the design and construction of a biogarden which harnesses the symbiotic relationship between plants, substrate, and microbial communities to effectively treat greywater in a natural and decentralized setting. To complement our biogarden system, we create a series of tools and resources to empower community members with the knowledge needed to fully understand the greywater issue and natural treatment solutions.

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## 2 Reactivities of Hydrated Electrons with Organic Compounds in Aqueous-Phase Advanced Reduction Processes

### 2.1 Introduction

Free radical-based technologies are attractive and promising processes for destroying a wide variety of organic contaminants. Advanced oxidation processes (AOPs) that generate highly reactive oxygenated radical species (e.g., hydroxyl radicals) ${ }^{1,2}$ and other reactive radicals (e.g., chlorine- ${ }^{-3,4}$, bromine- ${ }^{5}$ and nitrogen-derived radicals ${ }^{6,7}$ and carbonate radicals ${ }^{8}$ ) at ambient temperature and atmospheric pressure have been proven to degrade reduced forms of organic contaminants in water at full-scale treatment plants. Advanced reduction processes (ARPs) that generate reactive electrons in homogeneous solution ${ }^{9,10}$ and heterogeneous electrochemical ${ }^{11-13}$ or catalytic ${ }^{14}$ processes are effective in degrading the oxidized forms of organic and inorganic contaminants. Homogeneous, electrochemical, and a combination of both ARPs have been successfully applied for the degradation of conventional organic contaminants such as alkyl halides and emerging groups of contaminants such as per- and polyfluorinated alkyl substances (PFASs) ${ }^{15}$.

While the reactivities of reactive radical species in AOPs have been actively studied and some predictive approaches have been reported in the literature ${ }^{16}$, few studies have holistically focused on the reactivities of electrons in aqueous-phase ARPs. The reactivities of aqueous-phase hydrated electrons, $\mathrm{e}^{-}$aq, with a wide variety of individual organic compounds have been experimentally measured, and the second-order rate constants, $k_{\text {exp }}$, have been reported and compiled in the database ${ }^{17}$ (Figure 2.1). However, few studies have developed a predictive tool for the $k_{\text {exp }}$ values of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ due to a lack of mechanistic understanding of the reactivities with organic compounds. ${ }^{18,19}$ Nucleophilic electrons react at the electron-deficient sites of organic compounds. The three major reaction mechanisms include (1) association with the $\pi$ bond of a double bond; (2) concerted dissociative cleavage of a carbon halogen ( $\mathrm{C}-\mathrm{X}$ where $\mathrm{X}=\mathrm{F}, \mathrm{Cl}, \mathrm{Br}$ or I ) bond of haloalkanes or carbonnitrogen ( $\mathrm{C}-\mathrm{N}$ ) bond; and (3) stepwise cleavage of a C-X bond of haloalkanes and haloalkenes, a sulfur-sulfur (S-S) bond or a carbon-sulfur (C-S) bond of sulfides or disulfides. ${ }^{20}$ Each reaction mechanism depends on the molecular structures and functional groups present in the same molecule. The overall reactivities with $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ are reduced by electron-donating functional groups and increased by electron-withdrawing functional groups. However, the detailed mechanisms of multiple functional group compounds and the effect of these functional groups on the major reactivities have not been elucidated because of the difficulties in experimental investigations.


Figure 2.1. A box and whisker plot of experimentally measured second-order rate constants, $k_{\text {exp }}$, of structurally diverse aliphatic compounds with solvated electrons. (Note: refer to Figure A1 in Appendix A for information on how to read a box and whisker plot, and the meaning of the boxes, whiskers, and midpoints).

The use of quantum mechanics-based methods such as ab initio calculations or density functional theory (DFT) can complement experimental observations of chemical reactivities and provide mechanistic insight into reaction mechanisms. Several DFT-based methods were used to investigate the thermodynamics and kinetics of electron-induced reactions with halogenated compounds such as polychlorinated ethylenes ${ }^{21,22}$, polybrominated electrophiles ${ }^{23}$, and PFAS ${ }^{24-26}$. The dissociation and reductive cleavage of a given molecule were investigated based on the optimized electronic structures, bond dissociation energies and reduction potentials of the corresponding bond. The $k_{\text {exp }}$ values represent the overall reactivities, and thus, the elementary reaction mechanisms of the overall reaction cannot be known. Calculating the one-electron reduction potential ( $E_{\text {red,aq }}^{\circ}$, V ) in the aqueous phase of each component in a given molecule can provide information about most reactive sites and help determine the rate-determining reaction mechanism with electrons.

In this study, we use DFT to calculate the $E_{\text {red,aq }}^{\circ}$ values of conventional organic compounds with a wide variety of functional groups to determine the linear free energy relationships (LFERs) with the experimentally measured rate constants of $\mathrm{e}^{-}$aq. In addition, we use the 75 priority PFAS subset from the U.S. EPA ${ }^{27}$ and calculate the $E_{\text {red,aq }}^{\circ}$ values of all possible elementary reactions of each PFAS to determine its dominant reaction mechanism and reactive sites. The determined LFERs of conventional organic compounds are used to
predict the reactivities of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ with PFASs, which can be used as a screening tool for thousands of PFASs for electron-induced degradability. Figure 2.2 demonstrates the flowchart of methods used in this study from the determination of LFERs for conventional organic compounds to the prediction of $k_{\text {chem }}$ values for PFAS. While we demonstrate the prediction of $k_{\text {exp }}$ values for $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ in the homogeneous reduction processes, the reactivities of electrons via direct electron transfer on a heterogeneous-electrode can be extrapolated from the $\mathrm{e}^{-}$aq reactivities and the LFERs are useful for the heterogeneous processes.


Figure 2.2. Overall flowcharts of methodologies and logical steps.

### 2.2 Materials and Methods

### 2.2.1 Critical Data Evaluation

Experimentally measured second-order rate constants with the solvated electron ( $k_{\text {exp }}$ ) for 268 structurally diverse aliphatic compounds were obtained from the NIST database ${ }^{1}$ and compiled with the experimental conditions for the critical data evaluation in Table A3 in Appendix A. The statistical average of $k_{\exp }$ was adopted when multiple experimental values were reported for a given compound. All datapoints were investigated for experimental accuracy. Datapoints measured at an inadequate pH were removed from the dataset. All $k_{\text {exp }}$ values were corrected to an ionic strength of 0 M to ensure uniform experimental conditions ${ }^{2}$. The second-order reaction rate constant for the chemical reaction ( $k_{\mathrm{chem}}$ ) was calculated for each compound to eliminate diffusive effects. For reactions classified as diffusion limited ( $k_{\text {exp }}>$ diffusion limited rate constant $\left(k_{\mathrm{D}}\right)$ ), the $k_{\text {exp }}$ value was used in place of $k_{\text {chem }}$.

A thorough description of the procedure for correcting second-order rate constants for diffusive effects is found in our previous publication ${ }^{3}$. Experimentally measured secondorder rate constants for aqueous compounds ( $k_{\text {exp }}$ ) are made up of both the diffusion-limited rate constant ( $k_{\mathrm{D}}$ ) and the rate constant for the chemical reaction ( $k_{\mathrm{chem}}$ ), as shown in equation S1.

$$
\begin{equation*}
k_{\text {exp }}=\frac{k_{\mathrm{D}} k_{\mathrm{chem}}}{k_{\mathrm{D}}+k_{\text {chem }}} \tag{1}
\end{equation*}
$$

To eliminate the contribution of diffusive effects on the second-order rate constant, equation 1 was solved for $k_{\text {chem }}$. To determine $k_{\mathrm{D}}$ for a compound, the liquid phase diffusion coefficient $\left(D_{1}\right)$ of that compound needs to be calculated. The method to calculate $D_{1}$ varies depending on the charge state of the solute. For neutral compounds, the Hayduk-Laudie correlation ${ }^{4}$ as below

$$
\begin{equation*}
D_{1}=\frac{13.26 \times 10^{-5}}{\left(\mu_{\omega}\right)^{1.14}\left(V_{\mathrm{b}}\right)^{0.589}} \tag{2}
\end{equation*}
$$

where $\mu_{\omega}$ is the viscosity of water and $V_{\mathrm{b}}$ is the molar volume of the solute. For electrolyte compounds, the Nernst-Haskell correlation ${ }^{5}$ was used to calculate as below

$$
\begin{equation*}
D_{1}=\frac{R T\left[\left(\frac{1}{n_{+}}\right)+\left(\frac{1}{n_{-}}\right)\right]}{F^{2}\left[\left(\frac{1}{\lambda_{+}}\right)+\left(\frac{1}{\lambda_{-}}\right)\right]} \tag{3}
\end{equation*}
$$

where $R$ is the universal gas constant, $T$ is the absolute temperature in Kelvins, $F$ is Faraday's constant, $n_{+}$and $n$ - are the charge numbers of the cation and anion, respectively, and $\lambda_{+}$and $\lambda_{\text {- }}$ are the molar conductivities of the cation and anion, respectively. When molar conductivity values could not be found in the literature or databases, we assumed $k_{\text {exp }}=$ $k_{\text {chem }}$.

### 2.2.2 Reduction Mechanisms

Three major reaction mechanisms of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ include: (1) associative; (2) concerted dissociative; and, (3) stepwise dissociative mechanisms. In the associative mechanism, $\mathrm{e}^{-}$ aq reacts with the $\pi$ bond that can 'hold' an extra electron to form an anionic radical species ${ }^{20}$. Compounds containing carbonyl functional groups are examples of substances that undergo associative reactions:

$$
\begin{equation*}
\mathrm{RC}=\mathrm{O}+\mathrm{e}_{\mathrm{aq}}^{-} \rightarrow \mathrm{R}^{\circ} \mathrm{CO}^{-} \tag{4}
\end{equation*}
$$

Both concerted and stepwise mechanisms involve bond cleavage. In the concerted mechanism, single-electron transfer to a parent compound and bond cleavage occur simultaneously, as shown in equation 5. During the stepwise mechanism, the initial barrierless step of single-electron transfer results in the formation of an intermediate radical anion that has a longer lifetime than the bond vibration time (i.e., $\left.10^{-13} \mathrm{~s}\right)^{28}$. The intermediate radical anion then undergoes bond cleavage, as shown in equation 6 . The nonexistence of a radical anion is a sufficient condition for the concerted mechanism to
occur, but it is not a necessary condition. Thus, under the concerted mechanism, an intermediate radical anion may have a finite lifetime ${ }^{29}$.

$$
\begin{align*}
& \mathrm{RX}+\mathrm{e}_{\mathrm{aq}}^{-} \rightarrow \mathrm{R}^{\cdot}+\mathrm{X}^{-}  \tag{5}\\
& \mathrm{RX}^{-}+\mathrm{e}_{\mathrm{aq}}^{-} \rightarrow[\mathrm{RX}]^{--} \rightarrow \mathrm{R}^{\cdot}+\mathrm{X}^{-} \tag{6}
\end{align*}
$$

In general, it is suggested that compounds containing a $\sigma$ bond and/or a weak $\mathrm{C}-\mathrm{X}$ bond are reduced via a concerted mechanism, and compounds containing a $\pi$ bond (e.g., $\mathrm{C}=\mathrm{S}$, $\mathrm{S}=\mathrm{S}, \mathrm{NO}_{2}, \mathrm{CN}, \mathrm{C}=\mathrm{C}$ ), strong $\mathrm{C}-\mathrm{X}$ bonds (e.g., $\mathrm{C}-\mathrm{F}$ ), and/or electron withdrawing groups (e.g., $-\mathrm{F},-\mathrm{CN}, \mathrm{NO}_{2},-\mathrm{CO}$ ) are reduced via the stepwise mechanism. ${ }^{23,30}$ However, caution should be taken for compounds with strong electron withdrawing groups and halogenated alkenes because a concerted mechanism could possibly occur due to an unstable intermediate radical anion or the requirement of reduced reaction barriers. ${ }^{22,23}$

### 2.2.3 LFER Development

To determine which of these reduction mechanisms is the rate-determining step for a given molecule, we determined the LFER that relates the experimentally measured chemical reaction rate constant, $k_{\text {chem }}$, and the $E_{\text {red,aq }}^{\circ}$ values relative to the standard hydrogen electrode (SHE) through the relation described by equation 7. Assuming an elementary reaction proceeds by the same reaction mechanism, the log of the rate constant and the log of the equilibrium constant are linearly related. ${ }^{31}$ The natural $\log$ of the equilibrium constants has a linear relationship with the free energy reaction, $\Delta G^{\text {react }}{ }_{\text {aq }}$, which relates to the standard state reduction potential in equation 8 . Combining these two concepts enables the development of the LFER. Upon the calculation of the $\Delta E^{\circ}$ red,aq values, all possible $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ attacking sites for each compound were included, and the largest $E_{\text {red,aq }}^{\circ}$ value (i.e., the smallest free energy of formation) in a given molecule was used for the determination of the LFER. We determined the LFER for each reaction mechanism listed in equations 4-6 to investigate the correlation with $k_{\text {chem }}$ values.

$$
\begin{equation*}
\ln k_{\mathrm{chem}}=-\alpha E_{\mathrm{red}, \mathrm{aq}}^{\circ}+\beta \tag{7}
\end{equation*}
$$

In the above equation, $\alpha$ and $\beta$ are the coefficients that determine the slope representing the relationship between the reductive ability of the reaction site and the observed overall kinetics and the intercept representing the kinetics at the reference electrode, respectively. We argue that the LFER is a useful way to relate the kinetics (i.e., $k_{\text {chem }}$ values) with thermodynamic parameters (i.e., $E_{\text {red,aq }}^{\circ}$ values) and that determining the aqueous-phase free energies of activation, a parameter that drives the kinetics, for hundreds of reactions involving $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ is not practical for systematic investigation. Thus, we conducted potential energy surface scan to determine the reaction mechanism for a few compounds that may undergo more than one reaction mechanism described above.

For the associative and concerted reaction mechanisms, the $E_{\text {red,aq }}^{\circ}$ value was determined with equation 8 :

$$
\begin{equation*}
E_{\text {red,aq }}^{\circ}=-\left(\Delta G_{\mathrm{aq}}^{\text {react }} / n F\right)-E^{\circ}(\mathrm{SHE}) \tag{8}
\end{equation*}
$$

where $n$ is the number of electrons transferred, $F$ is Faraday's constant, and $E^{\circ}(\mathrm{SHE})=4.28$ V. Per the thermochemical (Born-Haber) cycle, $\Delta G_{\text {aq }}^{\text {react }}$, may be expressed as:

$$
\begin{equation*}
\Delta G_{\mathrm{aq}}^{\text {react }}=\Delta G_{\mathrm{gas}}^{\text {react }}+\Delta \Delta G_{\text {solv }}^{\text {react }} \tag{9}
\end{equation*}
$$

where $\Delta G_{\text {gas }}^{\text {react }}$ is the difference in the standard state gaseous phase Gibbs free energy of reaction between reactants and products and $\Delta \Delta G_{\text {solv }}^{\text {react }}$ is the difference in the standard state Gibbs free energy of solvation between reactants and products. All energies values were simulated at 298 K in this study.

Regarding the stepwise investigation, we calculated $E^{\circ}{ }_{\text {red,aq }}$ with equation $10^{26,32}$, which accounts for both the formation of the intermediate radical species and the resulting bond cleavage as an example of an RX bond ${ }^{26,32}$.

$$
\begin{equation*}
E_{\mathrm{red}, \mathrm{aq}}^{\circ}=\frac{1}{F} \times\left(-B D E+T \Delta S-\Delta \Delta G_{\mathrm{solv}}\right)+E_{\mathrm{x} \cdot \mathrm{x}-}^{\circ} \tag{10}
\end{equation*}
$$

where $B D E$ is the bond dissociation energy of the cleaved bond, $T$ is the absolute temperature in Kelvin, $\Delta S$ is the gaseous-phase entropy of the cleaved bond, $\Delta \Delta G_{\text {solv }}$ is the difference in solvation energy between the parent compound and the two radical products in equation 11, and $E^{\circ} \mathrm{X}^{\bullet} / \mathrm{X}$ - is the reduction potential of the cleaved aqueous atom.

$$
\begin{equation*}
\Delta \Delta G_{\text {solv }}=\Delta G_{\text {solv }}\left(\mathrm{R}^{*}\right)+\Delta G_{\text {solv }}\left(\mathrm{X}^{*}\right)-\Delta G_{\text {solv }}(\mathrm{RX}) \tag{11}
\end{equation*}
$$

The $B D E$ of the cleaved RX bond was calculated using the enthalpies $(H)$ of the parent compound and the two radical products produced upon cleavage (equation 12).

$$
\begin{equation*}
B D E=-\left[H(\mathrm{RX})-H\left(\mathrm{R}^{\bullet}\right)-H\left(\mathrm{X}^{*}\right)\right] \tag{12}
\end{equation*}
$$

To calculate the $E^{\circ}{ }_{\text {red,aq }}$ values for the determination of LFERs, single point energy calculations at the M06-2X functional ${ }^{33}$ and the Aug-cc-pVTZ basis set for all the mechanisms based on the optimized structures determined at M06-2X/cc-pVDZ or Aug-cc-pVTZ, unless detailed method was specified. We used M06-2X/LANL2DZ for compounds that contained iodine because the Dunning's basis set does not cover iodinated compounds. For PFASs, we used M06-2X with a combination of cc-pVDZ or Aug-ccpVTZ basis set. Table A1 in Appendix A shows the method and basis set used for the group of compounds. M06-2X is specifically designed for the accurate treatment of long-distance interaction and/or the stronger electron-acceptor properties of the $\mathrm{R}^{\bullet}$ fragments resulting from the dissociation of a C-R bond ${ }^{34}$, which makes it suitable for this study that investigates nucleophilic reactivity. The M06-2X functional was successfully applied for the reductive dissociation of polybrominated compounds. ${ }^{23}$ A continuum form of the
universal solvation model (SMD) ${ }^{35}$ was used in the aqueous-phase calculations to account for the impact of an aqueous environment. It is noted that we did not aim to obtain the absolute $E_{\text {red,aq }}^{\circ}$ values of each elementary reaction, as they are computationally prohibitive when obtaining highly accurate $\Delta G^{\text {react }}{ }_{\text {aq }}$ values for a number of compounds. Thus, we used M06-2X to obtain reliable relative $E_{\text {red,aq }}^{\circ}$ values so that we were able to relatively compare which reactive sites were dominant over other sites under the same reaction mechanism. The dominant reaction mechanism among the three major mechanisms was determined by the LFER with mechanistic insight into the reaction mechanisms, as the direct comparison of the $E_{\text {red,aq }}^{\circ}$ values obtained from equations 8 and 10 was not possible. The validation of the M06-2X method with various basis sets is provided in Table A2 in Appendix A. All DFT calculations were performed using Gaussian $16^{36}$ with the Michigan Tech highperformance cluster 'SUPERIOR' and homemade LINUX workstations.

### 2.3 Results and Discussion

### 2.3.1 Determination of Linear Free Energy Relationships

The critical data evaluation of $268 k_{\text {exp }}$ values (Figure 2.1 and Table A3 in Appendix A) in the literature selected $251 k_{\exp }$ values and calculated the chemical reaction rate constants by eliminating the diffusion contribution for the determination of LFERs (section 2.2.1). Figure 2.3 displays LFERs between the $k_{\text {chem }}$ values and our theoretically calculated $E_{\text {red,aq }}^{\circ}$ values for 251 organic compounds undergoing three major mechanisms: (a) associative, (b) concerted, and/or (c) stepwise. Table 2.1 summarizes all the data used to determine the LFERs. Tables A4 and A5 in Appendix A contains all the $E_{\text {red,aq }}^{\circ}$ values for all possible reactive sites in a given molecule for the three reaction mechanisms. Regarding the association, we determined the LFER to be $\ln k_{\text {chem }}=4.43 E_{\text {red,aq }}^{\circ}+31.76\left(\mathrm{r}^{2}=0.72, N=66\right.$, where $N$ is the number of compounds for the development of the LFER) (Figure 2.3a). When the carbon of the $\mathrm{C}=\mathrm{O}$ functional group bonds with $\mathrm{NH}_{2}$ or the OR functional group, the mesomeric effect of the - $\mathrm{CO}-\mathrm{NH}_{2}$ - or -CO-OR- functional group occurs and decreases the double-bond character of the $\mathrm{C}=\mathrm{O}$ functional group, creating new electrophilic centers with lower reactivity ${ }^{37}$. While we determined one unified LFER for associative mechanism with both $\mathrm{C}=\mathrm{O}$ of ketones, aldehydes and carboxylate groups (blue dots in Figure 2.3a) and O of carboxylic acids, alcohols, esters, and amides (red dots in Figure 2.3a), the functional groups affect the associative mechanism with O in a different way from those with $\mathrm{C}=\mathrm{O}$ functional group (see the next subsection). Compounds $17,33,45$, and 153 , whose $k_{\text {chem }}$ values are close to or exceed the diffusion limit ( $k_{\text {chem }}>2.5 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ ), were not included in either LFER. Compound 39, methyl trifluoroacetate, appears to be slightly off the LFER of the associative mechanism or that of the stepwise mechanism. Our investigation on the PES and spin density distribution supports the associative mechanism (see the detailed discussion in the reaction mechanism section below). Thus, we included this compound in the LFER of the associative mechanism. For the associative mechanism with the $\mathrm{C}=\mathrm{C}$ of alkenes, the LFER was determined to be $\ln k_{\text {chem }}=7.82 E_{\text {red,aq }}^{\circ}+41.25\left(\mathrm{r}^{2}=0.63, N=13\right)$ (Figure 2.3b). The reactions of the alkenes with $k_{\text {chem }}>5.3 \times 10^{9} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ were close to or exceeded the diffusion limit; therefore, the $k_{\text {chem }}$ values did not change with an increase in the $E_{\text {red,aq }}^{\circ}$ values. The sample deviation (SD) calculated with equation 13 was 0.084 for the associative mechanism and 0.13 for the associative mechanism with the $\mathrm{C}=\mathrm{C}$ functional
group. The SD values represent the statistical distribution of the experimental $k_{\mathrm{chem}}$ values from the predicted values, $k_{\text {predicted, }}$ within the normal distribution ${ }^{38}$.

$$
\begin{equation*}
\mathrm{SD}=\sqrt{\frac{1}{n-1} \sum_{i=1}^{n}\left(\frac{k_{\text {chem }, i}-k_{\text {predicted }, i}}{k_{\text {chem }, i}}\right)^{2}} \tag{13}
\end{equation*}
$$

For the concerted cleavage of the $\mathrm{C}-\mathrm{Cl}$ bond of haloalkanes and halocarboxylate, we determined the LFERs to be $\ln k_{\text {chem }}=5.66 E_{\text {red,aq }}^{\circ}+27.95\left(\mathrm{r}^{2}=0.73, N=19\right)$ and $\ln k_{\text {chem }}=$ $3.97 E_{\text {red,aq }}^{\circ}+28.92\left(r^{2}=0.99, N=4\right)$, respectively (Figure 2.3c). The SD values were 0.044 and 0.025 , respectively. All the $k_{\text {chem }}$ values of the haloalkane and halocarboxylate compounds that contain C-Br and C-I bonds were close to or exceeded the diffusion limit; therefore, we did not determine their LFERs. The presence of carboxylate functional groups impacted the $E_{\text {red,aq }}^{\circ}$ value of the cleavage of the $\mathrm{C}-\mathrm{Cl}$ bond in the halocarboxylates; thus, a different LFER was determined for the group of chlorinated halocarboxylates. The four chlorinated carboxylates also appeared to adhere to the LFER for stepwise mechanism. According to experimental works, the group of these compounds undergo both concerted and stepwise mechanisms ${ }^{21,22}$ and thus we keep these compounds in both LFERs. We also determined the LFER for the concerted cleavage of the C-N bond of alkyl ammonium $\left(\mathrm{RNH}_{3}{ }^{+}\right)$as $\ln k_{\mathrm{chem}}=4.92 E_{\text {red,aq }}^{\circ}+24.67\left(\mathrm{r}^{2}=0.98, \mathrm{~N}=7\right)($ Figure 2.3 c$)$ with the exception of tetramethylammonium (No. 166) and tetraethylammonium (No. 167), which contain a different base structure of $>\mathrm{N}^{+}-\mathrm{C}$. Additionally, we did not include compounds that contain oxygenated functional groups (No. 161, oxoethanaminium and No. 162, methoxyazanium) because of their dominant associative mechanism. The SD value was 0.051 .

For the stepwise mechanism, we determined the LFERs for compounds with (1) haloalkanes that contain CO functional groups (i.e., halocarboxylates, halooxygens and haloamides) or C-F bonds (fluorinated carboxylates), (2) haloalkenes, and (3) sulfides or disulfides for the stepwise mechanism to be the following: (1) $\ln k_{\text {chem }}=3.96 E_{\text {red,aq }}^{\circ}+40.29$ $\left(\mathrm{r}^{2}=0.69, N=22\right)$ or $\ln k_{\mathrm{chem}}=1.43 E_{\text {red,aq }}^{\circ}+22.58\left(\mathrm{r}^{2}=0.74, N=4\right)$, (2) $\ln k_{\mathrm{chem}}=10.36 E_{\text {red,aq }}^{\circ}$ $+77.25\left(\mathrm{r}^{2}=0.54, N=5\right)$, and (3) $\ln k_{\text {chem }}=4.45 E_{\text {red,aq }}^{\circ}+45.65\left(\mathrm{r}^{2}=0.57, N=8\right)$ (Figure 2.3d). Because of the high strength of a C-F bond, the slope of the LFER for fluorinated carboxylates is significantly smaller than that of other haloalkanes. The SD values were 0.048 for haloalkanes, 0.26 , for fluorinated carboxylates, 0.077 for haloalkenes, and 0.089 for disulfides. A detailed mechanistic discussion and prediction of PFAS are given below.



Figure 2.3. LFERs for the (a) associative mechanism with $\mathrm{C}=\mathrm{O}$ and O , (b) associative mechanism with $\mathrm{C}=\mathrm{C}$, (c) concerted mechanism, and (d) stepwise mechanism.

Table 2.1. $E_{\text {red,aq }}^{\circ}$ and $k_{\text {chem }}$ values of 251 organic compounds used to determine the LFERs. Compounds in regular font are for associative mechanism, those with underlines are for concerted mechanism, and those in italic are for stepwise mechanism.

| Class | No. | Name | Chemical Formula | $\begin{aligned} & \hline \Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \\ & \hline \end{aligned}$ | $\begin{gathered} E_{\text {red }}^{\circ} \\ (\mathrm{V} \text { vS SHE }) \end{gathered}$ | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | $\begin{gathered} \text { Ref. for } \\ k_{\text {exp }} \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Alkane | 1 | Methane | $\mathrm{CH}_{4}$ | 25.97 | -5.41 | $1.00 \times 10^{7}$ | 39 |
|  | 2 | Propane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3}$ | 23.74 | -5.31 | $2.10 \times 10^{6}$ | 40 |
|  | 3 | Butane | $\mathrm{C}_{4} \mathrm{H}_{10}$ | 22.77 | -5.27 | $2.40 \times 10^{6}$ | 40 |
| Carboxylate | 4 | Oxalate | OOCCOO- | -29.94 | -2.98 | $2.28 \times 10^{7}$ | 41-44 |
|  | 5 | Formate | $\mathrm{HCOO}^{-}$ | -9.93 | -3.85 | $5.04 \times 10^{5}$ | 41, 45 |
|  | 6 | Succinate | $\mathrm{OOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}$ | -8.72 | -3.90 | $1.59 \times 10^{7}$ | 37, 46 |
|  | 7 | Acetate | $\mathrm{CH}_{3} \mathrm{COO}^{-}$ | -8.07 | -3.93 | $1.05 \times 10^{6}$ | 45, 47 |
|  | 8 | Hydrogen oxalate | HOOCCOO | -52.21 | -2.02 | $3.65 \times 10^{9}$ | 40 |
|  | 9 | Malonate | ${ }^{-} \mathrm{OOC}-\mathrm{CH}_{2}-\mathrm{COO}^{-}$ | -9.07 | -3.89 | $1.00 \times 10^{7}$ | 46 |
|  | 10 | Malonate(1-) | $\mathrm{HOOC}-\mathrm{CH}_{2}-\mathrm{COO}^{-}$ | -35.93 | -2.72 | $5.06 \times 10^{8}$ | 46, 48 |
|  | 11 | Succinate(1-) | $\mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}$ | -17.65 | -3.51 | $2.05 \times 10^{8}$ | 37, 46 |
|  | 12 | Lactate | $\mathrm{CH}_{3} \mathrm{CHOHCOO}$ | -5.70 | -4.03 | $1.00 \times 10^{7}$ | 39 |
|  | 13 | Glycolate | $\mathrm{HOCH}_{2} \mathrm{COO}^{-}$ | -6.61 | -3.99 | $8.20 \times 10^{6}$ | 49 |
|  | 14 | Pyruvate | $\mathrm{CH}_{3} \mathrm{COCOO}^{-}$ | -50.94 | -2.07 | $6.80 \times 10^{9}$ | 39 |
|  | 15 | CID_4134252 | $\mathrm{HOCH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}$ | -13.59 | -3.69 | $1.00 \times 10^{6}$ | 50 |
|  | 16 | Malate | $\mathrm{OOCCH}_{2} \mathrm{CHOHCOO}$ | -11.81 | -3.77 | $6.01 \times 10^{7}$ | 51 |
| Carboxylic Acid | 17 | Oxalic acid | HOOCCOOH | -62.94 | -1.55 | $2.50 \times 10^{10}$ | 52 |
|  | 18 | Formic acid | HCOOH | -39.00 | -2.59 | $1.41 \times 10^{8}$ | 45 |
|  | 19 | Succinic acid | $\mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}$ | -35.30 | -2.75 | $2.30 \times 10^{8}$ | 46,53 |
|  | 20 | Propionic acid | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}$ | -35.03 | -2.76 | $2.20 \times 10^{7}$ | 53 |
|  | 21 | Acetic acid | $\mathrm{CH}_{3} \mathrm{COOH}$ | -32.16 | -2.89 | $2.02 \times 10^{8}$ | 45, 54 |
|  | 22 | Malonic acid | $\mathrm{HOOC}-\mathrm{CH}_{2}-\mathrm{COOH}$ | -40.83 | -2.51 | $3.03 \times 10^{9}$ | $\begin{gathered} 46,48, \\ 53 \end{gathered}$ |
|  | 23 | Lactic acid | $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{COOH}$ | -38.23 | -2.62 | $7.36 \times 10^{8}$ | 46,53 |
|  | 24 | Malic acid | $\mathrm{HOOCCH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{COOH}$ | -41.24 | -2.49 | $3.41 \times 10^{9}$ | 55 |
|  | 25 | Glycolic acid | $\mathrm{HOCH}_{2} \mathrm{COOH}$ | -37.42 | -2.66 | $4.38 \times 10^{8}$ | 53 |
| Alcohol | 26 | Methanediol | $\mathrm{CH}_{2}(\mathrm{OH})_{2}$ | -13.52 | -3.69 | $1.00 \times 10^{7}$ | 45, 56 |
|  | 27 | tert-Butanol | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{OH}$ | -6.33 | -4.01 | $4.00 \times 10^{5}$ | 47 |
|  | 28 | Butane-1,2,3,4 | $\mathrm{HOCH}_{2}\left[\mathrm{CH}(\mathrm{OH})_{2} \mathrm{CH}_{2} \mathrm{OH}\right.$ | -11.50 | -3.78 | $5.00 \times 10^{6}$ | 57 |
|  | 29 | Mannitol | $\mathrm{HOCH}_{2}[\mathrm{CH}(\mathrm{OH})]_{4} \mathrm{CH}_{2} \mathrm{OH}$ | -16.74 | -3.55 | $8.50 \times 10^{6}$ | 57, 58 |
| Ester | 30 | Methyl acetate | $\mathrm{CH}_{3} \mathrm{COOCH}_{3}$ | -33.56 | -2.82 | $8.73 \times 10^{7}$ | 59 |
|  | 31 | Methyl propionate | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{3}$ | -33.24 | -2.84 | $9.03 \times 10^{7}$ | 37 |
|  | 32 | Ethyl propionate | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOC}_{2} \mathrm{H}_{5}$ | -33.22 | -2.84 | $7.52 \times 10^{7}$ | 60 |
|  | 33 | Dimethyl oxalate | $\mathrm{CH}_{3} \mathrm{OOCCOOCH}_{3}$ | -59.03 | -1.72 | $1.04 \times 10^{11}$ | 48 |
|  | 34 | tert-butyl acetate | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCOOCH}_{3}$ | -30.20 | -2.97 | $2.30 \times 10^{7}$ | 37 |
|  | 35 | 2-Hydroxyethyl acetate | $\mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -33.27 | -2.84 | $2.60 \times 10^{7}$ | 61 |
|  | 36 | $\frac{\text { Di-tert-butyl }}{\text { peroxide }}$ | $\left.\mathrm{CH}_{3}\right)_{2} 3_{2} \mathrm{COOC}\left(\mathrm{CH}_{3}\right)_{3}$ | 44.93 | -6.23 | $\underline{1.41 \times 10^{8}}$ | 62 |
|  | 37 | Methylene glycol monoacetate | $\mathrm{HOCH}_{2} \mathrm{COOCH}_{3}$ | -37.37 | -2.66 | $4.90 \times 10^{8}$ | 37 |


| Class | No. | Name | Chemical Formula | $\begin{gathered} \Delta G_{\text {red,aq }}^{\circ} \\ \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{gathered}$ | $\begin{gathered} E_{\text {red }}^{\circ} \\ (\mathrm{V} \text { vS SHE }) \end{gathered}$ | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Ref. for $k_{\text {exp }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ester | 38 | Methyl methoxyacetate | $\mathrm{CH}_{3} \mathrm{OCH}_{2} \mathrm{COOCH}_{3}$ | -38.04 | -2.63 | $4.48 \times 10^{8}$ | 63 |
|  | 39 | Methyl trifluoroacetate | $\mathrm{CF}_{3} \mathrm{COOCH}_{3}$ | -42.28 | -2.45 | $2.06 \times 10^{9}$ | 37 |
|  | 40 | Ethyl glycinate | $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COOC}_{2} \mathrm{H}_{5}$ | -34.86 | -2.77 | $8.58 \times 10^{8}$ | 64 |
|  | 41 | Acetoxymethylamine | $\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{COOCH}_{3}$ | -32.45 | -2.87 | $3.14 \times 10^{8}$ | 37, 65 |
| Ether | 42 | Diethyl ether | $\left(\mathrm{C}_{2} \underline{H}_{5} \underline{2} 2 \underline{2}\right.$ | -38.95 | -2.59 | $\underline{1.00 \times 10^{7}}$ | 20 |
| Ketone | 43 | Acetone | $\mathrm{CH}_{3} \mathrm{COCH}_{3}$ | -38.95 | -2.59 | $8.90 \times 10^{9}$ | 66-70 |
|  | 44 | Methyl ethyl ketone | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}$ | -38.72 | -2.60 | $6.11 \times 10^{9}$ | 71 |
|  | 45 | 2,3-Butanedione | $\mathrm{CH}_{3} \mathrm{COCOCH}_{3}$ | -69.05 | -1.29 | $1.67 \times 10^{10}$ | 48,72 |
|  | 46 | Acetoin | $\mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}$ | -43.76 | -2.38 | $7.95 \times 10^{9}$ | 72 |
| Aldehyde | 47 | Acetaldehyde | $\mathrm{CH}_{3} \mathrm{CHO}$ | -44.97 | -2.33 | $6.11 \times 10^{9}$ | 45,48 |
|  | 48 | Propionaldehyde | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}$ | -44.42 | -2.35 | $4.43 \times 10^{9}$ | 68,71 |
| Halocarboxylate | 49 | Chloroacetate | $\mathrm{ClCH}_{2} \mathrm{COO}^{-}$ | 10.40 | -4.73 | $1.09 \times 10^{9}$ | $\begin{gathered} 67,69, \\ 73-74 \end{gathered}$ |
|  | 50 | 3-Chloropropanoate | $\mathrm{Cl}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}$ | 12.92 | -4.84 | $4.40 \times 10^{8}$ | 73 |
|  | 51 | Bromoacetate | $\mathrm{BrCH}_{2} \mathrm{COO}^{-}$ | 11.54 | -4.78 | $8.03 \times 10^{9}$ | 69 |
|  | 52 | 3-Bromopropanoate | $\mathrm{Br}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}$ | 15.24 | -4.94 | $2.70 \times 10^{9}$ | 69 |
|  | 53 | Fluoroacetate | $\mathrm{FCH}_{2} \mathrm{COO}^{-}$ | 66.82 | -7.18 | $1.20 \times 10^{6}$ | 69 |
|  | 54 | 2-Bromopropanoate | $\mathrm{CH}_{3} \mathrm{CHBrCOO}^{-}$ | 6.18 | -4.55 | $5.30 \times 10^{9}$ | 69 |
|  | 55 | 2-Chloropropanoate | $\mathrm{CH}_{3} \mathrm{CHClCOO}$ | 5.26 | -4.51 | $1.40 \times 10^{9}$ | 69 |
|  | 56 | Trichloroacetate | $\mathrm{Cl}_{3} \mathrm{CCOO}-$ | 1.91 | -4.36 | $1.22 \times 10^{10}$ | 69 |
|  | 57 | 2-Iodoacetate | $\mathrm{ICH}_{2} \mathrm{COO}-$ | 5.89 | -4.54 | $1.20 \times 10^{10}$ | 69 |
|  | 58 | 2-Iodopropanoate | $\mathrm{CH}_{3} \mathrm{CHICOO}^{-}$ | -1.08 | -4.23 | $6.60 \times 10^{9}$ | 69 |
|  | 59 | 3-Iodanylpropanoate | $\mathrm{ICH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}$ | 6.46 | -4.56 | $5.80 \times 10^{9}$ | 75 |
| Haloalkane | $\underline{60}$ | Chloromethane | $\mathrm{CH}_{3} \underline{\mathrm{Cl}}$ | -69.84 | $\underline{-1.25}$ | $\underline{8.33 \times 10^{8}}$ | 76-78 |
|  | 61 | Dibromomethane | $\mathrm{CH}_{2} \mathrm{Br}_{2}$ | $\underline{-73.00}$ | -1.11 | $\underline{1.10 \times 10^{11}}$ | $\underline{79}$ |
|  | 62 | Bromoform | $\mathrm{CHBr}_{3}$ | -80.06 | -0.81 | $\underline{1.67 \times 10^{10}}$ | $\underline{80}$ |
|  | $\underline{63}$ | Bromoethane | $\mathrm{CH}_{3} \underline{C H}_{2} \underline{-\mathrm{Br}}$ | -67.93 | $\underline{-1.33}$ | $\underline{1.89 \times 10^{10}}$ | $\underline{80-82}$ |
|  | 64 | Bromopropane | $\mathrm{CH}_{3} \underline{C H}_{2} \underline{C H}_{2}-\underline{B r}$ | -67.55 | $\underline{-1.35}$ | $\underline{1.47 \times 10^{10}}$ | 80,82 |
|  | 65 | Chloropropane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Cl}$ | -70.86 | -1.21 | $6.85 \times 10^{8}$ | $\frac{40,81}{\underline{82}}$ |
|  | 66 | Chloroethane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Cl}^{2}$ | -71.03 | $\underline{-1.20}$ | $\underline{7.21 \times 10^{8}}$ | 77 |
|  | 67 | 1-Bromo-2- chloroethane | $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \underline{\mathrm{Br}}$ | -70.61 | -1.22 | $\underline{1.18 \times 10^{10}}$ | $\underline{80}$ |
|  | 68 | Halothane | $\mathrm{CF}_{3} \mathrm{CHClBr}$ | -79.44 | -0.84 | $3.22 \times 10^{10}$ | $\underline{83}$ |
|  | $\underline{69}$ | 1,1- <br> Dichloroethane | $\mathrm{CH}_{3} \mathrm{CHCl}_{2}$ | -77.00 | -0.94 | $1.42 \times 10^{10}$ | $\underline{84}$ |
|  | 70 | Diiodomethane | $\mathrm{CH}_{\underline{2} \underline{\underline{2}} 2}^{2}$ | -80.13 | -0.81 | $3.40 \times 10^{10}$ | 79,85 |
|  | 71 | Iodoethane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{I}$ | -75.94 | -0.99 | $3.85 \times 10^{10}$ | 81, 82 |
|  | 72 | Dichloromethane | $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ | -75.69 | $\underline{-1.00}$ | $7.95 \times 10^{9}$ | $\underline{86}$ |
|  | $\underline{73}$ | Chloroform | $\mathrm{CHCl}_{3}$ | $\underline{-81.97}$ | -0.73 | $\underline{3.00 \times 10^{10}}$ | $\underline{39}$ |
|  | 74 | Trichlorofluoromethane | $\mathrm{CCl}_{3} \mathrm{~F}$ | -82.75 | -0.69 | $\underline{4.60 \times 10^{10}}$ | 87 |
|  | 75 | Dichlorodifluoromethane | $\mathrm{CF}_{2} \mathrm{Cl}_{2}$ | $\underline{-77.16}$ | -0.93 | $\underline{3.28 \times 10^{10}}$ | 87 |


| Class | No. | Name | Chemical Formula | $\begin{aligned} & \hline \Delta G_{\text {red,aq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{gathered} E_{E_{\text {red }}} \\ (\mathrm{V} \text { vS SHE }) \end{gathered}$ | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Ref. for $k_{\text {exp }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Haloalkane | 76 | Chlorotrifluoromethane | $\mathrm{CClF}_{3}$ | -71.19 | -1.19 | $\underline{5.36 \times 10^{9}}$ | 81 |
|  | $\underline{77}$ | $\frac{\text { Bromotrifluoro- }}{\text { methane }}$ | $\mathrm{CF}_{3} \underline{\mathrm{Br}}$ | -70.32 | -1.23 | $3.93 \times 10^{11}$ | 81 |
|  | 78 | Carbon tetrachloride | $\mathrm{CCl}_{4}$ | -91.15 | -0.33 | $\underline{7.61 \times 10^{10}}$ | 68,88 |
|  | 79 | $\frac{\text { Chlorodifluoro- }}{\text { methane }}$ | $\mathrm{CHClF}_{2}$ | -70.22 | -1.24 | $3.29 \times 10^{9}$ | $\underline{89}$ |
|  | $\underline{80}$ | 1,1,2- <br> Trichloroethane | $\mathrm{ClCH}_{2} \mathrm{CHCl}_{2}$ | -75.17 | -1.02 | $\underline{1.27 \times 10^{10}}$ | 84 |
|  | $\underline{81}$ | 1,1,1- <br> Trichloroethane | $\mathrm{CH}_{3} \mathrm{CCl}_{3}$ | -84.09 | -0.63 | $\underline{9.24 \times 10^{10}}$ | 77,84 |
|  | $\underline{82}$ | Hexachloroethane | $\mathrm{CCl}_{3} \mathrm{CCl}_{3}$ | -89.80 | -0.39 | $\underline{3.90 \times 10^{10}}$ | $\underline{84}$ |
|  | $\underline{83}$ | 2-Chlorobutane | $\mathrm{C}_{2} \underline{H}_{3} \underline{\mathrm{H}}^{\mathbf{C H}(\mathrm{Cl}) \mathrm{CH}_{3}}$ | -71.79 | -1.17 | $\underline{5.21 \times 10^{8}}$ | $\underline{82}$ |
|  | $\underline{84}$ | 1,2- <br> Dibromoethane | $\underline{\mathrm{BrCH}_{2}} \underline{\underline{\mathrm{CH}_{2}} \underline{\underline{\mathrm{Br}}} \mathbf{} \text { ( }}$ | -72.81 | -1.12 | $\underline{2.74 \times 10^{10}}$ | 80, 84 |
|  | $\underline{85}$ | 1,2- <br> Dichloroethane | $\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathbf{C l}$ | $\underline{-74.11}$ | $\underline{-1.07}$ | $\underline{1.91 \times 10^{9}}$ | 84,90 |
|  | $\underline{86}$ | $\begin{aligned} & \frac{1,1,2 \text {-Trichloro- }}{\frac{1,2,2-}{1}} \\ & \text { trifluoroethane } \end{aligned}$ | $\mathrm{ClCF}_{2} \mathrm{CCl}_{2} \mathrm{~F}$ | -80.52 | -0.79 | $\underline{3.17 \times 10^{10}}$ | $\underline{84}$ |
|  | $\underline{87}$ | 1-Iodopropane | $\mathrm{C}_{3} \underline{\underline{H}} \mathbf{-} \underline{\underline{I}}$ | -75.56 | $\underline{-1.00}$ | $\underline{2.73 \times 10^{10}}$ | $\underline{82}$ |
|  | $\underline{88}$ | 1-Iodobutane | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \underline{5}$ | -75.50 | $\underline{-1.01}$ | $\underline{2.29 \times 10^{10}}$ | 82 |
|  | $\underline{89}$ | 1-Bromobutane | $\mathrm{CH}_{3} \mathrm{CH}_{2} 2_{3} \underline{\underline{B r}}$ | -67.54 | -1.35 | $\underline{1.59 \times 10^{10}}$ | 80-82 |
|  | $\underline{90}$ | 1 -Chlorobutane | $\left.\mathrm{CH}_{3} \mathrm{CHH}_{2}\right)_{3} \mathrm{Cl}$ | -70.83 | -1.21 | $3.42 \times 10^{8}$ | $\begin{array}{r} \frac{40,54,}{81,82} \\ \hline \end{array}$ |
|  | $\underline{91}$ | $\underset{ }{\text { methylpropane }}$ | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}$ | -70.62 | -1.22 | $\underline{5.21 \times 10^{8}}$ | 82 |
|  | $\underline{92}$ | 1-Bromopentane | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2} 244_{4} \mathrm{Br}\right.$ | -67.45 | -1.36 | $\underline{1.17 \times 10^{10}}$ | 80 |
|  | $\underline{93}$ | $\begin{gathered} \text { 2-Bromo-2- } \\ \text { methylpropane } \end{gathered}$ | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}$ | -70.36 | -1.23 | $\underline{1.02 \times 10^{10}}$ | 80 |
|  | $\underline{94}$ | 2-Bromobutane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{Br}) \mathrm{CH}_{3}$ | -69.18 | -1.28 | $\underline{1.01 \times 10^{10}}$ | 80 |
|  | $\underline{95}$ | $\frac{\text { Trifluoroiodo- }}{\text { methane }}$ | $\mathrm{CF}_{3} \mathrm{I}$ | -77.06 | -0.94 | $\underline{2.77 \times 10^{10}}$ | 81 |
|  | $\underline{96}$ | Iodomethane | $\mathrm{CH}_{3} \mathrm{I}$ | -73.39 | -1.10 | $4.64 \times 10^{10}$ | 81,91 |
| Halooxygen | 97 | Isoflurane | $\mathrm{CHF}_{2} \mathrm{OCHClCF}_{3}$ | 0.87 | -4.32 | $5.80 \times 10^{9}$ | 84 |
|  | 98 | 1,1,1- <br> Trifluoroacetone | $\mathrm{CF}_{3} \mathrm{COCH}_{3}$ | 24.93 | -5.36 | $6.62 \times 10^{7}$ | 37 |
|  | 99 | Fluoroacetone | $\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{~F}$ | 19.34 | -5.12 | $9.77 \times 10^{8}$ | 37 |
|  | 100 | Methoxyflurane | $\mathrm{CH}_{3} \mathrm{OCF}_{2} \mathrm{CHCl}_{2}$ | 1.31 | -4.34 | $3.16 \times 10^{10}$ | 84 |
|  | 101 | 2-Chloroethanol | $\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | 15.25 | -4.94 | $5.34 \times 10^{8}$ | 92 |
|  | 102 | 2-Bromoethanol | $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | 18.64 | -5.09 | $1.71 \times 10^{9}$ | 69 |
|  | 103 | Chloroacetic acid | $\mathrm{ClCH}_{2} \mathrm{COOH}$ | 5.40 | -4.51 | $9.60 \times 10^{9}$ | 93 |
|  | 104 | Chloral hydrate | $\mathrm{CCl}_{3} \mathrm{CH}(\mathrm{OH})_{2}$ | -0.79 | -4.25 | $2.31 \times 10^{10}$ | 94 |
|  | 105 | Enflurane | $\mathrm{CHF}_{2} \mathrm{OCF}_{2} \mathrm{CHClF}$ | 4.14 | -4.46 | $3.03 \times 10^{9}$ | 84 |
| Cyanide | 106 | Acetonitrile | $\mathrm{CH}_{3} \mathrm{CN}$ | -14.83 | -3.64 | $3.74 \times 10^{7}$ | $\begin{gathered} 54,68, \\ 95 \end{gathered}$ |
|  | 107 | Succinonitrile | $\mathrm{NC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CN}$ | -21.84 | -3.33 | $1.83 \times 10^{9}$ | 96 |
|  | 108 | Trichloroacetonitrile | $\mathrm{CCl}_{3} \mathrm{CN}$ | -98.67 | $\underline{0.00}$ | $3.20 \times 10^{10}$ | 84 |
|  | 109 | Cyanamide | $\mathrm{H}_{2} \mathrm{NCN}$ | -21.23 | -3.36 | $1.60 \times 10^{9}$ | 96 |
| Amine | 110 | Methylamine | $\mathrm{CH}_{3} \mathrm{NH}_{2}$ | 19.28 | -5.12 | $9.00 \times 10^{5}$ | 97 |
|  | 111 | Butylamine | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{NH}_{2}$ | 17.07 | -5.02 | $1.10 \times 10^{6}$ | 98 |
|  | 112 | Propylamine | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ | 19.79 | -5.14 | $1.10 \times 10^{6}$ | 98 |


| Class | No. | Name | Chemical Formula | $\begin{aligned} & \Delta G_{\text {redaq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{gathered} E_{\text {red }}^{\circ} \\ (\mathrm{V} \text { vs SHE }) \end{gathered}$ | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Ref. for $k_{\text {exp }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Amine | 113 | Ethylamine | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}$ | 20.42 | -5.17 | $1.00 \times 10^{6}$ | 98 |
|  | 114 | Isobutylamine | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{NH}_{2}$ | 18.63 | -5.09 | $1.10 \times 10^{7}$ | 97 |
|  | 115 | Isoamylamine | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ | 20.07 | -5.15 | $1.00 \times 10^{6}$ | 97 |
|  | 116 | $1,2-$ Dimethylhydrazin | $\mathrm{CH}_{3} \mathrm{NHNHCH}_{3}$ | 27.98 | -5.49 | $6.10 \times 10^{6}$ | 99 |
|  | 117 | Methylhydrazine | $\mathrm{CH}_{3} \mathrm{NHNH}_{2}$ | 12.20 | -4.81 | $6.50 \times 10^{6}$ | 99 |
|  | 118 | Glycinate | $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}$ | -9.94 | -3.85 | $1.70 \times 10^{6}$ | 100 |
|  | 119 | Ethanolamine | $\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -0.27 | -4.27 | $2.00 \times 10^{7}$ | 101 |
|  | 120 | Isopropylamine | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHNH}_{2}$ | 18.20 | -5.07 | $1.50 \times 10^{6}$ | 97 |
|  | 121 | Tert-Butylamine | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{2}$ | 18.20 | -5.07 | $1.10 \times 10^{6}$ | 97 |
|  | 122 | beta-Alaninate | $\mathrm{NH}_{2}\left(\mathrm{CH}_{2}\right)_{2}-\mathrm{COO}^{-}$ | -9.80 | -3.85 | $4.20 \times 10^{6}$ | 102 |
|  | 123 | N,N- Diethylhydroxyl- | $\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{NOH}$ | -2.51 | -4.17 | $4.81 \times 10^{7}$ | 103 |
|  | 124 | tritiohydroxylamine | $\mathrm{CH}_{3} \mathrm{NHOH}$ | -15.92 | -3.59 | $2.42 \times 10^{8}$ | 65 |
|  | 125 | Amylamine | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{NH}_{2}$ | 21.11 | -5.20 | $1.00 \times 10^{6}$ | 98 |
|  | 126 | Trimethylhydrazine | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N}-\mathrm{NHCH}_{3}$ | -16.76 | -3.55 | $1.00 \times 10^{8}$ | 99 |
|  | 127 | 1,1-Dimethylhydrazine | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NNH}_{2}$ | 18.28 | -5.07 | $2.40 \times 10^{7}$ | 99 |
| Amide | 128 | Propionamide | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CONH}_{2}$ | -23.71 | -3.25 | $4.66 \times 10^{7}$ | $\begin{aligned} & 100, \\ & 104 \end{aligned}$ |
|  | 129 | N -Ethylacetamide | $\mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{5}$ | -23.75 | -3.25 | $1.40 \times 10^{7}$ | 64 |
|  | 130 | Methylacetamide | $\mathrm{CH}_{3} \mathrm{CONHCH}_{3}$ | -21.79 | -3.34 | $2.30 \times 10^{6}$ | 105 |
|  | 131 | Acetamide | $\mathrm{CH}_{3} \mathrm{CONH}_{2}$ | -25.72 | -3.16 | $3.84 \times 10^{7}$ | $\begin{gathered} 74, \\ 100, \\ 106 \end{gathered}$ |
|  | 132 | Urea | $\mathrm{H}_{2} \mathrm{NCONH}_{2}$ | -17.40 | -3.53 | $3.10 \times 10^{5}$ | 37, 74 |
|  | 133 | Glycinamide | $\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CONH}_{2}$ | -27.34 | -3.09 | $2.83 \times 10^{8}$ | 65 |
|  | 134 | Formamide | $\mathrm{HCONH}_{2}$ | -28.17 | -3.06 | $2.80 \times 10^{7}$ | $\begin{gathered} 73, \\ 100, \\ 106, \\ 107, \\ 108 \end{gathered}$ |
|  | 135 | 3-Chloropropionamide | $\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathrm{CONH}_{2}$ | 10.52 | -4.74 | $1.94 \times 10^{9}$ | 104 |
|  | 136 | (S)-2-Hydroxypropanamide | $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CONH}_{2}$ | -29.16 | -3.02 | $1.91 \times 10^{8}$ | 49 |
|  | 137 | Aceturate | $\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{COO}^{-}$ | -25.84 | -3.16 | $1.13 \times 10^{7}$ | 65,109 |
|  | 138 | Pivalamide | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCONH}_{2}$ | -27.03 | -3.11 | $1.50 \times 10^{7}$ | 100 |
|  | 139 | Malonamide | $\mathrm{H}_{2} \mathrm{NCOCH}_{2} \mathrm{CONH}_{2}$ | -30.47 | -2.96 | $1.15 \times 10^{9}$ | 110 |
|  | 140 | 2- <br> Hydroxyacetamide | $\mathrm{HOCH}_{2} \mathrm{CONH}_{2}$ | -29.10 | -3.02 | $2.93 \times 10^{8}$ | 49 |
|  | 141 | Biuret | $\mathrm{H}_{2} \mathrm{NCONHCONH}_{2}$ | -26.98 | -3.11 | $2.53 \times 10^{8}$ | 110 |
|  | 142 | 2-Chloropropionamide | $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{Cl}) \mathrm{CONH}_{2}$ | 0.91 | -4.32 | $7.58 \times 10^{9}$ | 104 |
|  | 143 | Iodoacetamide | $\mathrm{ICH}_{2} \mathrm{CONH}_{2}$ | -2.75 | -4.16 | $5.00 \times 10^{10}$ | 111 |
|  | 144 | Hydroxyurea | $\mathrm{HONHCONH}_{2}$ | -27.45 | -3.09 | $4.90 \times 10^{8}$ | 112 |
|  | 145 | Oxamate | $\mathrm{H}_{2} \mathrm{NCOCOO}^{-}$ | -44.35 | -2.36 | $5.70 \times 10^{9}$ | 110 |
|  | 146 | Succinamide | $\mathrm{H}_{2} \mathrm{NCOCH}_{2} \mathrm{CH}_{2} \mathrm{CONH}_{2}$ | -26.23 | -3.14 | $2.02 \times 10^{8}$ | 110 |


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| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Amide | 147 | Asparaginate | $\mathrm{H}_{2} \mathrm{NCOCH}_{2} \mathrm{CH}\left(\mathrm{NH}_{2}\right) \mathrm{COO}$ | -26.51 | -3.13 | $2.40 \times 10^{7}$ | 113 |
|  | 148 | N,N-Dimethyl- formamide | $\mathrm{HCON}\left(\mathrm{CH}_{3}\right)_{2}$ | -30.35 | -2.96 | $3.08 \times 10^{8}$ | $\begin{aligned} & \text { 100, } \\ & \text { 107, } \\ & 108 \end{aligned}$ |
|  | 149 | Methyl 2 acetamidoacetate | $\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{COOCH}_{3}$ | -38.38 | -2.62 | $3.34 \times 10^{8}$ | 110 |
|  | 150 | 2- <br> Formamidoacetate | $\mathrm{HCONHCH}_{2} \mathrm{COO}^{-}$ | -25.93 | -3.16 | $2.90 \times 10^{7}$ | 110 |
|  | 151 | N - <br> Methylformamide | $\mathrm{HCONHCH}_{3}$ | -25.68 | -3.17 | $4.31 \times 10^{7}$ | $\begin{aligned} & 100, \\ & 108 \end{aligned}$ |
|  | 152 | N -tert- <br> Butylacetamide | $\mathrm{CH}_{3} \mathrm{CONHC}\left(\mathrm{CH}_{3}\right)_{3}$ | -21.69 | -3.34 | $1.20 \times 10^{7}$ | 100 |
|  | 153 | Diacetamide | $\left(\mathrm{CH}_{3} \mathrm{CO}\right)_{2} \mathrm{NH}$ | -43.29 | -2.40 | $1.98 \times 10^{10}$ | 110 |
|  | 154 | $\mathrm{N}, \mathrm{N}-$ <br> Diethylacetamide | $\mathrm{CH}_{3} \mathrm{CON}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}$ | -23.89 | -3.24 | $8.00 \times 10^{6}$ | 100 |
|  | 155 | N,N-Dimethylacetamide | $\mathrm{CH}_{3} \mathrm{CON}\left(\mathrm{CH}_{3}\right)_{2}$ | -27.42 | -3.09 | $1.50 \times 10^{7}$ | $\begin{aligned} & 100, \\ & 105 \end{aligned}$ |
|  | 156 |  | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCON}\left(\mathrm{CH}_{3}\right)_{2}$ | -29.95 | -2.98 | $1.20 \times 10^{7}$ | 100 |
| Ammonia | 157 | Methyl ammoniumhydride | $\mathrm{CH}_{3} \underline{\mathrm{NH}}_{3}{ }^{ \pm}$ | -50.08 | -2.11 | $\underline{1.85 \times 10^{6}}$ | 97, 113 |
|  | $\underline{158}$ | Ethylammonium | $\mathrm{C}_{2} \underline{H}_{5} \underline{\mathrm{NH}}_{3}{ }^{ \pm}$ | -51.52 | -2.05 | $2.50 \times 10^{6}$ | $\underline{98}$ |
|  | 159 | $\frac{\text { Trideuterio(propyl }}{\text { )azanium }}$ | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{NH}_{3}{ }^{ \pm}$ | -50.99 | -2.07 | $\underline{2.80 \times 10^{6}}$ | 98 |
|  | 160 | Pentylazanium | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{NH}_{3}{ }^{ \pm}$ | -51.57 | -2.04 | $\underline{2.70 \times 10^{6}}$ | $\underline{98}$ |
|  | 161 | 2-Methoxy-2oxoethanaminium | $\mathrm{H}_{3} \mathrm{COOCCH}_{2} \underline{\mathrm{NH}}_{3}{ }^{ \pm}$ | -59.49 | -1.70 | $6.80 \times 10^{9}$ | $\underline{65}$ |
|  | $\underline{162}$ | Methoxyazanium | $\mathrm{CH}_{3} \mathrm{ONH}_{3}{ }^{ \pm}$ | -96.51 | -0.10 | $\underline{1.90 \times 10^{10}}$ | $\underline{65}$ |
|  | 163 | Tert- <br> butylammonium | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{3}{ }^{ \pm}$ | -53.40 | -1.96 | $\underline{1.10 \times 10^{6}}$ | $\underline{97}$ |
|  | $\underline{164}$ | $\xrightarrow{\text { 2-Methyl- }}$ | $\mathrm{CH}_{3} \mathrm{NHNH}_{3}{ }^{ \pm}$ | -80.62 | -0.78 | $\underline{1.40 \times 10^{9}}$ | $\underline{99}$ |
|  | $\underline{165}$ | 1,1-Dimethylhydrazinium | $\left.\mathrm{CH}_{3}\right)_{2} \mathrm{NNH}_{3}{ }^{ \pm}$ | -85.83 | -0.56 | $\underline{5.80 \times 10^{9}}$ | $\underline{99}$ |
|  | $\underline{166}$ | Tetramethyl- | $\left(\mathrm{CH}_{3}\right)_{4} \mathrm{~N}^{+}$ | -49.22 | -2.15 | $\underline{5.60 \times 10^{6}}$ | 114 |
|  | $\underline{167}$ | Tetraethylammonium | $\left(\mathrm{C}_{2} \underline{H}_{\underline{5}}^{5} 2 \underline{\mathrm{~N}}^{+}\right.$ | -52.94 | -1.98 | $1.20 \times 10^{7}$ | 114 |
| Hydrogen Sulfide | 168 | Cysteaminium | $\underline{\mathrm{HSCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{ \pm}}$ | $\underline{-51.15}$ | -2.06 | $\underline{2.25 \times 10^{10}}$ | $\begin{aligned} & \frac{115,}{116} \\ & \underline{116} \end{aligned}$ |
|  | $\underline{169}$ | $\frac{\text { 3-Sulfanylpropyl- }}{\text { azanium }}$ |  | -52.08 | -2.02 | $\underline{1.70 \times 10^{10}}$ | 117 |
| Alkyne | 170 | Acetylene | HC triplet bond CH | -21.82 | -3.33 | $2.00 \times 10^{7}$ | 118 |
|  | 171 | Propargyl alcohol | HC triplet bond $\mathrm{CCH}_{2} \mathrm{OH}$ | -24.16 | -3.23 | $2.12 \times 10^{8}$ | 68 |
| Sulfate | 172 | Ethanesulfonate | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{SO}_{3}{ }^{-}$ | 7.65 | -4.61 | $3.50 \times 10^{7}$ | 119 |
| Sulfoxide | 173 | Dibutyl sulphoxide | $\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{SO}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CH}_{3}\right]$ | 22.09 | -5.24 | $3.60 \times 10^{6}$ | 120 |
|  | 174 | Di-tert-butyl sulfoxide | $\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{Cl}_{2} \mathrm{SO}\right.$ | -63.62 | -1.52 | $1.50 \times 10^{7}$ | 120 |
|  | 175 | Methyl (methylsulfinyl)me thyl sulfide | $\mathrm{CH}_{3} \mathrm{SOCH}_{2} \mathrm{SCH}_{3}$ | 22.05 | -5.24 | $1.31 \times 10^{8}$ | 121 |
| Thiol | $\underline{176}$ | Methanethiol | $\mathrm{CH}_{3} \underline{\mathrm{SH}}$ | -47.75 | -2.21 | $\underline{1.08 \times 10^{10}}$ | $\underline{122}$ |
|  | $\underline{177}$ | Thiolactate | $\mathrm{CH}_{3}(\mathrm{CH}) \mathrm{SHCOO}^{-}$ | -58.46 | -1.75 | $\underline{2.89 \times 10^{9}}$ | 116 |
|  | $\underline{178}$ | 2-Mercaptopropionic acid | $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{SH}) \mathrm{COOH}$ | -62.50 | -1.57 | $\underline{4.08 \times 10^{9}}$ | 123 |
|  | $\underline{179}$ | Methyl thioglycolate | $\underline{H S C H}_{2} \underline{C O O C H}_{3}$ | $\underline{-56.08}$ | $\underline{-1.85}$ | $\underline{1.12 \times 10^{10}}$ | 116 |
|  | 180 | $\stackrel{\text { beta- }}{\text { Mercaptoethanol }}$ | $\underline{\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{OH}}$ | -49.88 | -2.12 | $1.73 \times 10^{10}$ | $\frac{115}{\underline{124}}$ |


| Class | No. | Name | Chemical Formula | $\begin{aligned} & \Delta G_{\text {red,aq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{gathered} E_{\mathrm{red}}^{\circ} \\ (\mathrm{V} \text { vs SHE }) \end{gathered}$ | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Ref. for $k_{\text {exp }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Thiol | $\underline{181}$ | $\begin{aligned} & \text { 2-Methyl-2- } \\ & \text { propanethiol } \end{aligned}$ | $\left.\left(\mathrm{CH}_{3}\right)_{2}\right)^{\mathrm{CSH}}$ | $\underline{-54.27}$ | -1.93 | $3.41 \times 10^{9}$ | $\underline{122}$ |
|  | $\underline{182}$ | 3-Mercaptopropionic acid | $\underline{\mathrm{HS}\left(\mathrm{CH}_{2} 2_{2} \mathrm{COOH}\right.}$ | $\underline{-50.10}$ | -2.11 | $\underline{6.91 \times 10^{9}}$ | $\underline{123}$ |
|  | $\underline{183}$ | Thioglycolate | $\mathrm{HSCH}_{2} \mathrm{COO}^{-}$ | $\underline{-54.30}$ | -1.93 | $\underline{3.03 \times 10^{9}}$ | $\underline{116}$ |
|  | 184 |  | $\frac{\mathrm{H}_{2}-\underline{\mathrm{NC}(=\mathrm{NH}) \mathrm{NHCH}_{2}} \underline{\mathrm{CH}}_{2} \underline{\mathrm{~S}}}{\underline{\mathrm{H}}}$ | $\underline{-51.25}$ | -2.06 | $\underline{1.02 \times 10^{11}}$ | $\underline{113}$ |
| Sulfide/ <br> Disulfide | 185 | Dimethylsulfide | $\mathrm{CH}_{3} \mathrm{SCH}_{3}$ | 52.27 | -6.55 | $2.00 \times 10^{7}$ | 125 |
|  | 186 | 3,3'-Dithiodipropionate | $\left(\mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}\right)_{2}$ | 20.22 | -5.16 | $4.35 \times 10^{9}$ | 126 |
|  | 187 | 2,2'-Disulfanediyldiacetate | $\left(\mathrm{SCH}_{2} \mathrm{COO}^{-}\right)_{2}$ | 25.32 | -5.38 | $4.30 \times 10^{9}$ | 126 |
|  | 188 | 2,2'-Sulfanediyldiacetate | $\mathrm{S}\left(\mathrm{CH}_{2} \mathrm{COO}^{-}\right)_{2}$ | 34.86 | -5.79 | $8.30 \times 10^{7}$ | 116 |
|  | 189 | $N$ - <br> Acetylcysteamine | $\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{CH}_{2} \mathrm{SH}$ | 29.28 | -5.55 | $1.43 \times 10^{10}$ | 116 |
|  | 190 | Cystamine | $\mathrm{S}_{2}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)_{2}$ | 24.23 | -5.33 | $5.85 \times 10^{10}$ | 126 |
|  | 191 | L-Cystine anion | $\mathrm{S}_{2}\left[\mathrm{CH}_{2} \mathrm{CH}\left(\mathrm{NH}_{2}\right) \mathrm{COO}^{-}\right]_{2}$ | 15.24 | -4.94 | $3.53 \times 10^{9}$ | $\begin{gathered} 39, \\ 115, \\ 126, \\ 127 \end{gathered}$ |
|  | 192 | $3,3^{\prime}-$ <br> Thiodipropanoate | $\mathrm{S}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}\right)_{2}$ | 33.51 | -5.73 | $5.80 \times 10^{7}$ | 116 |
| S- | $\underline{193}$ | 2-Hydroxy- ethanethiolate | $\mathrm{HOCH}_{2} \underline{\mathrm{CH}_{2}} \underline{\underline{S}}$ | $\underline{-15.20}$ | $\underline{-3.62}$ | $\underline{1.80 \times 10^{7}}$ | $\underline{115}$ |
|  | $\underline{194}$ | $\begin{aligned} & \frac{\text { 2-lambda1- }}{\text { Sulfanyl- }} \\ & \text { ethanamine } \end{aligned}$ | $\underline{\mathrm{H}}_{2} \mathrm{NCH}_{2} \underline{\mathrm{CH}}_{2} \underline{\mathrm{~S}^{-}}$ | $\underline{-16.84}$ | -3.55 | $\underline{9.55 \times 10^{8}}$ | $\frac{115}{\underline{116}}$ |
|  | $\underline{195}$ | 2-Acetamidoethanethiolate | $\mathrm{CH}_{3} \underline{\mathrm{CONHCH}}_{2} \underline{\mathrm{CH}}_{2} \underline{\mathrm{~S}^{-}}$ | -16.11 | -3.58 | $\underline{1.90 \times 10^{9}}$ | $\underline{116}$ |
| CS | 196 | Carbon disulfide | $\mathrm{CS}_{2}$ | -57.80 | -1.77 | $3.10 \times 10^{10}$ | 128, 45 |
|  | 197 | Thiourea | $\mathrm{H}_{2} \mathrm{NCSNH}_{2}$ | -18.12 | -3.49 | $3.29 \times 10^{9}$ | 20 |
|  | 198 | Thiosemicarbazide | $\mathrm{H}_{2} \mathrm{NNHCSNH}_{2}$ | -19.10 | -3.45 | $1.15 \times 10^{9}$ | 129 |
|  | 199 | $\mathrm{N}, \mathrm{N}^{\prime}-$ <br> Diethylthiourea | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NHCSNHCH}_{2} \mathrm{CH}$ | -19.13 | -3.45 | $5.10 \times 10^{8}$ | 129 |
| Nitro | 200 | Nitromethane | $\mathrm{CH}_{3} \mathrm{NO}_{2}$ | -61.02 | -1.63 | $1.80 \times 10^{11}$ | $\begin{gathered} 130- \\ 131 \end{gathered}$ |
|  | 201 | 1-Nitropropane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NO}_{2}$ | -60.85 | -1.64 | $2.70 \times 10^{10}$ | 132 |
|  | 202 | Nitroethane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NO}_{2}$ | -60.17 | -1.67 | $2.70 \times 10^{10}$ | 132 |
|  | 203 | 2-Methyl-2- <br> nitrosopropane | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}(\mathrm{NO})$ | -63.46 | -1.53 | $8.26 \times 10^{9}$ | 133 |
| PFAS | 204 | Trifluoroacetate | $\mathrm{CF}_{3} \mathrm{COO}^{-}$ | 76.90 | -7.61 | $1.65 \times 10^{6}$ | 69,134 |
|  | 205 | Perflurobutanoic Acid | $\mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{COO}^{-}$ | 57.88 | -6.79 | $7.10 \times 10^{6}$ | 134 |
|  | 206 | Perflurooctanoic $\qquad$ <br> Acid | $\mathrm{C}_{7} \mathrm{~F}_{15} \mathrm{COO}^{-}$ | 42.92 | -6.14 | $1.70 \times 10^{7}$ | 134 |
| Alkene | 207 | Allylamine | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{NH}_{2}$ | -23.13 | -3.28 | $1.20 \times 10^{7}$ | 97 |
|  | 208 | Acrylonitrile | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCN}$ | -53.94 | -1.94 | $2.78 \times 10^{10}$ | 135 |
|  | 209 | Allyl alcohol | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{OH}$ | -27.37 | -3.09 | $3.47 \times 10^{7}$ | $\begin{gathered} 54,68, \\ 70 \end{gathered}$ |
|  | 210 | Acrylic acid | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOH}$ | -59.27 | -1.71 | $1.03 \times 10^{12}$ | 136 |
|  | 211 | Acrylate | $\mathrm{CH}_{2}=\mathrm{CHCOO}^{-}$ | -40.74 | -2.51 | $5.30 \times 10^{9}$ | 136 |
|  | 212 | Methyl vinyl ketone | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOCH}_{3}$ | -63.32 | -1.53 | $2.78 \times 10^{9}$ | 137 |
|  | 213 | Methyl acrylate | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOCH}_{3}$ | -57.17 | -1.80 | $1.52 \times 10^{10}$ | 138 |
|  | 214 | Senecioic acid amide | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCONH}_{2}$ | -44.00 | -2.37 | $7.23 \times 10^{9}$ | 139 |


| Class | No. | Name | Chemical Formula | $\begin{gathered} \Delta G_{\text {redaq }}^{\circ} \\ \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right) \end{gathered}$ | $\begin{gathered} E_{\text {red }}^{\circ} \\ (\mathrm{V} \text { vs SHE }) \end{gathered}$ | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Ref. for $k_{\text {exp }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Alkene | 215 | Vinyl chloride | $\mathrm{CH}_{2}=\mathrm{CHCl}$ | 27.10 | -5.45 | $2.53 \times 10^{8}$ | 140 |
|  | 216 | Ethylene | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}_{2}$ | -24.75 | -3.21 | $3.00 \times 10^{5}$ | 54 |
|  | 217 | Ethenesulfonate | $\mathrm{CH}_{2}=\mathrm{CHSO}_{3}{ }^{-}$ | -37.67 | -2.65 | $2.30 \times 10^{9}$ | 141 |
|  | 218 | Tetrachloro ethylene | $\mathrm{Cl}_{2} \mathrm{C}=\mathrm{CCl}_{2}$ | 15.17 | -4.94 | $2.67 \times 10^{10}$ | 90, 140 |
|  | 219 | Crotonyl alcohol | $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCH}_{2} \mathrm{OH}$ | -24.31 | -3.23 | $5.51 \times 10^{7}$ | 54 |
|  | 220 | Crotonic acid | $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCOOH}$ | -54.36 | -1.92 | $6.62 \times 10^{10}$ | 136 |
|  | 221 | Dimethyl fumarate | $\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOOCH}$ | -76.95 | -0.94 | $3.30 \times 10^{10}$ | 110 |
|  | 222 | Divinyl sulfone | $\left(\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}\right)_{2} \mathrm{SO}_{2}$ | -55.62 | -1.87 | $1.66 \times 10^{10}$ | 137 |
|  | 223 | Methacrylic acid | $\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COOH}$ | -56.59 | -1.83 | $8.26 \times 10^{10}$ | 136 |
|  | 224 | Methyl methacrylate | $\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COOCH}_{3}$ | -54.41 | -1.92 | $2.72 \times 10^{10}$ | 139 |
|  | 225 | trans-1,2- <br> Dichloroethylene | $\mathrm{ClCH}=\mathrm{CHCl}$ | 22.70 | -5.26 | $1.08 \times 10^{10}$ | 140 |
|  | 226 | Trichloroethylene | $\mathrm{ClCH}=\mathrm{CCl}_{2}$ | 18.45 | -5.08 | $8.28 \times 10^{10}$ | 140 |
|  | 227 | cis-1,2- <br> Dichloroethylene | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CCl}_{2}$ | 19.86 | -5.14 | $3.86 \times 10^{11}$ | 140 |
|  | 228 | 1,3-Butadiene | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}=\mathrm{CH}_{2}$ | -42.65 | -2.43 | $1.19 \times 10^{10}$ | 20 |
|  | 229 | Acetaldehyde oxime | $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{NOH}$ | -30.63 | -2.95 | $7.22 \times 10^{7}$ | 37 |
|  | 230 | N,N-Dimethyl acrylamide | $\mathrm{CH}_{2}=\mathrm{CHCON}\left(\mathrm{CH}_{3}\right)_{2}$ | -51.04 | -2.07 | $4.51 \times 10^{10}$ | 139 |
|  | 231 | Methacrylamide | $\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{CONH}_{2}$ | -49.80 | -2.12 | $7.10 \times 10^{11}$ | 139 |
|  | 232 | Cyanoguanidine | $\mathrm{NCN}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2}$ | -31.89 | -2.90 | $1.96 \times 10^{10}$ | 142 |
|  | 233 | Tetracyano ethylene | $(\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}(\mathrm{CN})_{2}$ | 36.90 | -5.88 | $3.74 \times 10^{10}$ | 20 |
|  | 234 | Methacrylate | $\mathrm{CH}_{2}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COO}^{-}$ | -36.63 | -2.69 | $4.50 \times 10^{9}$ | 136 |
|  | 235 | 3-Buten-1-ol | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -22.99 | -3.28 | $2.45 \times 10^{6}$ | 54, 68 |
|  | 236 | 3-Buten-2-ol | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}(\mathrm{OH}) \mathrm{CH}_{3}$ | -26.41 | -3.13 | $5.91 \times 10^{7}$ | 54 |
|  | 237 | 3-Methylbut-2enoate | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCO}_{2}{ }^{-}$ | -31.71 | -2.91 | $6.40 \times 10^{8}$ | 143 |
|  | 238 | 3,3-Dimethyl acrylic acid | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCOOH}$ | -50.40 | -2.09 | $2.53 \times 10^{10}$ | $\begin{aligned} & 136, \\ & 143 \end{aligned}$ |
|  | 239 | Isocrotonate | $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCOO}^{-}$ | -35.70 | -2.73 | $1.30 \times 10^{9}$ | 136 |
|  | 240 | Hydrogen fumarate | $\mathrm{HOOCCH}=\mathrm{CHCOO}^{-}$ | -66.40 | -1.40 | $1.35 \times 10^{10}$ | 48, 110 |
|  | 241 | Monomethyl fumarate | $\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOO}^{-}$ | -64.43 | -1.49 | $1.30 \times 10^{10}$ | 110 |
|  | 242 | 2-Hydroxyethyl acrylate | $\mathrm{CH}_{2}=\mathrm{CHCOOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | -57.85 | -1.77 | $1.08 \times 10^{10}$ | 144 |
|  | 243 | trans-Aconitate (3) | $\begin{gathered} \mathrm{OOCCH}_{=} \mathrm{C}\left(\mathrm{COO}^{-}\right. \\ ) \mathrm{CH}_{2} \mathrm{COO}^{-} \end{gathered}$ | -45.03 | -2.33 | $1.80 \times 10^{8}$ | 51 |
|  | 244 | Acrylamide | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCONH}_{2}$ | -51.89 | -2.03 | $3.81 \times 10^{11}$ | 45, <br> 106, <br> 107, <br> 139, <br> 145, <br> 146 |
|  | 245 | Crotonamide | $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCONH}_{2}$ | -47.62 | -2.22 | $2.75 \times 10^{10}$ | 139 |
|  | 246 | $\begin{aligned} & \text { 4-(Ethylamino)-4- } \\ & \text { oxobut-2-enoate } \end{aligned}$ | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NHCOCH}=\mathrm{CHCOO}^{-}$ | -56.87 | -1.81 | $8.50 \times 10^{9}$ | 99 |
|  | 247 | cis-Dimethyl fumarate | $\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOOCH}$ | -73.51 | -1.09 | $3.20 \times 10^{10}$ | 110 |
|  | 248 | 4-Penten-2-OL | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}$ | -21.90 | -3.33 | $5.00 \times 10^{5}$ | 68 |
|  | 249 | Guanidine | $\mathrm{H}_{2} \mathrm{NC}(=\mathrm{NH}) \mathrm{NH}_{2}$ | -4.98 | -4.06 | $2.02 \times 10^{8}$ | 113 |


| Class | No. | Name | Chemical Formula | $\Delta G_{\text {red,aq }}^{\circ}$ <br> $\left(\mathrm{k}_{\text {cal }} / \mathrm{mol}\right)$ | $E_{\text {red }}^{\circ}$ <br> $(\mathrm{V}$ vs SHE $)$ | $k_{\text {chem }}$ <br> $\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ | Ref. for <br> $k_{\text {exp }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Alkene | 250 | Ethyl acrylate | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOC}_{2} \mathrm{H}_{5}$ | -57.33 | -1.79 | $1.34 \times 10^{10}$ | 138 |
|  | 251 | Acetone oxime | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{NOH}$ | -25.74 | -3.16 | $3.29 \times 10^{8}$ | 37,106 |

### 2.3.2 Outliers

The following seven compounds were identified as outliers and were discarded from the investigation: tert-butyl hydroperoxide, glyoxylic acid, o-methylhydroxylamine, methanol, ethanol and pyruvonitrile. The justification for removing each of these compounds from the dataset is described in more detail below.

The experimental pH for tert-butyl hydroperoxide $\left(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{COOH}, E_{\text {red,aq }}{ }^{\circ}=-1.02 \mathrm{~V}\right)$ was reported as $8.2^{6}$, which is significantly greater than the pKa of 4.75 . This disparity would result in dissociation of the OH group and thus an inaccurate $k_{\text {exp }}$ would be obtained for this carboxylic acid. Similarly, the experimental pH range for glyoxylic acid $(\mathrm{HOCCOOH}$, $E_{\text {red,aq }}=-1.20 \mathrm{~V}$ ) was reported as $3-4^{7}$, which encompasses the pKa of 3.3. Thus, it cannot be determined whether HOCCOOH was dissociated during the experiment which brings into question the accuracy of the reported $k_{\text {exp }}$ value. O-methylhydroxylamine $\left(\mathrm{CH}_{3} \mathrm{ONH}_{2}\right.$, $E_{\text {red,aq }}=-5.50 \mathrm{~V}$ ) is unlike any of the other amine and amide compounds in the dataset due to the presence of a single ether functional group. Due to this unique molecular structure, we were not able to achieve an accurate aqueous-phase optimization of this compound with M06-2X. For this reason and the inability to place this compound within one of the classes in our dataset, it was discarded from the investigation. The $k_{\exp }$ values for both methanol $\left(\mathrm{CH}_{3} \mathrm{OH}, E_{\text {red,aq }}=-4.32 \mathrm{~V}\right)$ and ethanol $\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}, E_{\text {red,aq }}=-4.33 \mathrm{~V}\right)$ appear to be significantly underestimated, with reported values of $1.0 \times 10^{4} \mathrm{M}^{-1} \mathrm{~s}^{-18}$ and $1.2 \times 10^{3} \mathrm{M}^{-1}$ $\mathrm{s}^{-19}$, respectively. These reaction rates exceed the lower measurement limit of the pulse radiolysis technique and therefore likely have some degree of uncertainty. Pyruvonitrile $\left(\mathrm{CH}_{3} \mathrm{COCN}, E_{\text {red,aq }}{ }^{\circ}=-1.51 \mathrm{~V}\right)$ is the only compound in our dataset that is a true statistical outlier as it is located over three standard deviations away from the average on the $E_{\text {red,aq }}{ }^{\circ}$ vs $k_{\text {chem }}$ plot. It is also the only compound in the cyanide class that contains a carbonyl group. While we did not experience any computational difficulties with this compound, the experimental data may be questionable. Previous publications ${ }^{10}$ have classified this datapoint as an outlier and the need for new experimental data for pyruvonitrile is the general consensus in the literature. For this reason, this datapoint was discarded from our investigation.

### 2.3.3 Impact of Functional Groups

The functional group(s) in the neighboring position of an $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ attacking site substantially impact the reactivities with $\mathrm{e}^{-}$aq. In general, electron donating groups such as alkyl and amine functional groups in the neighboring position(s) decrease the nucleophilic reactivity of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ by increasing the electron density of the reactive site. For example, the negatively charged oxygen of the $\mathrm{COO}^{-}$functional group acts as an electron donor to the adjacent $\mathrm{C}=\mathrm{O}$ bond due to its lone pair of electrons and hence reduces the reactivity of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ in association with $\mathrm{C}=\mathrm{O}$. In contrast, electron withdrawing functional groups such as ketones
and carboxylic acids decrease the electron density of the reactive site and hence increase the reactivity of $\mathrm{e}^{-}$aq. Figure 2.4 plots the total sum of the Taft constants ${ }^{144}$, $\sigma^{*}$, of neighboring functional group(s) against our $E_{\text {red,aq }}^{\circ}$ values for all the reaction mechanisms investigated in this study. The Taft constants of functional group(s) located in the neighboring position(s) of an $\mathrm{e}^{-}$aq attacking site are additive ${ }^{147,148}$. Overall, we confirm the excellent correlations of all three reaction mechanisms, indicating that our theoretically calculated $E_{\text {red,aq }}^{\circ}$ values represent the general electron donating/withdrawing properties of the functional groups of aliphatic compounds. As expected, all correlations exhibit positive slopes, which confirm that larger $E_{\text {red,aq }}^{\circ}$ values represent stronger electron-withdrawing functional groups (i.e., larger Taft constants). As shown by the LFERs in Figure 2.3, larger $E_{\text {red,aq }}^{\circ}$ values correlate with larger overall $k_{\text {chem }}$ values because of the increase in the nucleophilic reactivities of $\mathrm{e}^{-}$aq. Different correlations with Taft constants developed for the associative mechanism with CO and O confirm the different influence of neighboring functional groups resulting from inductive and mesomeric effects. The smaller slope (1.53) for the associative mechanism with O than that (1.69) for the associative mechanism with CO indicates the inhibition of reactivity resulting from the mesomeric effect. Hart et al. ${ }^{37}$ examined the negative slope between $\log k_{\text {exp }}$ and the Taft constants for groups of ketones with a limited number of data $(\mathrm{N}=10)$ and concluded that the slowing effect due to the mesomeric effect was more extensive than expected from inductive electrondonating/withdrawing effects. They also acknowledged that both mesomeric and inductive effects could apply to carboxylic compounds ( $\mathrm{N}=3$ ), and their data appeared to adhere to both correlations well. Notably, two compounds that we propose for the stepwise cleavage mechanism of the C-F bond of $\mathrm{CF}_{3} \mathrm{COCH}_{3}$ (No. 98) and $\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{~F}$ (No. 99) (see discussion on the reaction mechanism below) were included in the correlation with the Taft constant for the associative mechanism with CO by Hart. If these compounds and carboxylic compounds were removed from their correlation, a handful of compounds $(\mathrm{N}=4)$ would remain in close proximity, and a negative correlation between the $k_{\text {chem }}$ values and the sum of Taft constants would not be observed. Most likely, our extensive analysis of data ( $\mathrm{N}=66$ ) and the use of $E_{\text {red,aq }}^{\circ}$ values revealed a better comprehensive picture of the impact of functional groups.

Neighboring functional groups also affect the concerted cleavage mechanism of each C$\mathrm{Cl}, \mathrm{C}-\mathrm{NH}_{3}{ }^{+}$, and $\mathrm{S}-\mathrm{S}$ bond as well as the stepwise cleavage mechanism of each $\mathrm{C}-\mathrm{Cl}$ and S-S bond. The slopes of the correlations for $\mathrm{C}-\mathrm{Cl}$ bond cleavage for both concerted and stepwise mechanisms were found to be significantly steeper than those for $\mathrm{C}-\mathrm{N}$ and $\mathrm{C}-\mathrm{S}$ cleavages. The similar slopes of the correlations for $\mathrm{C}-\mathrm{Cl}$ bond between concerted and stepwise mechanisms indicate that the impact of neighboring functional groups is similar despite of the formation of intermediate species in the stepwise mechanism. While the Taft constants for $\mathrm{C}-\mathrm{C}$ bond cleavage were substantially different for various functional groups in the neighboring positions, the range of $E_{\text {red,aq }}^{\circ}$ values was within approximately 1 V . These results indicated the higher sensitivity of the $E_{\text {red,aq }}^{\circ}$ values associated with the properties of the electron-donating/withdrawing functional groups when compared with those examined for $\mathrm{C}-\mathrm{N}$ and $\mathrm{S}-\mathrm{S}$ bonds.


Figure 2.4. Sum of Taft constants against the theoretically calculated $E_{\text {red,aq }}^{\circ}$ values of each compound

### 2.3.4 Reaction Mechanisms

### 2.3.4.1 Associative Mechanism

When the $\pi$-fragment of a CO functional group is present in ketone, aldehyde and carboxylate, the initial injection of an electron occupies low-energy $\pi^{*}$-orbitals via associative mechanism to form a carbon-centered radical ${ }^{149,150}$. However, it is unclear whether association with $\mathrm{C}=\mathrm{O}$ is maintained or the stepwise cleavage of a $\mathrm{C}-\mathrm{X}$ bond occurs in the group of halooxygens. ${ }^{21,22,151}$ Our investigation of the PES of methyl trifluoroacetate (No. 39) and the product of radical anion as a function of one of dihedral angles showed the merging point of these PESs at approximately -70 degree (Figure A2 in Appendix A), indicating the possibility of stepwise mechanism. However, the spin density distributions of elongated C-F bond structures were located on the acetate carbonyl functional group with an increase in one of the C-F bonds, which confirmed the associative mechanism (Figure 2.5). Our investigation on the lowest unoccupied molecular orbital (LUMO)
represents no antibonding orbitals with regard to the C-F bond (Figure A3 in Appendix A), supporting the initial electron association with the CO functional group.


Figure 2.5. Distribution of charge (left) and spin density (right) of methyl trifluoroacetate (No.39) for different C-F bond lengths from top $1.324 \AA$ (optimized); $1.431 \AA, 1.538 \AA$, and $1.645 \AA$. The areas in dark blue indicate the high spin density.

The mesomeric effect described in the overall results move the reaction center from the $\mathrm{C}=\mathrm{O}$ functional group of carboxylic, ester, and acetamide compounds to the alkoxyl group of O . The partial positive charge generated on OH of carboxylic and alcohol, $\mathrm{C}-\mathrm{O}$ of ester, $\mathrm{C}-\mathrm{N}$ of acetamide is the site of $\mathrm{e}^{-}$aq addition in the mesomeric form, which were confirmed by our analysis on the charge distribution (Figure A4 in Appendix A). Although concerted cleavage of a C-O bond of esters or alcohol could occur, a better correlation of LFER for the association with O than those for the concerted cleavage of a $\mathrm{C}-\mathrm{O}$ bond is the evidence for the dominant associative mechanism (Figure A5 in Appendix A).
 are very close to or exceed the diffusion-limited rate. The association of $\mathrm{e}^{-}$aq with one of unsaturated carbons generates a radical anion intermediate described as a 3-electron 2orbital state of $\pi$ character ${ }^{22}$ with carbon atoms that are sp3 hybridized with a dangling lone pair of electrons on one carbon atom and an unpaired radical electron on the other carbon
atom. The initial injection of an electron produces a carbon-centered radical that further undergoes the reaction with second $\mathrm{e}^{-}{ }_{\text {aq }}$ to produce a stable unsaturated carbon after leaving the halogen functional group.

The group of nitro compounds include three $k_{\text {chem }}$ values for nitromethane (No. 200), 1nitropropane (No. 201), and nitroethane (No. 202). The $k_{\text {chem }}$ values for all the compounds are greater than $10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ exceeding the diffusion-limited. Our $E^{0}{ }_{\mathrm{aq}}$ values for the associative mechanism are approximately -1.6 V for all the compounds, whereas those for the concerted cleavage of $\mathrm{C}-\mathrm{NO}_{2}$ bond are approximately -2.2 V . This indicates the preference of the associative mechanism with $\mathrm{e}^{-}$aq and is supported by the spin density distribution on the $\mathrm{NO}_{2}$ functional group (Figure A6 in Appendix A). Due to the few datasets, we were not able to develop the LFER.

### 2.3.4.2 Concerted Dissociative Mechanism

## Haloalkane and Halocarboxylate

The concerted dissociative cleavage of a $\mathrm{C}-\mathrm{X}(\mathrm{X}=\mathrm{Cl}, \mathrm{Br}$, and I$)$ bond of haloalkanes is supported by the presence of $\sigma^{*}$ antibonding orbitals with respect to the $\mathrm{C}-\mathrm{X}$ bond. Injection of an electron into such orbitals is accompanied by the barrierless dissociation of the C-X bond and the reductive cleavage follows the concerted mechanism. ${ }^{21,22,152}$ Despite the fact that a carboxylate functional group was present in the given molecular structure of haloalkanes, we observed that the weak $\mathrm{C}-\mathrm{X}(\mathrm{X}=\mathrm{Br}$ and I$)$ bond of halocarboxylates underwent concerted reduction due to the inability to hold the $\mathrm{e}^{-}$aq. We investigated the spin density distribution in a given molecule to identify a possible attacking site by $\mathrm{e}^{-}$aq. The spin density distribution on four chlorinated carboxylates indicates the solvated electron was located on the carbon atom in the $\mathrm{C}-\mathrm{Cl}$ group (Figure A 7 in Appendix A), suggesting that the $\mathrm{C}-\mathrm{Cl}$ bond cleavage could occur upon the attack by the $\mathrm{e}^{-}-\mathrm{aq}$. It should be noted that we observed the significant elongation of a $\mathrm{C}-\mathrm{Cl}$ bond upon the structure optimization for 2-chloropropanoate ( $3.77 \AA$ of $\mathrm{C}-\mathrm{Cl}$ ) and trichloroacetate ( $3.58 \AA$ of $\mathrm{C}-\mathrm{Cl}$ ). These bond elongations suggests that the $\mathrm{C}-\mathrm{Cl}$ bonds may not cleave upon the attack by the solvated electron, and thus the stepwise reduction mechanism may occur. The $\mathrm{e}_{\mathrm{aq}}{ }_{\mathrm{q}}$ was likely held in the $\sigma^{*}$ antibonding orbital of chlorine, forming an intermediate radical anion species. Because of the uncertainty of the aqueous-phase PES, we were not able to confirm the dominant mechanism on these two chlorinated carboxylates.

The brominated and iodinated species appeared to undergo concerted reduction. In all radical anion structures, the $\mathrm{C}-\mathrm{X}(\mathrm{X}=\mathrm{Br}$ or I$)$ bond was elongated significantly and the $\mathrm{e}^{-}$ aq was located on the carbon of the C-X group (Figures A8 and A9 in Appendix A). Because we did not observe any associative mechanism of $\mathrm{e}^{-}{ }_{\text {aq }}$ with the $\mathrm{C}=\mathrm{O}$ functional group, the stepwise reduction mechanism seemed to be unlikely. The concerted mechanism is reasonable because the $\mathrm{C}-\mathrm{Br}$ bond strength is also relatively weak ( $285 \mathrm{~kJ} / \mathrm{mol}$ ) compared to $\mathrm{C}-\mathrm{Cl}$ and $\mathrm{C}-\mathrm{F}$, which is consistent with experimental finding ${ }^{23}$.

The C-N bond in general undergoes concerted dissociative cleavage. We determined two LFERs of ammonium compounds undergoing concerted and associative mechanisms and confirmed the concerted cleavage of a $\mathrm{C}-\mathrm{N}$ bond of ammonium functional group for the
rate determining step because of the strong correlation between $E^{\circ}{ }_{\text {red }}$ and $k_{\text {chem }}$ for this mechanism (Figure A10 in Appendix A). The group of cyanide included $3 k_{\text {chem }}$ values of acetonitrile (No.106), succinonitrile (No.107), and cyanamide (No.109). While the $k_{\text {chem }}$ value of acetonitrile was $10^{7}$-th order, the other two were $10^{9}$-th order. Our $E^{0}{ }_{\text {aq }}$ values for the concerted cleavage of $\mathrm{C}-\mathrm{CN}$ bond for these compounds ranged from -3.33 V to -3.06 V , whereas those for the association were from -3.64 V to -3.33 V . These indicate the preference of concerted cleavage of $\mathrm{C}-\mathrm{CN}$ bond to form cyanide ion $\left(\mathrm{CN}^{-}\right)$and carboncentered radicals. Our investigation on the spin density of cyanide compounds indicated the high spin density at the cyanide functional group (Figure A11 in Appendix A). Due to the small number of compounds, we were not able to develop the LFER.

The group of thiol contained 12 compounds containing at least one -SH functional group. As discussed above, the C-S bond is generally the weak point of a molecule because of its bond weakness in comparison to the $\mathrm{C}-\mathrm{C}$ and $\mathrm{C}-\mathrm{H}$ bonds. In the thiol compounds, the $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ likely attacks the C-S group and results in the immediate bond cleavage due to a lack of antibonding $\sigma^{*}$ orbitals on the -SH functional group to hold the extra electron. Or the $\mathrm{e}^{-}{ }_{\text {aq }}$ associates with the $\mathrm{C}=\mathrm{O}$ bond and loosens the $\mathrm{C}-\mathrm{S}$ bond to cleave in the stepwise mechanism. Among all compounds containing thiol functional group, we did not observe any clear LFERs for both mechanisms (Figure A12 in Appendix A). However, for thiols that do not contain $\mathrm{C}=\mathrm{O}$ functional group, we observed the acceptable LFER for concerted mechanism due to the limited number of data. Therefore, this class of compounds is likely reduced by the concerted mechanism, generating $\mathrm{R}^{*}$ and $\mathrm{HS}^{-} .{ }^{153}$

### 2.3.4.3 Stepwise Mechanism

## Halocarboxylates, Halooxygens, Chlorinated Amides, and Haloalkenes

We observed the consistent stepwise mechanisms for halocarboxylates (No. 49-59), halooxygens (No. 97-105), and chlorinated amides (No. 135 and No. 142) because of the presence of $\mathrm{COO}^{-}, \mathrm{OH}$ and CO functional groups, which are consistent with previous experimental observations ${ }^{20,21,22}$. When haloalkanes hold electron-withdrawing and $\pi$ acceptor functional groups or other $\pi$-fragments, the electrons may initially occupy lowenergy $\pi^{*}$-orbitals and the reduction of these molecules may result in the transient formation of radical anions. ${ }^{154}$ For the fluorinated carboxylates (No. 53 and 204-206), we determined the different trend from other halocarboxylates because of the abnormally strong C-F bond. While the optimized structure did not show the elongation of the C-F bond, our spin density observation of fluoroacetate confirms the association of $\mathrm{e}^{-}$aq with the carboxylate functional group (Figure A13 in Appendix A). In addition, the LUMO of fluoroacetates confirms antibonding orbitals with regard to the C-F bonds (Figure A14 in Appendix A). The singly occupied molecular orbitals (SOMO) of the vertically excited radical anions $\left(\mathrm{C}_{-} \mathrm{F}^{*}\right)^{*}$ are characterized by essentially the same shapes (Figure A15 in Appendix A). Geometry optimization of these intermediate radical anion resulted in the significant elongation of one of the C-F bonds and formation of the $\{\mathrm{C} \ldots \mathrm{F}\}^{\circ}$. The electronic structure of the radical anion intermediate as a 3-electron 2-orbital state of p character with carbon atoms that are sp 3 rather than sp 2 hybridized with a dangling lone
pair of electrons on one carbon atom and an unpaired radical electron on the other carbon atom.

Electron-withdrawing functional groups adjacent to a CO functional group induce a shortening of the $\mathrm{C}=\mathrm{O}$ bond ${ }^{155}$ (e.g., $1.30 \AA$ of $\mathrm{CF}_{3} \mathrm{COCH}_{3}$ (no. 98) and $1.31 \AA$ of $\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{~F}$ (no. 99) compared to $1.32 \AA$ of $\mathrm{CH}_{3} \mathrm{COCH}_{3}$ from our optimized structures), which leads to a lower electron density in the $\pi$ orbitals, resulting in the higher reactivity toward $\mathrm{e}^{-}$aq. However, the $k_{\text {chem }}$ values of $\mathrm{CF}_{3} \mathrm{COCH}_{3}$ and $\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{~F}$ do not appear to follow this trend and show substantially smaller rate constants (i.e., $10^{7}-10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ ) for associative mechanism. We propose that these two compounds undergo stepwise mechanism where $\mathrm{e}^{-}$aq associates with $\mathrm{CO} \pi$ bond and elongates the C-F bond, followed by the cleavage of the C-F bond. The $E_{\text {red,aq }}^{\circ}$ values of these compounds for the stepwise mechanism are -5.36 V for $\mathrm{CF}_{3} \mathrm{COCH}_{3}$ and -5.12 V for $\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{~F}$. We confirmed that these $E_{\text {red,aq }}^{\circ}$ values adhere to the LFER developed for halooxygen/halocarboxylate undergoing stepwise. It should be noted that the aqueous-phase PES of radical anions of these compounds (i.e., intermediate) as a function of dihedral angle has uncertainties in the energy values and we were not able to confirm the stepwise mechanism. Our investigation on the spin density distribution shown in Figures A16-A19 in Appendix A for both compounds provide the evidence of electron association and elongation of the C-F bond, which support the stepwise mechanism. Furthermore, the LUMO of both compounds (Figure A20 in Appendix A) was the evidence of stepwise cleavage that holds the electron in the one of the C-F bonds. Based on our investigation, we only propose stepwise mechanisms for these two compounds and further study is needed to confirm the reaction mechanism.

## Sulfides, Disulfides, Sulfoxide

A total of 8 compounds were investigated for the group of sulfides that contain a -C-S-Cfunctional group and disulfide that has a -C-S-S-C- functional group. We determined the LFER for the stepwise mechanism that cleave the C-S bond of sulfides and the S-S bond of disulfides. We did not observe any correlation for the concerted mechanism (Figure A21 in Appendix A). Although some sulfides (No. 186, 187, 191, and 192) contain $\mathrm{COO}^{-}$ functional group that implicates the initial association with $\mathrm{e}_{\mathrm{aq}}^{-}$, those functional groups are located far from the C-S and S-S sites and do not appear to impact the elongation of those bonds upon the injection of a first electron. Upon the attack by $\mathrm{e}^{-}$aq, the $\mathrm{S}-\mathrm{S}$ or $\mathrm{C}-\mathrm{S}$ bond initially elongates which results in a decrease in the energy of the antibonding $\sigma^{*}$ orbital that localizes over the elongated S-S or C-S bond. This antibonding orbital temporarily holds the $\mathrm{e}^{-}$aq for more than one vibration, creating a three-electron bonded radical anion intermediate structure CSSC* or a C-centered radical. ${ }^{156}$ After the formation of this radical anion, the S-S bond cleaves, resulting in the following products: RS* and RS ${ }^{-}$via a stepwise mechanism. ${ }^{157,158}$

The sulfoxide class (No. 173-175) has the characteristic of a central $\mathrm{S}=\mathrm{O}$ double bond. The presence of a $\pi$-bond which allows for electron localization, accessible antibonding $\pi^{*}$ orbitals, and two weak C-S bonds suggest that this class of compounds is reduced via the stepwise mechanism. The $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ likely attacks the sulfur atom, resulting in the elongation of
a C-S bond, as was observed in the sulfide and disulfide class. Simultaneously, the $\pi$-bond transforms into a $\sigma$ bond by shifting two electrons to the oxygen atom, creating a negative charge on the oxygen.

## Alkanes and Amines

Compounds belonging to alkane and amines are generally difficult to reduce due to a lack of electron withdrawing functional groups in their chemical structures. We estimated $E_{\text {red }}^{\circ}$ values for the alkane class to be low with the values ranging from -5.27 V to -5.41 V . The $k_{\text {chem }}$ values are also significantly small in the range from $10^{6}$ and $10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}$. For these reasons, we do not include any data in the groups of alkanes and amines in the analysis of LFERs.

### 2.3.5 Prediction of the Reactivities with PFASs

We investigate the reactivities of $\mathrm{e}^{-}$aq with the 75 priority PFAS subset from the U.S. EPA. The 75 PFASs were grouped based on the functional groups. The $E_{\text {red,aq }}^{\circ}$ values for (1) the associative mechanism with $\mathrm{C}=\mathrm{O}$ and influenced by $\pi_{C=O}^{*}$ orbitals, ${ }^{159,160}$ (2) the associative mechanism with O , and (3) the stepwise C-F cleavage mechanism for all possible attacking sites in a given PFAS are summarized in Table 2.2. Figure 2.7 displays the range of $E_{\text {red,aq }}^{\circ}$ values for the stepwise cleavage of a C-F bond at different positions for the selected groups of PFASs investigated in this study. For this plot, we used M06-2X/cc-pVDZ for both structural optimization and frequency calculations and used the LFER determined from the same method to avoid significant computational time. Notably, we verified that the trend of all energies from representative PFASs was consistent between M06-2X/cc-pVDZ and M06-2X/Aug-cc-pVTZ (Table A6 in Appendix A). The group of polyfluorocarboxylates (PFCAs) has 7 PFASs with $E_{\text {red,aq }}^{\circ}$ values in the range from -4.1 V to -2.3 V for the associative mechanism with $\mathrm{C}=\mathrm{O}$ and in the range from -7.3 V to -6.0 V for the stepwise C-F cleavage mechanism. From the largest $E_{\text {red,aq }}^{\circ}$ value in each reaction mechanism along with the LFER ( $\ln k_{\mathrm{chem}}=1.82 E_{\text {red,aq }}^{\circ}+27.80$ in Figure A22 in Appendix A), the $k_{\mathrm{chem}}$ values in neutral solution were predicted to range from $6.9 \times 10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ to $3.8 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for the associative mechanism and $4.5 \times 10^{6} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ to $2.1 \times 10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for the stepwise cleavage mechanism of a $\mathrm{C}-\mathrm{F}$ bond. The predicted $k_{\mathrm{chem}}$ values of perfluorobutanoic acid ( 3 carbon chains, $6.87 \times 10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ ), perfluorohexanoic acid ( 5 carbon chains, $6.66 \times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ ), perfluorooctanoic acid ( 7 carbon chains, $5.78 \times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ ) and perfluorononanoic acid ( 8 carbon chains, $7.96 \times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ ) for the associative mechanism with $\mathrm{C}=\mathrm{O}$ were in excellent agreement with the recently reported $k_{\exp }$ values of $(5.4 \pm 1.2) \times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for perfluorobutanoic acid, $(5.4 \pm 0.1) \times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for perfluorohexanoic acid, $(7.1 \pm 0.6) \times 10^{8}$ $\mathrm{M}^{-1} \mathrm{~s}^{-1}$ for perfluorooctanoic acid, and $(6.4 \pm 0.4) \times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for perfluorononanoic acid. ${ }^{151}$ Although this experimental study did not determine the mechanism for those measured rate constants, we believe they measured the rates of the associative mechanism. In contrast, the $k_{\text {exp }}$ values for C-F cleavage $\left(10^{6}-10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ were previously reported ${ }^{134}$ and used for the determination of our LFERs (compound No. 204-206), which confirm the significantly smaller $k_{\text {chem }}$ values of the stepwise cleavage mechanism of a C-F bond. The predicted $k_{\text {chem }}$ values in three reaction mechanisms for all 75 PFASs are shown in Figure 2.6. The $k_{\text {chem }}$ values that exceeded the diffusion limit $\left(3 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}\right.$ and $\left.\ln k=24.1\right)$ were not included
in either figure. The $k_{\text {chem }}$ values predicted for the 75 PFASs that undergo the stepwise cleavage mechanism of a C-F bond range from $6.9 \times 10^{7}$ to $3.7 \times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}$. In contrast, 19 $k_{\text {chem }}$ values range from $4.9 \times 10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ to $3 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for the associative mechanism with $\mathrm{C}=\mathrm{O}, 23 k_{\text {chem }}$ values range from $1.3 \times 10^{6}$ to $3 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for the associative mechanism with O , and $4 k_{\text {chem }}$ values are above the diffusion limit for the $\mathrm{C}=\mathrm{C}$ associative mechanism. We did not determine the LFERs for the functional groups of sulfonic acid $\left.\left(\mathrm{SO}_{3}\right)^{-}\right)$, phosphinic acid $\left(\mathrm{PO}(\mathrm{OH})_{2}\right)$, sulfonamide $\left(\mathrm{SO}_{2} \mathrm{NH}\right)$, and sulfonyl $\left(\mathrm{SO}_{2}\right)$; thus, no rate constant predictions were conducted. The investigation of the $E_{\text {red,aq }}^{\circ}$ values at all possible $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ attacking sites for all possible $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ reaction mechanisms highlights the significantly lower reactivity of $\mathrm{e}^{-}$aq for the stepwise cleavage mechanism of a C-F bond and higher reactivity of $\mathrm{e}^{-}$aq with functional groups in a given PFAS structure.


Figure 2.6. Predicted $\mathrm{k}_{\mathrm{chem}}$ values for PFASs. The $E_{\text {red,aq }}^{\circ}$ values were calculated based on structural optimization at the level of M06-2X/cc-pVDZ and single point energy calculation at the level of M06-2X/Aug-cc-pVTZ and the LFER developed based on the same method and basis set. (Note: refer to Figure A1 in Appendix A for information on how to read a box and whisker plot, and the meaning of the boxes, whiskers, and midpoints).

Table 2.2. The $E_{\text {red,aq }}^{\circ}$ values calculated for all possible attacking sites in PFASs

| Class | Compound Name | Attacking Site | 2D Structure | $E_{\text {red,aq }}^{\circ}(\mathrm{V}$ vs SHE) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Stepwise (C-F cleavage) | $\begin{array}{\|c\|} \hline \text { Concerted } \\ \text { (C-F cleavage) } \\ \hline \end{array}$ | Association w/ functional group |
|  | Perfluorobutanoic acid (PFBA) | alpha |  | -6.86 | -3.45 |  |
|  |  | beta |  | -7.13 | -3.69 | -4.10 |
|  |  | terminal |  | -7.46 | -4.05 |  |
|  | Perfluorooctanoic acid (PFOA) | alpha |  | -6.14 | -3.48 |  |
|  |  | beta |  | -6.28 | -3.62 |  |
|  |  | gamma |  | -6.25 | -3.58 |  |
|  |  | delta | , | -6.24 | -3.56 | $-3.50$ |
|  |  | epsilon |  | -6.30 | -3.55 |  |
|  |  | zeta |  | -6.30 | -3.60 |  |
|  |  | terminal |  | -6.66 | -4.01 |  |
|  | Perfluorohexanoic acid | alpha |  | -6.49 | -3.49 |  |
|  |  | beta |  | -6.60 | -3.62 |  |
|  |  | gamma |  | -6.63 | -3.56 | -3.46 |
|  |  | delta |  | -6.68 | -3.62 |  |
|  |  | terminal |  | -7.02 | -4.02 |  |
|  | Perfluorononanoic acid | alpha |  | -6.01 | -3.53 | -3.41 |
|  |  | beta |  | -6.12 | -3.65 |  |
|  |  | gamma |  | -6.10 | -3.60 |  |
|  |  | delta |  | -6.09 | -3.59 |  |
|  |  | epsilon |  | -6.12 | -3.57 |  |
|  |  | zeta |  | -6.12 | -3.52 |  |
|  |  | eta |  | -6.12 | -3.60 |  |
|  |  | terminal |  | -6.55 | -4.08 |  |
|  | Ammonium perfluorooctanoate | alpha |  | -6.14 | -3.48 | $-3.50$ |
|  |  | beta |  | -6.28 | -3.62 |  |
|  |  | gamma |  | -6.25 | -3.58 |  |
|  |  | delta |  | -6.24 | -3.56 |  |
|  |  | epsilon |  | -6.30 | -3.55 |  |
|  |  | zeta |  | -6.30 | -3.60 |  |
|  |  | terminal |  | -6.66 | -4.01 |  |





| Class | Compound Name | Attacking Site | 2D Structure | $E_{\text {red, }{ }^{\circ}(\mathrm{V} \text { vs SHE) }}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Stepwise (C-F cleavage) | $\begin{gathered} \text { Concerted } \\ \text { (C-F cleavage) } \end{gathered}$ | Association w/ functional group |
| Fluorotelomer Alcohols (FTOHs) | 4:2 Fluorotelomer alcohol | alpha |  | -6.86 | -3.71 | -4.20 |
|  |  | beta |  | -6.81 | -3.65 |  |
|  |  | gamma |  | -6.80 | -3.64 |  |
|  |  | terminal |  | -7.14 | -4.02 |  |
|  | 6:2 Fluorotelomer alcohol | alpha |  | -6.50 | -3.56 | -3.49 |
|  |  | beta |  | -6.45 | -3.46 |  |
|  |  | gamma |  | -6.40 | -3.38 |  |
|  |  | delta |  | -6.32 | -3.37 |  |
|  |  | epsilon |  | -6.39 | -3.43 |  |
|  |  | terminal |  | -6.78 | -3.87 |  |
|  | 4:4 Fluorotelomer alcohol | alpha |  | -6.60 | -3.68 | -3.93 |
|  |  | beta |  | -- | -- |  |
|  |  | gamma |  | -6.54 | -3.59 |  |
|  |  | terminal |  | -6.94 | -4.03 |  |
|  | 8:2 Fluorotelomer alcohol | alpha |  | -- | -- | -3.08 |
|  |  | beta |  | -6.07 | -3.32 |  |
|  |  | gamma |  | -6.05 | -3.28 |  |
|  |  | delta |  | -5.92 | -3.24 |  |
|  |  | epsilon |  | -5.92 | -3.24 |  |
|  |  | zeta |  | -5.99 | -3.25 |  |
|  |  | eta |  | -6.08 | -3.37 |  |
|  |  | terminal |  | -- | -- |  |
|  | 11:1 Fluorotelomer alcohol | alpha |  | -5.70 | -3.20 | -3.02 |
|  |  | beta |  | -5.68 | -3.12 |  |
|  |  | gamma |  | -5.58 | -3.05 |  |
|  |  | delta |  | -5.54 | -3.03 |  |
|  |  | epsilon |  | -5.55 | -3.01 |  |
|  |  | zeta | , | -5.53 | -3.01 |  |
|  |  | eta |  | -5.57 | -3.04 |  |
|  |  | theta |  | -5.52 | -3.01 |  |
|  |  | iota |  | -5.60 | -3.03 |  |
|  |  | kappa |  | -5.61 | -3.09 |  |
|  |  | terminal |  | -- | -- |  |





| Class | Compound Name | Attacking Site | 2D Structure | $E_{\text {redaq }}^{\circ}$ ( V vs SHE) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Stepwise (C-F cleavage) | Concerted $($ C-F cleavage $)$ | Association w/ functional group |
| Perfluoroalkyl Anhydrides | Pentafluoropropanoic anhydride | alpha terminal |  | $\begin{aligned} & -6.26 \\ & -7.12 \end{aligned}$ | $\begin{aligned} & -3.20 \\ & -4.06 \end{aligned}$ | -1.35 |
| Polyfluoroalkyl Acyl Fluorides | 5H-Octafluoropentanoyl fluoride | alpha <br> beta <br> gamma <br> terminal |  | $\begin{aligned} & -6.35 \\ & -6.80 \\ & -6.80 \\ & -6.91 \end{aligned}$ | $\begin{aligned} & \hline-3.17 \\ & -3.59 \\ & -3.59 \\ & -3.72 \end{aligned}$ | -1.74 |
| Polyfluoroalkyl Aldehydes | 5H-Perfluoropentanal | alpha <br> beta <br> gamma <br> terminal |  | $\begin{aligned} & \hline-6.34 \\ & -6.81 \\ & -6.85 \\ & -6.95 \end{aligned}$ | $\begin{array}{r} \hline-3.13 \\ -3.56 \\ -3.59 \\ -3.73 \\ \hline \end{array}$ | -1.74 |
|  | Sevoflurane | alpha <br> beta terminal |  | $\begin{aligned} & -7.08 \\ & -7.48 \\ & -7.50 \end{aligned}$ | $\begin{aligned} & -3.74 \\ & -4.12 \\ & -4.14 \end{aligned}$ | -2.67 |
|  | Flurothyl | terminal |  | -7.66 | -4.14 | -3.07 |
| Polyfluoroalkyl Ethers | Perfluoroisobutyl methyl ether | $\begin{gathered} \hline \text { alpha } \\ \text { beta } \\ \text { gamma } \\ \text { terminal } \\ \hline \end{gathered}$ |  | $\begin{aligned} & \hline-7.13 \\ & -6.46 \\ & -7.27 \\ & -7.26 \\ & \hline \end{aligned}$ | $\begin{aligned} & \hline-3.89 \\ & -3.17 \\ & -4.04 \\ & -4.02 \\ & \hline \end{aligned}$ | -2.16 |
|  | tris(Trifluoroethoxy)methane | terminal |  | -7.01 | -4.21 | -4.55 |
|  | Difluoromethyl 1H,1H-perfluoropropyl | alpha <br> beta terminal |  | $\begin{aligned} & -7.32 \\ & -7.03 \\ & -7.42 \end{aligned}$ | $\begin{aligned} & -4.07 \\ & -3.69 \\ & -4.10 \end{aligned}$ | -2.11 |








Figure 2.7. Theoretically calculated $E_{\text {red,aq }}^{\circ}$ values for the cleavage of a C-F bond at different positions of various PFASs. The $E_{\text {red,aq }}^{\circ}$ values were calculated based on M06-2X/cc-pVDZ. (Note: refer to Figure A1 in Appendix A for information on how to read a box and whisker plot, and the meaning of the boxes, whiskers, and midpoints).

The attachment of an $\mathrm{e}^{-}$aq to the group of PFCAs $(\mathrm{N}=8)$ occurred near the $\alpha$-carbon, and the resultant intermediate radical dianions were the most stable due to resonance stabilization by the $\pi$-system of carboxylate functional groups, which is consistent with previous predictions on $\mathrm{PFOA}^{152}$ and perfluoropentanoic acid (PFPeA) ${ }^{24}$. Attachment near the $\alpha$-carbon was also observed for the group of perfluoroalkyl phosphinates (PFPiAs) due to the phosphonate functional group, perfluoroalkyl ether carboxylates (PFECA), perfluoroalkyl amides, polyfluoroalkyl aldehydes and acyl fluorides, and semifluorinated alkenes (SFAenes). In contrast, the group of perfluoroalkane sulfonates (PFSA) (N=5) showed preferable attachment of an $\mathrm{e}_{\text {aq }}$ near the $\beta$ - or $\gamma$-carbon with the largest $E_{\text {red,aq }}^{\circ}$ values due to the inability of $\pi$-stabilization due to the trigonal geometry of the sulfonate functional group ${ }^{24}$. A similar trend was observed for the groups of fluorotelomer alcohols (FTOH) and polyfluorinated alcohols, fluorotelomer acrylates (FTACs), perfluoroalkane sulfonamides (FASAs), perfluoroalkane sulfonyl chlorides (PASCs), and fluorotelomer carboxylates (FTCAs). The investigation of the $E_{\text {red,aq }}^{\circ}$ values at all possible e ${ }_{\text {aq }}$ attacking sites for PFASs that contain a wide variety of functional groups highlights significant differences in regard to the most preferable reactive sites of $\mathrm{e}^{-}$aq. While the scope of the current study is on the initial reactivities of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ with a wide variety of organic compounds and PFASs, investigating the subsequent degradation pathways is underway. The cleavage of a C-F bond in a PFAS is the major goal for practical PFAS remediation using reductive technologies, and our LFERs and predicted $k_{\text {chem }}$ values for the stepwise cleavage mechanism of a C-F bond present significant challenges in cleaving a C-F bond from a kinetics point of view.

### 2.4 Practical Implications

For practical implications, we develop an unsteady-state kinetic model for the homogeneous aqueous-phase UV/sulfite system to degrade a model compound (e.g., PFAS) with input parameters that are consistent with experimental observations in the literature ${ }^{153}$ (Table 2.3 and 2.4). It should be noted that the model was used to assess the impact of the initial rate constant prediction accuracy on the time-dependent fate and the predicted results do not necessarily indicate the degradation of a model compound in an environmental matrix. Figure 2.8 represents the time-dependent concentration profile of a parent compound that has $k_{\text {chem }}=1.0 \times 10^{6} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ with $\mathrm{e}^{-}$aq. The profiles were also predicted by changing the $k_{\text {chem }}$ values by a difference of a factor of $1.2,2$, and 5 . Estimating the rate constant impacted the profile of the parent compound by $33 \%$ for $k_{\text {chem }}$ values with a factor of $1.2,77 \%$ with a factor of 2 , and $100 \%$ with a factor of 5.0 at 300 hrs . While our LFER for the C-F stepwise cleavage mechanism has the ability to predict the $k_{\text {chem }}$ values within the difference of a factor of 1.2, this prediction demonstrates the importance of an accurate rate constant of a target compound in estimating the decay of an environmentally relevant contaminant that requires significant amount of time (e.g., PFASs).

Table 2.3. Experimental conditions used for simulating the fate of a model compound in the UV/sulfite process.

| Parameter | Input Value |
| :---: | :---: |
| UV light type | 18 W LPUV |
| UV light intensity $\left(I_{0}\right)$ | 3.85 Einstein $/ \mathrm{L} \cdot \mathrm{S}$ |
| Effective path length $(b)$ | 2.85 cm |
| Volume $(V)$ | 572 mL |
| Quantum yield of sulfite $(\varphi)$ | 0.1 |
| Extinction coefficient of sulfite $(\varepsilon)$ | $17.7 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| Solution pH | 9.5 |
| Temperature | $20^{\circ} \mathrm{C}$ |
| Sulfite dose | 10 mM |

Table 2.4. Experimental reactions considered in the UV/sulfite model.

| Chemical Reaction | Second-Order Rate Constant |
| :---: | :---: |
| $\mathrm{UV}+\mathrm{HSO}_{3}-/ \mathrm{SO}_{3}{ }^{2-} \rightarrow \mathrm{SO}_{3}{ }^{-}+\mathrm{e}_{\mathrm{aq}}^{-}$ | See Table 2.3 |
| $\mathrm{e}_{\mathrm{aq}}{ }^{-}+\mathrm{R}(\mathrm{PFAS}) \rightarrow$ product | $\mathrm{k}_{1}=1.0 \times 10^{6} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ with a difference of a factor of 1.2, 2, 5 |
| $\mathrm{SO}_{3}^{\cdot}+\mathrm{SO}_{3}^{-} \rightarrow \mathrm{S}_{2} \mathrm{O}_{6}^{2-}$ | $2 \mathrm{k}_{2}=1.0 \times 10^{6} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ |
| $\mathrm{SO}_{3}^{\cdot}+\mathrm{SO}_{3}^{\cdot}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{SO}_{4}^{2-}+\mathrm{H}^{+}+\mathrm{HSO}_{3}^{-}$ | $\mathrm{k}_{3} / \mathrm{k}_{2}=0.37$ |
| $\mathrm{e}_{\mathrm{aq}}^{-}+\mathrm{H}^{+} \rightarrow \mathrm{H}^{\cdot}$ | $\mathrm{k}_{4}=2.3 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ |
| $\mathrm{e}_{\mathrm{aq}}{ }^{-}+\mathrm{H}^{-}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2}+\mathrm{OH}^{-}$ | $\mathrm{k}_{5}=3.0 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ |


| $\mathrm{e}_{\mathrm{aq}}^{-}+\mathrm{e}_{\mathrm{aq}}^{-}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2}+2 \mathrm{OH}^{-}$ | $2 \mathrm{k}_{6}=1.1 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ |
| :---: | :---: |
| $\mathrm{e}_{\mathrm{aq}}{ }^{-}+\mathrm{S}_{2} \mathrm{O}_{6}^{2-} \rightarrow \mathrm{SO}_{3}{ }^{2-}+\mathrm{SO}_{3}{ }^{-}$ | $\mathrm{k}_{7}=2.0 \times 10^{5} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ |



Figure 2.8. Time-dependent concentration of a target compound with $k_{\text {chem }}=1.0 \times 10^{6} \mathrm{M}^{-1} \mathrm{~s}^{-}$ ${ }^{1}$ and different predicted values by a difference of a factor of $1.2,2$, and 5 in UV/sulfite process ${ }^{153}$.

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## 3 Development of a Group Contribution Method to Predict the Aqueous-Phase Reactivities of Hydrated Electrons with Conventional and Emerging Groups of Organic Compounds

### 3.1 Introduction

Advanced reduction processes (ARPs) that generate reactive radicals (e.g., superoxide anion radicals ${ }^{1}$ ) and electrons in homogeneous solution ${ }^{2}$ and heterogeneous electrochemical ${ }^{3,4}$ or catalytic ${ }^{5}$ processes are effective in degrading the oxidized forms of organic and inorganic contaminants ${ }^{6,7}$. In particular, homogeneous, electrochemical, or a combination of both ARPs has been successfully applied to degrade conventional organic pollutants, such as alkyl halides ${ }^{3,4}$, and emerging groups of pollutants such as per- and polyfluorinated alkyl substances (PFASs) ${ }^{8}$.

While the second-order rate constants, $k_{\exp }$, of the hydrated electrons, $\mathrm{e}^{-}{ }_{\mathrm{aq}}$, for various conventional organic compounds and a limited number of fluorinated compounds were measured and compiled in the NIST dataset ${ }^{9}$, few studies have established prediction tools for the $k_{\text {exp }}$ values. Quantitative structure-activity relationships (QSARs) have been developed based on molecular descriptors ${ }^{10,11}$; however, such QSARs are highly empirical and molecular descriptors are not readily available. Therefore, if a large number of datasets are available in the literature, the group contribution method (GCM) is an attractive and promising approach for developing a computational tool to estimate the rate constant ${ }^{12-16}$. GCM fragments the structure of a given compound based on the reactivities with $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ and impacts of neighboring functional groups. The benefit of GCM is that it requires only structural information that may hold the physical chemical properties of functional groups.

Three major reaction mechanisms of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ with aliphatic organic compounds include (1) association with the $\pi$ bond of a double bond ${ }^{17}$; (2) concerted dissociative cleavage of a carbon halogen ( $\mathrm{C}-\mathrm{X}$, where $\mathrm{X}=\mathrm{F}, \mathrm{Cl}, \mathrm{Br}$, or I) bond of haloalkanes ${ }^{18}$ or a carbon-nitrogen (C-N) bond ${ }^{17}$; and (3) stepwise cleavage of a $\mathrm{C}-\mathrm{X}$ bond of haloalkanes and haloalkenes, a sulfur-sulfur (S-S) bond, or a carbon-sulfur (C-S) bond of sulfides or disulfides ${ }^{17}$. In our previous study, the calculation of aqueous-phase one-electron reduction potentials of all possible reactive sites of 250 organic compounds revealed the possible attacking site by $\mathrm{e}^{-}$ aq in the structure of a given molecule ${ }^{19}$. Furthermore, the functional groups present in the molecular structure were found to significantly impact the reactivity of $\mathrm{e}^{-}$aq. With the understanding that functional groups and chemical structure play a significant role in determining compound reactivity with $\mathrm{e}^{-}{ }_{\mathrm{aq}}$, the next logical step was to develop a GCM which is capable of estimating $k_{\text {chem }}$ for a wide variety of diverse organic compounds using only structural information.

In this study, we develop a GCM for $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ (GCMe) by fragmenting structures of a wide variety of conventional and emerging groups of compounds based on the mechanistic understanding of $\mathrm{e}^{-}$aq reactivities with those of organic compounds. We calibrate the parameters representing the reactivities with base structure and the impact from the
neighboring functional group for single functional group compounds with the $k_{\text {exp }}$ values. Then, the parameters are validated by comparing the estimated $k$ values for multiple functional group compounds. Finally, we predict the $k$ values for the emerging groups of PFASs. An MS Excel spreadsheet that can be used to calculate the $k$ values of hydrated electrons as supporting material is also provided. Such computational tools with inputs of only structural information will be useful to screen hundreds of organic compounds to prioritize the important group of compounds for degradation in an aqueous phase ARP. The tool can also be used to study the fate of a targeted compound degradation induced by $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ for the prior design and assessment of treatment feasibility.

### 3.2 Materials and Methods

### 3.2.1 Critical Data Evaluation

Experimentally measured $k_{\text {exp }}$ with $\mathrm{e}^{-}$aq for 262 structurally diverse aliphatic and aromatic compounds were obtained from the NIST database ${ }^{20}$. All $k_{\exp }$ values were critically evaluated based on the experimental conditions used in the original study, as described below. Deprotonated compounds measured at pH less than their $p \mathrm{Ka}$ values and vice versa were removed from the calibration due to experimental inaccuracies. All $k_{\text {exp }}$ values were corrected to an ionic strength of 0 M to ensure uniform experimental conditions ${ }^{21}$. When multiple experimental values were reported for a given compound, the statistical average of $k_{\text {exp }}$ values was adopted. The $k_{\text {exp }}$ for the chemical reaction was calculated for each compound to eliminate the impact of diffusion, as described in our previous study ${ }^{19}$.

### 3.2.2 Group Contribution Method for Hydrated Electrons

The basis of GCMe is that the overall second-order rate constant of a compound reacting with a single reductant, $\mathrm{e}^{-}$aq, is the sum of partial rate constants that can be estimated based on the Arrhenius kinetic theory ${ }^{22,23}$. The Arrhenius activation energy, $E_{\mathrm{a}}$, for each elementary reaction is the sum of the base $E_{\mathrm{a}}$, which is attributed to $\mathrm{e}^{-}$aq interacting with the reactive site and the $E_{\mathrm{a}}$ of the neighboring functional group(s) that contributes to the reactivity at the reactive site. Four major mechanisms of the reductant $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ with aliphatic compounds were included in the GCMe, which were (1) association with a carbon-oxygen double bond $(\mathrm{C}=\mathrm{O})^{17},(2)$ concerted or stepwise cleavage of a carbon-halogen bond $(\mathrm{C}-\mathrm{X}$, where $\mathrm{X}=\mathrm{F}, \mathrm{Cl}, \mathrm{Br}$, and I$)^{18}$, (3) association with a carbon-carbon double bond $(\mathrm{C}=\mathrm{C})^{17}$, and (4) interaction with sulfur ( S )- or nitrogen ( N )-atom-containing functional groups, including association and cleavage of a carbon-sulfur (C-S), a sulfur-sulfur (S-S), or a carbon-nitrogen $(\mathrm{C}-\mathrm{N})$ bond ${ }^{17}$. As for aromatic compounds, aforementioned four major reaction mechanisms occur on the side chain of a benzene ring (see details below). The partial second-order rate constant for each reaction mechanism was denoted as $k_{\text {aso-co }}, k_{\mathrm{clv}}$, $k_{\text {aso-CC, }} k_{\text {int-SN }}$, and $k_{\text {arm }}$ for association with $\mathrm{C}=\mathrm{O}$, cleavage of a $\mathrm{C}-\mathrm{X}$ bond, association with $\mathrm{C}=\mathrm{C}$, interaction with S or N , and interaction with the side chain of aromatic compounds, respectively. The overall second-order reaction rate of an organic compound, $k_{\text {overall }}$, can be written in an additive manner based on Benson's additivity of thermodynamics ${ }^{24}$, as shown in equation 1.

$$
\begin{equation*}
k_{\mathrm{overall}}=k_{\mathrm{aso}-\mathrm{CO}}+k_{\mathrm{clv}}+k_{\mathrm{aso-CC}}+k_{\mathrm{int}-\mathrm{SN}}+k_{\mathrm{arm}} \tag{1}
\end{equation*}
$$

The methods for determining each partial rate constant are described in the following sections.

### 3.2.2.1 Associative Mechanism

The high electron density in the orbitals above and below the $\pi$-bond of $\mathrm{C}=\mathrm{O}, \mathrm{C}=\mathrm{C}$, and the functional group(s) as well as the polarity caused by the electronegative oxygen create an electron deficiency in the carbon atoms, which is the association site of $\mathrm{e}^{-}$aq. Organic compounds containing $-\mathrm{CO}-\mathrm{NH}_{2}-$ or $-\mathrm{CO}-\mathrm{OR}-$ (where R is the functional group) showed lower reactivity with $\mathrm{e}^{-}$aq due to the mesomeric effect ${ }^{25}$, creating new electrophilic centers. Nevertheless, to avoid the increase in the number of calibration parameters, we accounted one unified association mechanism for $\mathrm{C}=\mathrm{O}$ among carboxylates, carboxylic acids, ester and amides. The neighboring functional group(s) contributes to the $E_{\mathrm{a}}$ at the reactive site with $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ by increasing or decreasing the $E_{\mathrm{a}}$ due to electron-withdrawing or -donating ability. Consequently, $k_{\text {aso }}$ can be written as follows:
where the structure is the base structure of $\mathrm{CO}, \mathrm{CC}$, or $\mathrm{SN}, A$ is the Arrhenius frequency factor that is constant under the same reaction mechanism in each base structure, $\mathrm{R}_{i}$ is the functional group of $i, R$ is the gas constant and $T$ is the absolute temperature. For example, for the base structure of CO , using the rate constant of $k_{\mathrm{CO}}$ and the group contribution factor, $X_{\mathrm{Ri}}$, of $\mathrm{R}_{i}$ functional group below,

$$
\begin{align*}
& k_{\mathrm{CO}}=A_{\mathrm{CO}} e^{-\left[E_{\mathrm{a} . \mathrm{CO}}^{0}\right]} / \mathrm{RT}  \tag{3}\\
& X_{\mathrm{R}_{i}}=e^{-E_{\mathrm{La.asococo}}^{\mathrm{R}_{i}}} / \mathrm{RT} \tag{4}
\end{align*}
$$

Thus, the partial rate constant for association with $\mathrm{C}=\mathrm{O}$ can be written as

$$
\begin{equation*}
k_{\mathrm{aso}-\mathrm{CO}}=k_{\mathrm{CO}} X_{\mathrm{R}_{i}} \tag{5}
\end{equation*}
$$

### 3.2.2.2 Concerted or Stepwise Cleavage of a C-X Bond

When a $\mathrm{C}-\mathrm{X}$ bond is present in a molecular structure, the bond is split by $\mathrm{e}^{-}$aq through the concerted or stepwise mechanism ${ }^{3,4}$. The neighboring functional group(s) of the $\mathrm{C}-\mathrm{X}$ bond impacts the cleavage by donating or withdrawing the electrons from the targeted $\mathrm{C}-\mathrm{X}$ bond. Consequently, the rate constant for the cleavage of a $\mathrm{C}-\mathrm{X}$ bond $k_{\mathrm{C}-\mathrm{x}}$ can be written as follows:

$$
\begin{equation*}
k_{\mathrm{C}-\mathrm{X}}=A_{\mathrm{C}-\mathrm{X}} \mathrm{e}^{-\left[E_{\mathrm{a} \cdot \mathrm{C} \cdot \mathrm{X}}^{0}+E_{\mathrm{a} . \mathrm{C} \cdot \mathrm{X}}^{\mathrm{R}_{i}}\right]} / \mathrm{RT} \tag{6}
\end{equation*}
$$

where the $E_{\mathrm{a}, \mathrm{C}-\mathrm{X}}^{0}$ is the $E_{\mathrm{a}}$ for the C-X bond split, and $E_{\mathrm{a}, \mathrm{C}-\mathrm{X}}^{\mathrm{R}_{i}}$ is the $E_{\mathrm{a}}$ of a functional group of $\mathrm{R}_{i}$ next to the $\mathrm{C}-\mathrm{X}$ bond. For example, for a $\mathrm{C}-\mathrm{Cl}$ bond, using the rate constant of $k_{\mathrm{C}-\mathrm{Cl}}$ and the group contribution factor of $\mathrm{R}_{i}$ functional group below,

$$
\begin{align*}
& k_{\mathrm{C}-\mathrm{Cl}}=A_{\mathrm{C}-\mathrm{Cl}} e^{-\left[E_{\mathrm{c}, \mathrm{Cl}}^{0}\right]} / \mathrm{RT}  \tag{7}\\
& Y_{\mathrm{R}_{i}}=e^{-E_{\mathrm{a}, \mathrm{C}, \mathrm{Cl}}^{\mathrm{R}_{i}}} / \mathrm{RT} \tag{8}
\end{align*}
$$

Thus, the partial rate constant for cleavage of $\mathrm{C}-\mathrm{Cl}$ can be written as

$$
\begin{equation*}
k_{\mathrm{clv}}=k_{\mathrm{C}-\mathrm{Cl}} Y_{\mathrm{R}_{i}} \tag{9}
\end{equation*}
$$

### 3.2.2.3 Interaction with S- or N-atom-containing Compounds through the Association or Cleavage of a C-S or a C-N Bond

Compounds containing S - or N -atoms undergo concerted dissociative cleavage or stepwise cleavage mechanisms ${ }^{17}$. The $\mathrm{C}-\mathrm{N}$ of an alkyl ammonium functional group and the $\mathrm{C}-\mathrm{S}$ bond of a thiol functional group undergo concerted cleavage due to a lack of antibonding $\sigma^{*}$ orbitals. The $S-S$ or $C-S$ bond initially elongates, resulting in a decrease of energy of the antibonding $\sigma^{*}$ orbital that localizes over the elongated $\mathrm{S}-\mathrm{S}$ bond or $\mathrm{C}-\mathrm{S}$ bond ${ }^{26}$. This antibonding orbital temporarily holds the $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ for more than one vibration, creating a three-electron bonded radical anion intermediate, $\mathrm{CSSC}^{*-}$ or C -centered radical ${ }^{27,28}$. From these mechanisms, the group rate constants were defined based on the structure of their reactive sites (e.g., $-\mathrm{C} \equiv \mathrm{N},-\mathrm{NH}_{3}{ }^{+},-\mathrm{NO}_{2}, \mathrm{NO},>\mathrm{C}=\mathrm{N},-\mathrm{SO}_{3}{ }^{-},-\mathrm{S}=\mathrm{O},-\mathrm{S}-$, $-\mathrm{S}-\mathrm{S}-,-\mathrm{SH},-\mathrm{S}^{-}$, and $-\mathrm{C}=\mathrm{S}$ ). The impacts of neighboring functional groups on the reactive site were not considered in the calibration for two reasons: (1) limited number of data available for calibration and (2) insignificant impact observed by neighboring functional groups on the $k_{\exp }$ values with the exception of a group of ammonium compounds. Consequently, the rate constant for the interaction with S - or N -atom-containing compounds $k_{\mathrm{SN}}$ can be written as follows:

$$
\begin{equation*}
k_{\mathrm{int}-\mathrm{SN}}=A_{\mathrm{SN}} e^{-\left[E_{\mathrm{aSN}}^{o}\right]} / \mathrm{RT} \tag{10}
\end{equation*}
$$

where the $A_{\mathrm{SN}}$ and $E_{\mathrm{a}, \mathrm{SN}}^{0}$ is the Arrhenius $A$ and $E_{\mathrm{a}}$ for the interaction with S - or N -atomcontaining functional group. For example, for a $-\mathrm{S}=\mathrm{O}$ bond, the partial rate constant of $k_{\text {so }}$ can be written as below,

$$
\begin{equation*}
k_{\mathrm{int}-\mathrm{SN}}=k_{\mathrm{SO}} \tag{11}
\end{equation*}
$$

Where

$$
\begin{equation*}
k_{\mathrm{so}}=A_{\mathrm{so}} e^{-\left[E_{\mathrm{a} . \mathrm{So}}^{0}\right]} / \mathrm{RT} \tag{12}
\end{equation*}
$$

### 3.2.2.4 Aromatic Compounds

As the reactivity of $\mathrm{e}^{-}$aq with benzene is low (i.e., $k_{\exp }=7.2 \times 10^{6} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ ) $29-32$, the presence of a functional group significantly impacts the reactivity (e.g., $k_{\exp }=10^{9}-10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for bromobenzene or nitrobenzene and $k_{\text {exp }}=2.28 \times 10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}^{33-35}$ ), indicating the negligible reactivity with the aromatic ring. Consequently, the reaction of $\mathrm{e}^{-}{ }_{\text {aq }}$ with the benzene ring was not included. This treatment can also be justified according to the experimentally observed reaction mechanisms with halo- and nitrobenzenes (i.e., nucleophilic substitution to form a negatively charged carbanion) ${ }^{36-39}$. Moreover, the localized reactions of $\mathrm{e}^{-}$aq with aromatic compounds support the major reaction occurring on the functional groups. Thus, only group rate constants on the alkyl side chain on the benzene ring were factored. For the di- and trifunctional groups on the benzene ring, the formation of a localized electron-deficient center is impacted by the functional groups and their locations ${ }^{17}$. Thus, isomers (i.e., the position of the functional group on the ring relative to a targeted bond) were accounted for using different group contribution factors. 27 group contribution factors were determined for isomers containing the nine branched functional groups: $-\mathrm{CH}_{3},-\mathrm{OH},-\mathrm{O}^{-},-\mathrm{COO}^{-},-\mathrm{F},-\mathrm{Cl},-\mathrm{Br},-\mathrm{I}$, and $-\mathrm{NH}_{2}$. Equation 13 represents the general equation for calculating $k$.

$$
\begin{equation*}
k_{\mathrm{arm}}=A_{\mathrm{R}_{i}}^{\prime} e^{-\left[E_{\mathrm{a} . \mathrm{amm}}^{0}+E_{\mathrm{a} . \mathrm{imm}}^{R}\right]} / \mathrm{RT} \tag{13}
\end{equation*}
$$

For mono-substituted benzene, only group rate constant represents the partial rate constant as below

$$
\begin{equation*}
k_{\mathrm{arm}}=A_{\mathrm{R}_{i}}^{\prime} e^{-\left[E_{\mathrm{a} . \mathrm{am}}^{0}\right]} / \mathrm{RT} \tag{14}
\end{equation*}
$$

By assigning the group rate constant for the side chain reactive site and the group contribution factor of functional group at the position relative to the reactive site,

$$
\begin{align*}
& k_{\text {(base) }}^{\prime}=A_{\text {(base) }}^{\prime} e^{-\left[E_{\text {a.amp(base) }}^{0}\right]} / \mathrm{RT}  \tag{15}\\
& \sum_{i} Z_{i}=e^{-\left(\sum E_{\text {a.amp(position) }}^{R_{i}} / \mathrm{RT}\right)} \tag{16}
\end{align*}
$$

For example, for a $\mathrm{C}-\mathrm{Cl}$ bond cleavage on the alkyl side chain of dichlorobenzene, the rate constant can be shown for 1,2-, 1,3-, and 1,4-dichlorobenzene, respectively as below

$$
\begin{align*}
& k_{\mathrm{arm}}=k_{\mathrm{C}-\mathrm{Cl}}^{\prime} Z_{\mathrm{C}-\mathrm{Cl}(\mathrm{o})}  \tag{17}\\
& k_{\mathrm{arm}}=k_{\mathrm{C}-\mathrm{Cl}}^{\prime} Z_{\mathrm{C}-\mathrm{Cl}(\mathrm{~m})}  \tag{18}\\
& k_{\mathrm{arm}}=k_{\mathrm{C}-\mathrm{Cl}}^{\prime} Z_{\mathrm{C}-\mathrm{Cl}(\mathrm{p})} \tag{19}
\end{align*}
$$

For the cleavage of a $\mathrm{C}-\mathrm{Cl}$ bond of 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, and $1,2,4$-trichlorobenzene ( $\mathrm{C}-\mathrm{Cl}$ bond at 1 position is cleaved and other two Cl functional groups impact the $\mathrm{C}-\mathrm{Cl}$ bond cleavage) can be written as

$$
\begin{align*}
& k_{\mathrm{arm}}=k_{\mathrm{C}-\mathrm{Cl}}^{\prime} Z_{\mathrm{Cl}(0)} Z_{\mathrm{Cl}(0)}  \tag{20}\\
& k_{\mathrm{arm}}=k_{\mathrm{C}-\mathrm{Cl}}^{\prime} Z_{\mathrm{Cl}(\mathrm{~m})} Z_{\mathrm{Cl}(\mathrm{~m})}  \tag{21}\\
& k_{\mathrm{arm}}=k_{\mathrm{C}-\mathrm{Cl}}^{\prime} Z_{\mathrm{Cl}(0)} Z_{\mathrm{Cl}(\mathrm{p})} \tag{22}
\end{align*}
$$

### 3.2.2.5 Datasets

A total of 262 structurally diverse aqueous organic compounds, including 181 aliphatic and 81 aromatic compounds in 24 groups based on the types of functional groups, are selected. While the NIST datasets ${ }^{20}$ contained 3 alkanes and 13 aliphatic amines, the $k_{\exp }$ values were between $10^{5}-10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}$, and the $k_{\exp }$ values did not vary significantly regardless the changes in the alkyl chain lengths and positions. More importantly, nucleophilic $\mathrm{e}^{-}{ }_{\text {aq }}$ does not react with alkyl and amine functional groups; thus, these $k_{\text {exp }}$ values in the GCMe development are not included. Further, $189 k_{\exp }$ values ( $72 \%$ ) are used for calibration and $73 k_{\exp }$ values ( $28 \%$ ) for validation. The compounds selected for calibration contain only a single reactive site in which only one mechanism occurs. This ensures the calibrated compounds are not impacted by other reaction mechanisms; for example, di-tert-butyl
 validation undergo multiple reduction mechanisms as they contain multiple reactive sites. For example, monomethyl fumarate $\left(\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOO}^{-}\right)$undergoes either association with $\mathrm{C}=\mathrm{C}$ or $\mathrm{C}=\mathrm{O}$. The parameters for aliphatic and aromatic compounds were separately calibrated to differentiate the impact of the ring structure on the branched functional groups in the aromatic compounds. For aliphatic compounds, group rate constants and group contribution factors associated with $\mathrm{C}=\mathrm{O}$ are calibrated first. Then, using these calibrated parameters, the other three mechanisms are subsequently calibrated. Hydrogen $(\mathrm{H})$ is used as a reference for the group contribution factors and is assigned a value of 1 . All parameters in the GCMe are determined by minimizing the objective function (OF) using the genetic algorithms ${ }^{40,41}$ in equation 23.

$$
\begin{equation*}
\mathrm{OF}=\sqrt{\frac{1}{N-1} \sum_{i=1}^{N}\left[\left(k_{\text {exp }, i}-k_{\text {calc }, i}\right) / k_{\text {exp }, i}\right]^{2}} \tag{23}
\end{equation*}
$$

where $k_{\text {exp }, i}$ and $k_{\text {calc, } i}$ are the experimentally determined and GCMe-calculated $k$ values of a compound $i$, respectively, and $N$ is the total number of compounds. The error goal (EG) of the calibration and validation were set to a difference of a factor of 2 and 5, respectively, to account for the experiment error of measurements by pulse radiolysis ${ }^{20,42}$.

### 3.3 Results and Discussion

### 3.3.1 Overall Results

Figure 3.1 plots the $k_{\text {calc }}$ values of 262 aliphatic and aromatic compounds against $k_{\text {exp }}$ values from both calibration and validation. Through calibration, 106 parameters, including 37 group rate constants and 69 group contribution factors, were determined with a total of 189 $k_{\text {exp }}$ values. Tables B1-5 in Appendix B show all the group rate constants and group contribution factors. Tables B6 and B7 in Appendix B contain all the values used in calibration and validation, respectively. It was found that $79 \%$ ( 150 compounds) and $92 \%$ ( 174 compounds) of the $k_{\text {calc }}$ values were within a difference of a factor of 2 and 5 from $k_{\text {exp }}$ values, respectively (Table 3.1). The OF value determined in equation 23 represents sample deviation (SD) ${ }^{43}$, in which the number of fitted data is distributed within one standard deviation from the mean value under the assumption of the normal sample distribution. The SD value weighs all $k_{\text {calc }}$ values equally; hence, the outweighed data point will not significantly impact the overall correlation. The least-square fit determines a correlation coefficient of $r^{2}$ as 0.86 . Although the approach is significantly different from our GCMe, the overall correlation of our GCMe appeared to be superior to those that were reported by QSARs, with an $r^{2}$ of 0.75 for aliphatic compounds ( $n=100$ ) and $r^{2}$ of 0.70 for aromatic compounds $(\mathrm{n}=147)^{10,11}$.

Next, using the calibrated group rate constants and group contribution factors, a total of 73 $k_{\text {exp }}$ multifunctional group compounds were calculated for validation. The SD value was 0.653 with $30 \%$ ( 22 compounds), and $53 \%$ ( 39 compounds) of the $k_{\text {calc }}$ values were within a difference of a factor of 2 and 5 from $k_{\text {exp }}$ values, respectively. Table 3.1 summarizes the statistical results with the total number of compounds used for calibration and validation.


Figure 3.1. Calculated $k_{\text {calc }}$ obtained through calibration and validation against the experimentally measured $k_{\exp }$ for 262 compounds with $\mathrm{e}^{-}{ }_{\text {aq. }}$. Horizontal error bars indicate the range of the reported experimental rate constants for a given compound.

Table 3.1. Summary of experimental data, parameters, and statistical results.

|  | Total | Calibration |  |  |  |  | Validation |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | \# of $k_{\text {exp }}$ | \# of $k_{\text {calc }}$ | \# of group rate constants | \# of group contribution factors |  | nd (\%) of ata <br> in EG <br> Factor of 5 | \# of $k_{\text {calc }}$ | Numberand <br> withi <br> Factor of 2 | (\%) of data <br> EG <br> Factor of 5 |
| Overall | 262 | 189 | 37 | 69 | 150 (79\%) | 174 (92\%) | 73 | 22 (30\%) | 39 (53\%) |
| Association with $\mathrm{C}=\mathrm{O}$ | 72 | 43 | 3 | 18 | 32 (74\%) | 37 (86\%) | 29 | 8 (28\%) | 13 (45\%) |
| Concerted or stepwise C-X cleavage | 43 | 29 | 5 | 9 | 25 (86\%) | 29 (100\%) | 14 | 5 (36\%) | 11 (79\%) |
| Association with $\mathrm{C}=\mathrm{C}$ | 20 | 16 | 6 | 9 | 13 (81\%) | 13 (81\%) | 4 | 1 (25\%) | 2 (50\%) |
| Association with S - or N -containing functional groups; cleavage of C-S or C-N | 46 | 20 | 12 | 1 | 17 (85\%) | 19 (95\%) | 26 | 8 (31\%) | 13 (50\%) |
| Aromatic compounds | 81 | 81 | 11 | 32 | 63 (78\%) | 76 (94\%) | 0 | -- | -- |

### 3.3.2 Association with a $\mathrm{C}=\mathrm{O}$ Bond

For the association mechanism with a $\mathrm{C}=\mathrm{O}$ bond, 43 compounds, including 5 carboxylates, 6 carboxylic acids, 4 alcohols, 5 esters, 3 ketones, 2 aldehydes, and 18 amides, were used to calibrate 3 group rate constants and 18 group contribution factors. The SD value of the calibration was 0.435 , with $74 \%$ ( 32 compounds) and $86 \%$ ( 37 compounds) of the datapoints falling within a difference of a factor of 2 and 5 , respectively. Three group rate constants were considered: (1) $k_{\mathrm{C}=\mathrm{O}}$ for carboxylates, carboxylic acids, esters, and acetamides, (2) $k_{\mathrm{O}}$ for alcohols, and (3) $k_{\mathrm{C}=\mathrm{O}(\mathrm{II})}$ for ketones and aldehydes owing to significantly higher reactivities than $k_{\mathrm{C}=0}{ }^{9}$. The group rate constant of $k_{\mathrm{C}=\mathrm{O} \text { (II) }}$ was also used in esters and amides that contain multiple carbonyl groups (such as dimethyl oxalate, malonamide, and biuret) because of the significantly larger $k_{\text {exp }}$ values due to the presence of a second $\mathrm{C}=\mathrm{O}$ functional group ${ }^{9}$. The alkyl functional group(s) in the medium position of dicarboxylate did not appear to impact the overall $k_{\text {exp }}$ values for oxalate, malonate, and succinate. Thus, one group contribution factor was assigned for $\mathrm{COO}^{-}, \mathrm{CH}_{2} \mathrm{COO}^{-}$, and $\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}$. In contrast, the number of $\mathrm{CH}_{2}$ alkyl functional groups in the medium position of dicarboxylic acid considerably impacted the $k_{\text {exp }}$ values, affording $k_{\text {exp }}$ in the range of $10^{8}-10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1} .{ }^{9}$ Thus, three separate group contribution factors were determined for $\mathrm{COOH}, \mathrm{CH}_{2} \mathrm{COOH}$, and $\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}$, respectively. Similar to the carboxylate functional groups, other functional groups that exhibited a similar impact on the overall $k_{\text {exp }}$ values were combined into a single group contribution factor to reduce the total number of parameters for calibration (e.g., alkyl functional groups of $\mathrm{CH}_{2}, \mathrm{CH}_{3}$, $\mathrm{CH}_{2} \mathrm{CH}_{2}, \mathrm{CH}_{2} \mathrm{CH}_{3}$, and $\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}$, alcohol functional groups of CHOH and $\mathrm{CH}_{2} \mathrm{OH}$, ether functional group of $\mathrm{OCH}_{3}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$, and $\mathrm{OC}\left(\mathrm{CH}_{3}\right)_{3}$, amine functional groups of NH and $\mathrm{NH}_{2}$, alkyl amine functional groups of $\mathrm{NHCH}_{2}, \mathrm{NHCH}_{3}$, and amide, and carbonyl functional groups of $\mathrm{NHC}=\mathrm{O}, \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}$, and $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}$ ).

The group contribution factors of $\mathrm{O}^{-}$in formate and $\mathrm{NH}_{2}$ in urea were determined using compound-specific group contribution factors as the $k_{\text {exp }}$ values were significantly smaller (i.e., $10^{5} \mathrm{M}^{-1} \mathrm{~s}^{-125}$ ) than those that were determined for other compounds $\left(10^{7}-10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$
because of the lack of any well-defined electrophilic center ${ }^{44}$. As GCMe determines the $\mathrm{O}^{-}$ and $\mathrm{NH}_{2}$ from longer chain functional groups, it is not able to account for those appeared in the smallest chain. This is a common issue in the GCM application for small molecular weight compounds observed for hydroxyl radicals as well ${ }^{45}$.

The validation process was conducted using the calibrated group rate and contributing factors for 29 multifunctional compounds, including 8 carboxylates, 3 carboxylic acids, 6 esters, 1 ketone, 3 amines, and 8 amides. The SD value was 0.69 , and $28 \%$ ( 8 compounds) and $45 \%$ ( 13 compounds) of the datapoints were within a difference of a factor of 2 and 5 , respectively. Methyl trifluoroacetate $\left(\mathrm{CF}_{3} \mathrm{COOCH}_{3}\right)$ was included as a validation compound in a group for association with $\mathrm{C}=\mathrm{O}$ even though it undergoes two types of mechanisms: stepwise cleavage of the $\mathrm{C}-\mathrm{F}$ bond and association with $\mathrm{C}=\mathrm{O}$. Our previous LFER study confirmed the associative mechanism during reduction based on potential energy surface, spin density, and lowest unoccupied molecular orbital investigations ${ }^{19}$.

### 3.3.3 Concerted or Stepwise Cleavage of a C-X Halogen Bond

For the cleavage mechanism of a $\mathrm{C}-\mathrm{X}$ halogen bond, a total of 29 compounds, including 10 haloalkanes, 5 halooxygens, 11 halocarboxylates, and 3 PFASs, were used to calibrate five group rate constants and nine group contribution factors. The SD value was 0.296, and $86 \%$ ( 25 compounds) and $100 \%$ ( 29 compounds) of $k_{\text {calc }}$ values were within a difference of a factor of 2 and 5 from $k_{\text {exp }}$ values, respectively. The calibration only used chlorinated haloalkanes because the $k_{\exp }$ values for all brominated and iodinated alkanes significantly exceeded the diffusion limit rate constants ${ }^{19}$. However, the group rate constants and group contribution factors of bromine- or iodine-containing compounds were calibrated from halooxygens and halocarboxylates. The compounds in the halooxygen and halocarboxylate groups contained two possible reactive sites undergoing: (1) cleavage of a $\mathrm{C}-\mathrm{X}$ bond and (2) association with a $\mathrm{C}=\mathrm{O}$ bond. For these compounds, group rate constants for the association previously determined were used to calibrate only the parameters for the cleavage mechanism.

The group rate constants for each of the four halogen atoms: $k_{\mathrm{C}-\mathrm{F}}, k_{\mathrm{C}-\mathrm{Cl}}, k_{\mathrm{C}-\mathrm{Br}}$, and $k_{\mathrm{C}-\mathrm{I}}(1.80$ $\times 10^{8}, 1.45 \times 10^{9}, 6.30 \times 10^{9}$, and $1.35 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$, respectively) were found to follow the trend with the bond dissociation energy of each $\mathrm{C}-\mathrm{X}$ bond ${ }^{46}$, indicating the consistency with the general physical-chemical properties of calibrated group rate constants. The $k_{\text {exp }}$ values of three PFASs-trifluoroacetate, perfluorobutanoic acid, and perfluorooctanoic acid-were included in the calibration. However, the $k_{\text {exp }}$ values were significantly smaller than those of other fluorinated compounds (e.g., fluoroacetone, methoxyflurane, and enflurane) due to the presence of long-chain alkyl groups and other functional groups ${ }^{47}$. Therefore, another group rate constant, $k_{\mathrm{C}-\mathrm{F}(\mathrm{II})}$, was determined $\left(9.52 \times 10^{4} \mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ for the group of PFASs. It should be noted that halogenated compounds with strong electronwithdrawing functional groups may undergo a stepwise mechanism where $\mathrm{e}^{-}{ }_{\text {aq }}$ associates with the electron-withdrawing functional group (e.g., $\mathrm{C}=\mathrm{O}$ ) and elongates the $\mathrm{C}-\mathrm{F}$ bond, followed by the cleavage of the $\mathrm{C}-\mathrm{F}$ bond ${ }^{3,4}$. Hence, to avoid this complication, current GCMe adapts only cleavage of any $\mathrm{C}-\mathrm{X}$ bond regardless of the concerted or stepwise mechanism. While this simplification of a $\mathrm{C}-\mathrm{X}$ bond cleavage did not appear to reflect the
embedded reaction mechanism, calibrated group rate constants and group contribution factors seemed to follow the general chemical and physical properties. A total of 14 multifunctional compounds, including 7 haloalkanes and 7 halooxygens, were used for the validation. The SD value was 0.53 , and $36 \%$ ( 5 compounds) and $79 \%$ ( 11 compounds) of $k_{\text {calc }}$ values were within a difference of a factor of 2 and 5 from the $k_{\text {exp }}$ values, respectively.

### 3.3.4 Association with a $\mathrm{C}=\mathrm{C}$ Bond

For the association with a $\mathrm{C}=\mathrm{C}$ bond, 16 alkenes were used to calibrate six group rate constants and nine group contribution factors. The SD value was 0.407 , and $81 \%$ ( 13 compounds) of $k_{\text {calc }}$ values were within a difference of a factor of 2 from $k_{\text {exp }}$ values. Six group rate constants were accounted for, including $k_{\mathrm{H} 2 \mathrm{C}=\mathrm{CH} 2,} k_{\mathrm{H} 2 \mathrm{C}=\mathrm{CH}}, k_{\mathrm{C}=\mathrm{CH} 2}, k_{\mathrm{HC}=\mathrm{CH}(\mathrm{cis})}$, $k_{\mathrm{HC}=\mathrm{CH}(\text { (rans }),}$ and $k_{\mathrm{C}=\mathrm{CH}}$, to ensure the structural impact from isomers and the number of functional groups to the reactivities with $\mathrm{e}^{-}{ }_{\text {aq. }}$. The determined group rate constants were found to increase with a smaller number of hydrogens on unsaturated carbon(s) (i.e., $k_{\mathrm{H} 2 \mathrm{C}=\mathrm{CH} 2}=1.50 \times 10^{5} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ vs. $k_{\mathrm{C}=\mathrm{CH}}=8.25 \times 10^{10} \mathrm{M}^{-1} \mathrm{~s}^{-1}$ ), indicating that the functional group(s) significantly enhances the reactivity for association with a $\mathrm{C}=\mathrm{C}$ bond. Our previous study determined that chlorinated alkenes (e.g., vinyl chloride $\left(\mathrm{CH}_{2}=\mathrm{CHCl}\right)$ and trans-1,2-dichloroethylene $(\mathrm{ClCH}=\mathrm{CHCl})$ ) were reduced solely through the association with a $\pi$-bond that is impacted by the presence of chlorine atoms ${ }^{19}$. Due to the limited number of available $k_{\text {exp }}$ values, the nearest functional group on the side chain of a $\mathrm{C}=\mathrm{C}$ bond and the next nearest functional group were integrated to be one group contribution factor. For example, $\mathrm{CH}_{2}, \mathrm{CH}_{2} \mathrm{CH}_{2}$, and $\mathrm{CH}_{2} \mathrm{NH}_{2}$ each were integrated into one group contribution factor, including $\mathrm{CH}_{2} \mathrm{OH}$ and CHOH for one, and $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ and $\mathrm{CH}_{2} \mathrm{CHOH}$ for one. A total of four alkenes were used for validation. The SD value was 0.74 , and $50 \%$ ( 2 compounds) of the $k_{\text {calc }}$ values were within a difference of a factor of 5 from $k_{\text {exp }}$ values.

### 3.3.5 Interaction with S - or N -atom-containing Compounds

For the association with $\mathrm{S}=\mathrm{S}$ and $\mathrm{NO}_{2}$ or cleavage of a $\mathrm{C}-\mathrm{S}$ or $\mathrm{C}-\mathrm{N}$ bond, 20 compounds, including one cyanide, 5 ammonia, one sulfate, 2 sulfoxide, 2 thiol, 1 sulfide, 1 disulfide, 1 S -, $2 \mathrm{CS}, 3$ nitro, and 1 imine were used to calibrate 12 group rate constants and one group contribution factor that represents alkyl functional groups (i.e., $\mathrm{CH}_{3}, \mathrm{CH}_{2} \mathrm{CH}_{3}$, $\mathrm{CH}_{2} \mathrm{CH}_{2}$, and $\left.\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$. The diversity in the structures of the reactive sites afforded the calibrated group rate constants ranging from $4.2 \times 10^{6}$ (i.e., $k_{\mathrm{S}=\mathrm{O}}$ ) to $2.7 \times 10^{10}$ (i.e., $k_{\mathrm{NO} 2}$ ). Most compounds used in the calibration contained only one S - or N -atom functional group, which reduced the degree of freedom to 8 and identical calibrated $k_{\text {calc }}$ values regardless of the length of the alkyl chain. For example, thiourea $\left(k_{\exp }=3.3 \times 10^{9}\right)^{48}$ and thiosemicarbazide $\left(1.2 \times 10^{9}\right)^{48}$ have identical $k_{\text {calc }}$ values of $1.38 \times 10^{9}$ because only one group rate constant, $k_{\mathrm{CS}}$, was calibrated for these compounds. Unfortunately, this is one limitation of the current GCMe. However, due to data scarcity, this approach was accepted for calibration and validation (see below). The SD value was 0.316, and 85\% (17 compounds) and $95 \%$ ( 19 compounds) of the $k_{\text {calc }}$ values that were within a difference of a factor of 2 and 5 from the $k_{\text {exp }}$ values, respectively.

A total of 26 multifunctional S - or N -atom-containing compounds were used for validation, including 1 sulfoxide, 3 cyanides, 1 ammonia, 2 hydrogen sulfides, 6 thiols, 6
sulfides/disulfides, 2 S-, 2 CS , and 3 imines. Using only one group rate constant for the same group of compounds, the $k_{\text {calc }}$ values for validation indicate identical values. Regardless of this limitation, the SD value was 0.706 , and $31 \%$ ( 8 compounds) and $50 \%$ ( 13 compounds) of the $k_{\text {calc }}$ was within a difference of a factor of 2 and 5 from the $k_{\text {exp }}$ values, respectively. The poor validation results for this mechanism can be attributed to the large number of unique reactive sites grouped into this mechanism and the scarcity of experimental data for the reactivity of S - and N -containing compounds with $\mathrm{e}^{-}$aq. The calibration dataset, which only contains 20 compounds, was used to calibrate individual group rate constants for 12 unique reactive sites. This mechanism has the smallest compound to group rate constant ratio ( $\sim 2: 1$ ) compared to the ratios for all of the other mechanisms incorporated into the GCMe (3:1-14:1). This greatly limits the ability of the GCMe in estimating accurate second-order rate constants for compounds undergoing this mechanism, as some of the group rate constants were determined using only a single compound ( $k_{\mathrm{C}=\mathrm{N}}, k_{\mathrm{SO} 3-}, k_{\mathrm{S}}, k_{\mathrm{S}-}, k_{\mathrm{N}=\mathrm{O}}, k_{\mathrm{C}=\mathrm{N}}$ ). Additionally, the very limited dataset made it impossible to determine group contribution factors for each of the reactive sites (with the exception of alkyl functional groups for $k={ }_{\mathrm{NH} 3+}$ because of its decent class size of $n=5$ ).

The combination of poorly calibrated group rate constants due to scarce data and the absence of group contribution factors resulted in poor validation results. However, this scarcity of data communicates two important findings. First, neighboring functional groups play a significant role in the reactivity of S - and N -containing compounds. For example, $k_{\text {pred }}\left(3.74 \times 10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ of compound no. 159 , cyanamide ( $\mathrm{H}_{2} \mathrm{NCN}$ ), is two orders of magnitude lower than $k_{\text {chem }}\left(1.60 \times 10^{9} \mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ because the impact of the $-\mathrm{NH}_{2}$ neighboring functional group could not be considered. Second, the impact of multiple reactive sites are not linearly additive. For example, compound no. 177, carbon disulfide ( $\mathrm{CS}_{2}$ ), contains two $-\mathrm{C}=\mathrm{S}$ reactive sites and no neighboring functional groups, yet, $k_{\text {pred }}$ of this compound (2.76 $\left.\times 10^{9} \mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ is estimated to be one order of magnitude lower than $k_{\text {chem }}\left(3.10 \times 10^{10} \mathrm{M}^{-1}\right.$ $\mathrm{s}^{-1}$ ). This could be a result of computation uncertainty because $k_{\mathrm{C}=\mathrm{S}}$ was determined using only two compounds, or because reactivity does not in fact increase linearly as the number of identical reactive sites increase within a compound. In order to confirm this speculation and to improve the overall accuracy of the GCMe for this mechanism, a larger experimental dataset is necessary.

### 3.3.6 Aromatic Compounds

For aromatic compounds with single- and multifunctional groups, 81 compounds, including 14 mono-, 58 di-, and 9 trisubstituted benzenes, were used to calibrate 11 group rate constants and 32 group contribution factors. First, only $k_{\text {exp }}$ values for monosubstituted benzenes were used to determine the group rate constants of 11 aliphatic functional groups on the benzene side chain. The group rate constants for di- and trisubstituted benzenes and group contribution factors using those calibrated group rate constants were determined. While there are common functional groups under the same reaction mechanisms between aliphatic and aromatic compounds (note: aliphatic side chains on a benzene ring), the impact of aromatic structure is in the localization of electron density of a benzene ring to form an electron-deficient center and the reaction on the side chain through association and cleavage of a $\mathrm{C}-\mathrm{X}$ bond ${ }^{44}$. Thus, we determined the group rate constants and contribution
factors separately for aromatic compounds. The SD was 0.348 , and $78 \%$ ( 63 compounds) and $94 \%$ ( 76 compounds) of the $k_{\text {calc }}$ values were within a difference of a factor of 2 and 5 from the $k_{\text {exp }}$ values, respectively. Due to limited data availability, we could not conduct the validation.

### 3.3.7 Relationships Between the Group Contribution Factors and Taft Constants

Figure 3.2 shows the relationship between calibrated group contribution factors and the Taft constant ${ }^{49}$. The Taft constant was used to determine the impact of neighboring functional group(s) on the main mechanisms in aliphatic compounds. In general, the reactivities of nucleophilic $\mathrm{e}^{-}$aq were enhanced by the presence of electron-withdrawing functional groups and reduced by the electron-donating ones. The positive slope of an overall correlation supports the general trend; functional groups with larger group contribution factors (i.e., more electron-withdrawing groups) correlate with the larger Taft constant. A group of greater electron-withdrawing functional groups (i.e., halogenated ones) appears with larger group contribution factors, followed by a group of oxygenated groups (i.e., carboxylate, carbonyl, and alcohols) and a group of amines and alkyl functional groups. The positive correlation verifies the physical-chemical properties of calibrated group contribution factors.

The purpose of Figure 3.2 is to show the positive relationship between Taft constants and the electron-withdrawing and -donating group contribution factors. While the positive correlation is clear, the correlation itself appears weak ( $r^{2}=0.57$ ), which results from three factors. First, group contribution factors were determined for each mechanism separately because the impact of the neighboring functional group varies slightly depending on which reactive site is present. For example, the Taft constant ( $\sigma^{*}$ ) for $\mathrm{O}^{-}$is approximately -3.0, but the group contribution factors $(\mathrm{Y})$ for this functional group range from approximately 0.0 to 0.5 for the mechanisms of association with $\mathrm{C}=\mathrm{O}$ and mono-, di-, and tri-substituted benzenes. Although the range for Y is relatively small among these three mechanisms, it creates a looser correlation among the datasets. Second, due to the limited dataset size, some functional groups were grouped into a single group contribution factor. For example, only a single group contribution factor was generated for $\mathrm{COO}^{-}, \mathrm{CH}_{2} \mathrm{COO}^{-}$, and $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}$even though each of these functional groups are associated with different $\sigma^{*}$. In these cases, the average of the Taft constants was taken and plotted against Y , which contributes to a weaker correlation. Finally, plotting all five mechanisms together (as shown in Figure 3.2) weakens the correlation because of the slight differences in the values generated for the group contribution factors. Each mechanism shows a positive correlation, but the slopes differ. Figure B. 1 in appendix B shows the Y versus Taft plot for only the C-X cleavage mechanism and has a much stronger correlation $\left(r^{2}=0.92\right)$ than the master plot.

The significant $\mathrm{e}^{-}$aq reactions with aromatic compounds occurred on the branched aliphatic chain of the benzene ring; thus, the Taft constants were also used to investigate the impact of these functional groups. Previously, a linear correlation was observed between the Hammett constants at para-position and the relative reactivity of various monosubstituted
benzenes to benzene, implying the reactivity of $\mathrm{e}^{-}{ }_{\text {aq }}$ with electrophilic centers ${ }^{44}$. Anbar and Hart discussed the limitation of Hammett constants and the additivity of the parameters and concluded that the reaction of $\mathrm{e}^{-}$aq may be rather localized, being impacted by the overall $\pi$-electron density of the monosubstituted functional group and the formation of the localized electron-deficient center by multifunctional groups ${ }^{35}$. For multifunctional compounds, the electron-donating functional groups at para-position reduced the overall reactivities with $\mathrm{e}^{-}{ }_{\text {aq }}$ the most compared to those at ortho- and meta-position due to the notable increases in the $\pi$-electron density of the ring by resonance effect. The electronwithdrawing functional groups at the para-position enhance the overall reactivities with $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ the most compared to those at ortho- and meta-positions due to induction's exceptional electron withdrawing effects. The observations here are consistent with the experimentally determined reactivities with multiple functional compounds on a ring.


Figure 3.2. Relationship between calibrated group contribution factors and the Taft constants

### 3.3.8 Prediction of Reaction Rate Constants of $\mathrm{e}^{-}$aq with PFASs

The presence of multiple potential reactive sites and a wide variety of functional groups, in addition to the $\mathrm{C}-\mathrm{F}$ bonds in PFASs, makes it challenging to predict the reactivities with $\mathrm{e}^{-}$aq. For validation and prediction, the EPA- 75 dataset ${ }^{50}$ was selected because of its structural diversity. However, the perfluoroalkyl phosphonic and phosphinic acid (PFPA \& PFPiA) classes were not included in the prediction due to the absence of phosphonate group rate constants and group contribution factors. Two overall rate equations were written to predict the corresponding reaction rate constants, including the cleavage of a C F bond and the sum of all reaction mechanisms. Figure 3.3 demonstrates a whisker plot of predicted rate constants with PFASs in different groups and Table B8 in Appendix B contain all validated and predicted rate constants for PFASs. A limited number of $k_{\text {calc }}$ values for the PFCA and PFSA groups were validated for both cleavages of a $\mathrm{C}-\mathrm{F}$ bond and overall reaction mechanisms based on the available $k_{\exp }$ values in the literature. The predicted overall rate constants ranged from $10^{8}$ to $10^{11} \mathrm{M}^{-1} \mathrm{~s}^{-1}$, whereas those with the C F cleavage ranged from $10^{6}$ to $10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}$, suggesting that electron-withdrawing functional groups that undergo association, such as $-\mathrm{C}=\mathrm{O},-\mathrm{SO}_{3}{ }^{-}$, and $>\mathrm{C}=\mathrm{C}<$, increased their reactivity with $\mathrm{e}^{-}$aq. Similarly, the alkenes and SFAene groups showed the greatest reactivities with $\mathrm{e}^{-}$aq due to the presence of the $\mathrm{C}=\mathrm{C}$ bond. The predicted $k_{\text {pred }}$ values for the overall mechanism in the groups of FTOH, polyfluoroalkyl ethers, and polyfluorinated alcohol were not shown due to insignificant differences in the $k_{\text {pred }}$ values observed between the cleavage of $\mathrm{C}-\mathrm{F}$ bonds and the overall mechanism. These differences are due to the presence of -OH and -O - functional groups that have low reactivity with $\mathrm{e}^{-}{ }_{\mathrm{aq}}$.


Figure 3.3. Validated and predicted reaction rate constants of $\mathrm{e}^{-}{ }_{\mathrm{aq}}$ with PFASs in EPA-75 priority PFAS datasets. (Note: refer to Figure A1 in Appendix A for information on how to read a box and whisker plot, and the meaning of the boxes, whiskers, and midpoints).

### 3.3.9 Limitation of GCMe and Engineering Implications

One of the limitations of GCMe is that it cannot estimate the rate constants for the reactions close to the diffusion-control limit because it is based on the group additivity of the rate constants. Additionally, the rate constant expression based on the thermochemical additivity may not thoroughly reflect the reaction mechanisms in the aqueous phase because of unknown reaction mechanisms. In addition, there are insufficient experimental datasets, as was discussed in section 3.3.5., leading to weakly calibrated group rate constants. As a result, the group contribution factors with the electron-donating and withdrawing abilities, i.e., the Taft constant, did not exhibit a strong correlation. Furthermore, the rate constants estimated by the GCMe are only as accurate as the experimental data on which they are based. The observed inconsistencies in the experimental data may have resulted from the difference in experimental protocols, such as the differences in the analytical approach, difference in the experimental environment (i.e. temperature, pH , ionic strength, sample purity), and mis-interpreted or -reported results. For the datasets that can be characterized by these inconsistencies and insufficiencies, additional experimental studies are required to obtain better calibration.

Although the GCMe used only experimentally reported rate constants based on the thermochemical additivity of the activation energies, the group contribution factors linearly correlated with the general inductive constants for most cases. In addition, the rate constants for the compounds with multifunctional groups were validated and compared with the experimental rate constants. The GCMe can be used to estimate most of the multifunctional group rate constants within a difference of a factor of $2(30 \%)$ and $5(53 \%)$ from the experimental values. This equates to $71 \%, 85 \%$, and $99 \%$ of the GCMe estimated rate constants for the validation compounds falling within one-half, one, and two orders of magnitude of the experimental rate constants, respectively. Therefore, the GCMe can be used to estimate the rate constants for many compounds with any type of functional groups for which we have sufficient data to calibrate the group rate constants and group contribution factors. Overall, the GCMe can be used to estimate the second-order rate constants of organic contaminants reacting with $\mathrm{e}^{-}{ }^{-}$aq within the EG , and this may be acceptable for the design of solvated-electron-based ARPs, depending on how sensitive the model is to the rate constants.

### 3.4 Chapter 3 References

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## 4 Development of a Biogarden to Demonstrate Sustainable Greywater Treatment in the Monteverde, Costa Rica Community.

### 4.1 Introduction

Goal 6 of the United Nations (UN) Sustainable Development Goals (SDGs) is to ensure global access to water and sanitation for all ${ }^{1}$. However, the UN's 2022 data indicates that six out of ten people globally lack access to safely managed sanitation facilities ${ }^{2}$, implying that large amounts of wastewater enter the environment untreated. Costa Rica, a developing country located in Central America, is no stranger to this concept. It is estimated that each Costa Rican uses approximately 187 liters of water per day, which is discharged as $\sim 85 \%$ greywater and $\sim 15 \%$ blackwater $^{3}$. While blackwater is typically treated by a decentralized septic tank combined with a drainage field, it is common practice to discharge greywater directly into roads, the environment, and in nearby bodies of water. This practice creates erosion, leads to eutrophication of water bodies, contaminates flora and fauna, and, when ponded, becomes a mosquito breeding ground ${ }^{4}$. According to the national Ley de Augas (water laws), all households and businesses are required to treat their greywater before discharging it into the environment. The law ${ }^{5}$ limits the discharge of biological oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids (TDS) to 40 $\mathrm{mg} / \mathrm{L}, 150 \mathrm{mg} / \mathrm{L}$, and $50 \mathrm{mg} / \mathrm{L}$, respectively, and limits fecal coliforms to less than 100 $\mathrm{cfu} / 100 \mathrm{~mL}$. Discharge water temperature and pH must fall within the ranges of $15^{\circ} \mathrm{C}$ $40^{\circ} \mathrm{C}$ and 5-9, respectively ${ }^{5}$. The Costa Rica water discharge laws are stricter than those established by the World Health Organization ${ }^{6}$. However, even with these established limits, minimal enforcement, small fines, and a widespread practice of dumping result in less than $4 \%$ of greywater in Costa Rica receiving treatment before discharge ${ }^{7}$.

The practice of dumping greywater is especially of concern in the Monteverde Zone because of its altitude of $1,300 \mathrm{~m}-1,600 \mathrm{~m}$. Located in north-western Costa Rica at the top of the Guacimal watershed, this zone is comprised of the towns of Monteverde, Santa Elena, and Cerro Planos, and is famously known for its 10,500 hectares ( 26,000 acres) Cloud Forest Reserve that is home to an abundance of biodiversity and attracts both tourists and scientists ${ }^{8}$. The Cloud Forest Reserve yields a large and consistent supply of fresh drinking water that is distributed to lower-altitude communities through the Rio Guacimal (Guacimal river) that outlets into the Pacific Ocean at sea level ${ }^{9}$. While this watershed plays a critical role in delivering drinking water to the many towns found within its $181 \mathrm{~km}^{2}$ area ${ }^{9}$, it also poses a serious issue: all greywater discharged in this watershed will flow to downstream communities, contaminating their drinking water supplies. This issue is especially of concern during Costa Rica's rainy season (May-October) because greywater discharged in roads and ditches is swept away by runoff, producing a larger organic load to the river.

A sociological study ${ }^{10}$ conducted in the Monteverde Zone identified three main barriers to greywater treatment in Costa Rica: no governmental involvement, lack of infrastructure, and cultural perception. While the government has taken the first step toward correcting the greywater discharge problem by establishing water laws, they have failed to create
infrastructure for treatment, provide funding and resources to communities, and educate their citizens on the importance of greywater treatment. This study found that the general public perceives greywater in the environment as a nuisance because of its strong odor and visually unappealing characteristics, however, many of them lack a general understanding of greywater beyond what can be observed by the five senses. It was determined that fewer than $50 \%$ of people surveyed understand the difference between greywater and blackwater, and, when asked to agree or disagree with the following statement, "greywater negatively affects my neighborhood", more than $75 \%$ disagreed. The few that did agree with this statement understand the negative impacts of greywater through the lens of personal loss, such as the death of livestock and crops from greywater contamination. These individuals have associated the term todo malo (all bad) with greywater. While the cultural view of greywater shows less than a basic understanding of the issue, a vast majority ( $89 \%$ ) of community members surveyed showed interest in learning more about greywater and how to effectively treat it.

Greywater can be broken down into two types: light and dark. Light greywater is wastewater resulting from human hygiene (i.e. showering, handwashing) and dark greywater is wastewater from laundry machines, dishwashers, and kitchen sinks ${ }^{11,12}$. There is a distinction between the two types of greywater because the latter often contains higher organic loads and may contain FOGs (fats, oils, grease). Compared to blackwater, both types of greywaters are characteristic of lower organic, nutrient, and pathogenic loading, making it possible to treat on-site. With laws in place, but no readily available infrastructure or resources, an affordable, decentralized, and environmentally friendly treatment system is necessary. Biojardineras, also known as biogardens, constructed wetlands, or reedbeds, (hereafter referred to as biogardens) are promising low-cost, lowenergy use, nature-based solutions for greywater treatment in Costa Rica and other developing countries ${ }^{13,14}$.

Biogardens are self-sustaining systems that depend on the symbiotic relationships between native aquatic plants, substrate, and microbial communities to form a biofilter that effectively treats greywater ${ }^{15-17}$. Biogardens are characterized as either surface flow or subsurface flow ${ }^{18,19}$ with the latter being the ideal choice because it can handle higher organic loads and is safer for the public ${ }^{20}$. The lack of an exposed water surface in this type of system greatly reduces the risk of humans coming into contact with the contaminated water and prevents the accumulation of disease-carrying insects. However, subsurface flow biogardens typically require a larger surface area than surface flow and are often more difficult to control once established ${ }^{21}$. Flow regimes in biogardens can be characterized as horizontal flow or vertical flow with the latter requiring intermittent feeding that is often achieved by a pump ${ }^{22}$. A schematic of a horizontal subsurface flow (HSSF) biogarden is shown in Figure 4.1. A standard biogarden is capable of treating water through the following chemical and physical processes: sedimentation, filtration, precipitation, adsorption, plant uptake, and microbial decomposition ${ }^{23,24}$. According to the literature, existing biogardens for greywater treatment in other tropical, developing countries, such as Singapore and Nicaragua, have exhibited $75 \%-95 \%$ removal of COD, BOD, phosphorus, nitrogen, and total suspended solids (TSS), proving their effectiveness ${ }^{25-28}$.


Figure 4.1. Cross-section schematic of a horizontal subsurface flow biogarden.
In this study, we develop a HSSF biogarden system on the Centro Educacion Creativa (CEC) campus in the Monteverde Zone to effectively treat the campus kitchen's greywater before it is discharged into the environment. This biogarden system serves as a local example of a nature-based solution to the greywater issue in Costa Rica. In addition to the engineering design and implementation of this system, we create a series of open-access tools and resources to aid in educating the public on the issue of greywater and naturebased treatment solutions. The combination of a working biogarden and the set of openaccess tools empowers community members with a thorough understanding of the greywater issue and the knowledge needed to successfully design and build their own biogarden system for their home or business. In a global context, this is one step closer to achieving SDG 6 and ensuring safe access to water and sanitation for all.

### 4.2 Materials and Methods

### 4.2.1 Preliminary Investigation

### 4.2.1.1 Site Investigation

In early September of 2021, I visited the CEC campus (located at 85CJ+3M8, Carretera Monteverde a Tilaran) where I met with the principal and staff to understand water usage and discharge on their campus. I also received a site tour where I inspected the existing greywater drainage system and determined if any of the existing infrastructure could be repurposed for the biogarden. Conversations with the kitchen staff revealed the kitchen use and cleaning schedules. During the academic year (mid-August through the end of May), the kitchen is typically used between the hours of 8am and 4pm Monday through Friday and anywhere from 25 to 50 meals are prepared each day. Meals are prepared for the $\sim 25$ staff members and any students who signed up for school lunch that day. Approximately four times a year on special occasions, the kitchen staff will prepare meals for all students
and staff (125-175 people). When important guests visit the school (i.e. politicians, external teachers), which occurs about once a month, the kitchen staff will prepare additional meals for them. Occasionally, the kitchen will also be used for cooking classes. During the month of July, classes are not in session, but the campus and kitchen are used for various summer camps throughout the month. The only times during the year when the campus and kitchen are officially closed are the month of June and approximately 3 weeks in December/January for the holiday break. The kitchen is cleaned on an as-needed basis with a minimum cleaning of once per week. Only biodegradable cleaners are used on the sink.

Ingredients typically used for food preparation in the CEC kitchen include vegetables, fruit, tuna, red and white meat, eggs, dairy products, animal fats, oils (fish oil, avocado oil, vegetable oil), legumes, and grains. The kitchen staff shared that food scraps are disposed of in the campus compost bin and in the kitchen sinks, and grease is disposed of in the kitchen sinks. Inspection of the kitchen sinks revealed that no drain strainers were installed and thus both food scraps and grease could enter the drainage system. Upon further inspection of the existing drainage system, I observed a buildup of organic matter and solidified grease that was presumably multiple years old, suggesting that heavily contaminated greywater was entering the environment. The kitchen greywater is discharged to a heavily vegetated area near the southeast end of campus that is approximately 40 meters from the kitchen (Figure 4.2). I verified that there are no bodies of water within a 100 -meter radius of this discharge point.


Figure 4.2. Centro Educacion Creativa campus, located in the Monteverde Zone.

### 4.2.1.2 Hydraulic \& Chemical Loading

In September of 2021, I took a set of baseline effluent water quality samples of the kitchen greywater to measure various parameters. Temperature, pH , conductivity, TDS, salinity, and dissolved oxygen (DO) were measured with the USI 556 MPS probe and turbidity was measured using the LaMotte 2020we device. The MPS probe and LaMotte device were provided by the Monteverde Institute (MVI) and calibrated per the manufacturer's instructions. Due to limited equipment at MVI, COD, BOD, nitrate ( $\mathrm{NO}_{3}{ }^{-}$), and phosphate $\left(\mathrm{PO}_{4}{ }^{3-}\right)$ were measured by the Escuela de Ingeniería de Biosistemas at the University of Costa Rica (UCR). COD, $\mathrm{BOD}, \mathrm{NO}_{3}{ }^{-}$, and $\mathrm{PO}_{4}{ }^{3-}$ samples were analyzed per the U.S. EPA reactor digestion method (Hach method 8000), the dilution method (Hach method 8043), the salicylate method (Hach method 8155), and the U.S. EPA PhosVer 3 (ascorbic acid) method (Hach method 8048), respectively. Note that UCR did not possess BOD analysis equipment until 2023 and thus BOD measurements will be missing from 2021 and 2022 data tables in the results section. All water samples were collected in 2 mL plastic vials and taken from an accessible concrete drainage basin that was connected to the kitchen's discharge pipe. Samples taken by the Escuela de Ingeniería de Biosistemas team were stored in a cooler on ice during transport to the UCR lab and were then stored in a freezer until the team was ready to run the analysis. All samples collected by UCR were analyzed within 24 hours of collection. To determine hydraulic loading, the campus kitchen's weekly greywater discharge volume was tracked over the next month using an existing mechanical water meter that was installed on the kitchen's effluent water pipe.

### 4.2.1.3 Storm Events

Because the biogarden system will be open to the atmosphere, it was necessary to analyze historical rainfall data to determine the amount of rainwater that would enter the biogarden during storm events which will impact hydraulic residence time. With many unique microclimates spread throughout Costa Rica, the annual rainfall varies significantly across regions. Therefore, it was vital to use rainfall data that was collected at a weather station close to the CEC in order to ensure the most accurate possible consideration of precipitation. MVI, which has a micro weather station that collects rainwater data and is located only 1.8 km from the CEC, was determined to be the nearest weather station. Daily, monthly, and yearly rainfall data from the most recent 12 years (2010-2021) was gathered from the micro weather station and used for analysis.

### 4.2.1.4 Plant Research

In order to learn about native macrophytes with long root structures that will work well in the CEC biogarden, I consulted multiple books on native flora ${ }^{29}$ and spoke with the local plant specialist, Willow Zuchowski. The criteria for plant selection were based on the microclimate of the biogarden location and included the following: ability to (1) survive at an altitude of $1,300 \mathrm{~m}$ with annual temperature ranges of $15^{\circ} \mathrm{C}$ to $29^{\circ} \mathrm{C}$, (2) grow well in a partially-shaded environment, and (3) survive periodic droughts and floods which will occur during the dry and wet seasons, respectively. Research was also conducted on plant species that were successfully implemented in other biogardens in the surrounding areas, such as the biogarden on MVI's property.

### 4.2.2 System Design

Based on the effluent water quality results from chemical testing, the following system components were determined to be necessary for effective treatment of the CEC kitchen greywater: primary filtration, grease trap, settling tank(s), HSSF biogarden basin, and a clarifier. Simple mesh strainers that cover the sink drains were selected for primary filtration with the purpose of preventing food waste and large particles from entering the system. The grease trap was sized and designed per the International Plumbing Code ${ }^{30}$ specifications for a small industrial-sized kitchen. The settling tanks and clarifier were sized for gravitational settlement of sand- and gravel-sized particles using Stoke's Law (equation 1) where $v_{\mathrm{s}}$ is the settling velocity of the particle, $g$ is gravity, $\mathrm{p}_{p}$ and $\mathrm{p}_{w}$ are the densities of the particle and water, respectively, $d_{\mathrm{p}}$ is the diameter of the particle, and $\mu$ is the dynamic viscosity. Values for $\mathrm{p}_{p}, \mathrm{p}_{w}, d_{\mathrm{p}}$, and $\mu$ were taken from online databases, assuming an average water temperature of $20^{\circ} \mathrm{C}$.

$$
\begin{equation*}
v_{s}=\frac{g\left(\rho_{p}-\rho_{\omega}\right) d_{p}^{2}}{18 \mu} \tag{1}
\end{equation*}
$$

To ensure particles will settle out during the settling tank hydraulic residence time, critical settling velocity was calculated which is the minimum rate at which a particle must settle in order to reach the sludge zone before it exits the basin. Critical settling velocity or $v_{\mathrm{c}}$ is calculated using equation 2 where $Q$ is the process flow rate and $A$ is the area of the top of the basin settling zone. Particles with a settling velocity $v_{\mathrm{s}}$ greater than or equal to $v_{\mathrm{c}}$ will settle out of the water before it flows out of the tank.

$$
\begin{equation*}
v_{c}=\frac{Q}{A} \tag{2}
\end{equation*}
$$

The design of the HSSF biogarden basin was centered around achieving a minimum removal efficiency of $78 \%$ for COD in order to ensure the treated water complies with the legal discharge limit ( $150 \mathrm{mg} / \mathrm{L}$ ). Since the system will be located on a school campus, a subsurface flow style was selected for the biogarden to reduce the risk of students coming into contact with the greywater and to prevent the accumulation of possible diseasecarrying insects, such as mosquitos. A horizontal flow regime was selected over a vertical flow regime because it does not require a pump and campus space was not an issue. The biogarden design was based off of an ideal plug-flow reactor (PFR) with attached biological growth because water is expected to flow through the basin as a plug at a slow rate with little mixing occurring. However, tracer study results have shown that the effluent curve of biogardens does not match that of an ideal PFR, and thus it is argued that PFR kinetics do not apply to subsurface flow biogardens ${ }^{31-33}$. While biogardens will typically never behave ideally because they are a nature-based system, the effluent curves resemble that of a PFR much more closely than that of a completely mixed flow reactor (CMFR), and thus the PFR model is the most appropriate choice for subsurface flow biogarden design ${ }^{34}$. Additionally, studies have shown that subsurface flow biogarden effluent curves are similar to those of facultative ponds and other wastewater treatment systems that are designed around the assumption of PFR conditions ${ }^{34}$, further solidifying the choice to
design the CEC biogarden based on a PFR. The mass balance for an ideal PFR is shown in equation 3 where $Q$ is the maximum possible greywater discharge entering the biogarden, $C$ is the concentration of the pollutant of interest (in this case, COD), $V$ is the basin volume, $r$ is the reaction rate, and $t$ is time. In this mass balance, both $V$ and $t$ are independent variables that influence $C$, the dependent variable.

$$
\begin{equation*}
-Q \frac{\partial C}{\partial V}+r=\frac{\partial C}{\partial t} \tag{3}
\end{equation*}
$$

The 10-year storm event was also considered because the proposed location of the biogarden is open to the atmosphere. A water balance for the biogarden basin is shown below in equation 4 where $I_{\mathrm{B}}$ is inflow to the biogarden from the settling tanks, $P$ is precipitation, $O_{\mathrm{B}}$ is outflow from the biogarden to the clarifier, ET is evaporation and transpiration, and $\Delta S$ is the change in storage (volume of water in the basin). Note that the biogarden will be constructed so that no runoff enters the basin, hence why a term for runoff is not included in the water balance.

$$
\begin{equation*}
I_{\mathrm{B}}+P-O_{\mathrm{B}}-E T=\Delta S \tag{4}
\end{equation*}
$$

In addition to assuming an ideal PFR for design purposes, the biogarden was also assumed to perform at steady-state. It is important to note that, under normal operating conditions, the biogarden will not perform under steady-state conditions due to fluctuations in the hydraulic and chemical loading that result from the school's kitchen use schedule. However, in order to ensure the biogarden effectively treats the greywater during a possible maximum discharge event, steady-state performance with a consistent maximum hydraulic and chemical loading entering the biogarden is assumed for design purposes. Under the steady-state assumption, equation 3 can be solved for hydraulic residence time $(\tau)$ to yield equation 5 where $C_{0}$ and $C$ are the initial and final concentrations of COD, respectively, and $k_{\mathrm{A}}$ is the approximate first-order kinetic constant for COD degradation by microorganisms. Since $k_{\mathrm{A}}$ could not be measured due to a lack of equipment, an approximate value was taken from a study ${ }^{35}$ that measured the rate of COD degradation in by microorganisms in a tropical biogarden environment.

$$
\begin{equation*}
\tau=\frac{1}{k_{\mathrm{A}}} \ln \left(\frac{C_{0}}{C}\right) \tag{5}
\end{equation*}
$$

With the knowledge that $\tau=V / Q$, equation 5 can be rearranged to yield equation 6 where $A$ is the surface area of the biogarden, and $W$ and $L$ are the width and length of the biogarden, respectively. Equation 6 can be solved for $A$ using known values for $Q, k_{\mathrm{A}}, C_{0}$, and $C$.

$$
\begin{equation*}
A=W L=\frac{Q}{k_{\mathrm{A}}} \log \left(\frac{C_{0}}{C}\right) \tag{6}
\end{equation*}
$$

Values for $W$ and $L$ were determined using the 3:1 length-to-width ratio constraint per the United State Environmental Protection Agency (U.S. EPA) constructed wetland guidelines ${ }^{34}$. The height of water in the biogarden, $H$, was determined using the U.S. EPA constraint of limiting the maximum water depth to 0.6 m when the $3: 1$ ratio is used for length and width ${ }^{34}$. These two constraints ensure that a low hydraulic gradient can be achieved which will help to maintain flow conditions that are nearly laminar. The water depth constraint is based on the average root depth of macrophytes. Biogardens that are designed outside of this constraint will have depths that exceed the macrophyte root penetration depth, resulting in an uneven distribution of oxygen throughout the bed profile and possible dead zones which will in turn affect the efficiency of nitrification processes and microbial degradation of other contaminants. The grade of the biogarden basin was calculated with the purpose of maintaining an appropriate hydraulic gradient during times when there is no hydraulic loading to the biogarden.

With a known $L, W$, and $H, \tau$ for effective COD removal can be calculated using equation 7 below where $\varepsilon$ is the porosity of the substrate and Q includes the rate of rainfall entering the biogarden during the 10 -year storm event.

$$
\begin{equation*}
\tau=\frac{\varepsilon W H L}{Q} \tag{7}
\end{equation*}
$$

With all biogarden parameters determined, the next step involved calculating the flow limit that should not be exceeded to ensure subsurface flow conditions can be maintained. Darcy's law, which describes the flow regime through a porous media, is shown in equation 8 below where $Q_{\text {limit }}$ is the flow limit for subsurface conditions, $k_{\mathrm{s}}$ is the hydraulic conductivity of the substrate, $S$ is the hydraulic gradient of the surface of the water, and $A$ is the cross-sectional area of the biogarden perpendicular to flow (i.e. $W \times H$ ). It is common practice to determine the "effective" $k$ s for a system by performing tests that involve measuring hydraulic conductivity under a variety of hydraulic gradients. However, due to limited resources, these pre-design tests could not be conducted, so, instead, an appropriate value for $k_{\mathrm{S}}$ was selected from the available databases.

$$
\begin{equation*}
Q_{\text {limit }}=k_{\mathrm{S}} \times A \times S \tag{8}
\end{equation*}
$$

Physical limitations exist that make Darcy's law not strictly pertinent to the design of subsurface flow biogardens, specifically: (1) Darcy's law assumes laminar flow conditions which is not fully accurate as some turbulence is expected because of the gravel-sized substrate, and (2) a constant and uniform flow is also assumed which is unlikely because the flow will presumably vary throughout the biogarden basin due to the hydrologic cycle (evaporation and precipitation), and short circuiting may also occur because of uneven substrate porosity ${ }^{34}$. Nonetheless, Darcy's Law is the most applicable and accessible model for use in the design of subsurface flow biogardens ${ }^{34}$. The use of Darcy's Law becomes even more appropriate when the following system conditions ${ }^{34}$ are met: (1) the substrate used is $<4 \mathrm{~cm}$ in size, (2) the biogarden basin is constructed in a way that minimizes the possibility of short circuiting, (3) the design is based on the smallest possible hydraulic
gradient, and (4) $Q_{\text {limit }}$ is assumed to be an average flow that accounts for gains and losses that may occur with precipitation and evaporation. We determined our biogarden basin to meet these conditions and thus Darcy's Law is applicable.

Because the settling tanks are only sized to remove sand- and gravel-sized particles during maximum flow events, there is a chance that silt- and clay-sized inorganic particles will accumulate in the biogarden basin overtime, impacting the hydraulic conductivity and flow conditions. Thus, to account for this, the following safety factors ${ }^{34}$ were included in the calculation of $Q_{\text {limit: }}$ (1) $k_{\mathrm{s}}$ was set to be $1 / 3$ of its effective value and (2) the value used for $S$ was $<10 \%$ of its maximum potential. If $Q_{\text {limit }}$ is calculated to be greater than $Q$, then the necessary pressure head to overcome resistance to flow through the substrate is available and thus subsurface flow conditions will be maintained ${ }^{34}$.

The selection of the plastic liner and the substrate was limited to what was available to be sourced locally for little to no cost. A locally available medium-sized gravel substrate with a size of 4 cm and an approximate porosity of $40 \%$ was selected to fill the biogarden. This type of substrate is known as Piedra cuatra and is native to the Monteverde Zone. A highdensity polyethylene (HDPE) plastic sheet was purchased at a local hardware store and used to line the biogarden basin.

### 4.2.3 Construction Process

After the biogarden system design was complete, materials were located and brought to the CEC campus. All required materials (sand, substrate, plastic barrels, plastic liner, piping, plants) were sourced locally. Construction of the system began in October of 2021 and occurred mainly by hand with the help of community volunteers, MVI staff, and the CEC maintenance staff. Parents of CEC students were especially helpful with the construction efforts because of their automatic enrollment in the CEC's community service program which requires each family to contribute 50 hours of service during the academic year. All system components were tied into the existing PVC pipe drainage system, which was previously installed at a slight pitch, creating a gravity-fed system that does not require any pumps. For each component, 50 mm -diameter PVC pipes were selected for seamless connectivity to the existing drainage system.

Individual system components were constructed per standard Costa Rica construction procedures. For the grease trap, a hole with dimensions slightly larger than the design was dug. Next, wood forms were added to create the walls, base, and chamber divider. Then, cement was poured into the forms and allowed to harden. Any gaps between the cement and the hole were backfilled with soil. The checkpoint was constructed in a similar manner as the grease trap. To construct the settling tanks and clarifier, holes were dug to a size slightly larger than the plastic barrels. The barrels were placed in the holes and backfilled with soil. A rectangular wood form was setup around the barrels and filled with cement to lock the barrels in place.

To construct the biogarden, the basin was dug by hand and then lined with the impermeable plastic liner (top left and top right images in figure 4.3). We ensured the edge of the plastic liner extended beyond the limits of the basin to eliminate gaps where greywater could
potentially leak out. The liner was covered with 10 cm of sand to protect it from substrate punctures (bottom left image in figure 4.3). Inflow and outflow pipes were installed on the north and south ends of the biogarden, respectively, and connected to the settling tank outflow pipe and clarifier inflow pipe, respectively. The horizontal inflow/outflow pipe was connected to a PVC tee that joined two components: (1) a vertical pipe on the upper end with a hole in the top cap for ventilation, and (2) a horizontal pipe on the lower end that extends the width of the biogarden and contains 3 cm -wide holes to allow for even distribution of water flow into or out of the biogarden (Figure 4.4). The outlet of the outflow pipe was installed at a height approximately 3 cm lower than the inlet of the inflow pipe to prevent backwashing. Large boulders were carefully piled around the inflow and outflow piping to protect the pipes from the weight of the substrate and to prevent the substrate from entering the pipes and potentially causing clogs (bottom left image in figure 4.3). The remainder of the biogarden basin was filled with the substrate. Large boulders were placed around the perimeter of the biogarden on top of the liner edges in order to keep them from flapping in the wind and for aesthetic purposes. A short berm was built around the biogarden using dirt for the purpose of preventing rainfall runoff from entering the biogarden.



Figure 4.3. Top left: empty biogarden basin with inflow and outflow piping installed. Top right: HDPE plastic liner installed in biogarden basin. Bottom left: 10 cm of sand layered on top of the plastic liner base and large boulders placed around the inflow piping. Bottom right: remainder of the basin filled with substrate.


Figure 4.4. Biogarden inflow piping setup.

Plants were sourced directly from the local reserves, specifically, the cloud forest reserve located on the CEC campus and the Los Pinos reserve. As a local researcher who was working on a project that benefited the local community, I had permission to enter the reserves, locate the plants I needed, dig them up, and transport them back to the CEC for transplanting. Young plants that had experienced less than one growth year were selected from the reserves because they were the most likely to survive the transplant and successfully adapt to their new growing conditions. Consideration of the plants' sun/shade conditions in the reserves was an important factor in plant selection as it would be easiest to select plants that were growing in conditions mimicked by the biogarden (i.e. partial shade). Plants were watered with a hose for a few days after the transplant to help them adapt.

### 4.3 Results and Discussion

### 4.3.1 Rainwater Analysis

Rainfall data from 2010 to 2021 was collected from the MVI micro weather station and compiled into data tables (Tables $\mathrm{C} 1-\mathrm{C} 7$ in Appendix C). Annual rainfall in the Monteverde Zone ranges from 1659 mm to 4092 mm with the years 2012 and 2020 having the lowest and highest recorded rainfall, respectively (Figure 4.5). Average monthly rainfall over this 12-year period ranges from 3.33 mm (January) to 515.38 mm (October) with the highest and lowest monthly rainfall occurring in October of 2019 and February/March of 2019, 2017, and 2016, respectively, with recorded values of 915 mm and 0 mm , respectively (Figure 4.6). Average daily rainfall over this period ranges from 0.46 mm (March) to 17.43 mm (October) (Figure 4.7). The maximum rainfall event occurred in 2017 with a recorded value of 364 mm of rain in a single day in October. This single, maximum rainfall event was considered the 12 -year storm event in the Monteverde Zone and used for design purposes. Based on the calculated surface area of the biogarden basin (discussed in next section), it was determined that a volume of 1.97 cubic meters of rainwater will fall into the basin over the course of 24 hours, flowing in at a rate of approximately $1.4 \mathrm{~L} / \mathrm{min}$ during the 12 -year storm event. To account for this additional possible inflow, the basin volume was expanded by $26.8 \%$ to ensure it has enough capacity for the maximum storm event while still effectively treating contaminants to compliance levels.


Figure 4.5. Annual rainfall data in Monteverde from 2010-2021 (data source: MVI micro weather station)


Figure 4.6. Average monthly rainfall data in Monteverde from 2010-2021 (data source: MVI micro weather station)


Figure 4.7. Average daily rainfall data in Monteverde from 2010-2021 (data source: MVI micro weather station)

It is important to note that, within the 12 years of available data from MVI, the maximum recorded daily, monthly, and annual rainfall occurred in recent years (2019 and 2020), hinting that rain patterns in the Monteverde Zone are shifting, possibly as a result of climate change. While there is not enough data in the MVI database to confirm this, a larger database was found, "Datos Casa LaVal", that contains 40 years' worth of rainfall and temperature data collected in the Monteverde Zone and is thus more appropriate for investigating climate change impacts to historical rainfall trends. In general, climate change impacts rainfall and drought intensity, rather than annual volume of rainfall, hence why no general trends are apparent in Figure 4.5. To effectively analyze this dataset, average daily rainfall and number of rainfall days in a select month were averaged over a decade. Decades were then compared over the 40-year period and trends were identified. March and October, the historically driest and wettest months in Costa Rica, respectively, were selected as the months of interest because data trends would be the clearest in these extreme months. Rainfall data was also analyzed for the full dry season, January through April. It is important to note that Costa Rica experiences occasional mist during the dry season as a result of the formation of orographic clouds from air that is pushed over the continental divide from the Caribbean Sea. Mist data is reported in the large database as rainfall because it was collected by the rain gauge, however, these values were excluded from this investigation because mist is not officially classified as a form of precipitation because it stays suspended in the air.

In October, we observe a general increase in the amount of rainfall received in a single day over the course of 40 years (Figure 4.8, left), with 1981-1990 delivering an average of 16.56 mm rain/day and the most recent decade, 2011-2020, delivering nearly 4 mm more
at 20.21 mm rain $/$ day. Furthermore, we observe a sharp increase in the intensity of single rainfall events in October over the 40 -year period (Figure 4.8, right). In the first three decades (1981-2010), the average maximum daily rainfall event hovers around $78-81 \mathrm{~mm}$ rain/day, but, in the fourth and most recent decade (2011-2020), the maximum rainfall event increases by nearly 30 mm rain $/$ day. A closer inspection of the data revealed that the two most intensive single day rainfall events occurred in 2017 and 2018 with measurements of 316 - and $187-\mathrm{mm}$ rain/day. These results suggests that daily rainfall events in October are intensifying in the Monteverde Zone. Similarly, in March, Costa Rica's driest month, daily rainfall events are decreasing in intensity with 1981-1990 averaging 4.81 mm rain/day while daily rainfall drops to less than $1 \mathrm{~mm} /$ day in 2011-2020 (Figure 4.9, left). Correspondingly, the average number of rainless days in March over the four decades is clearly increasing (Figure 4.9 , right) with 2011-2020 being characteristic of approximately two more rainless days than 1981-1990. These results suggest that drought is intensifying in the Monteverde Zone in March. Looking at the dry season as a whole, we do not observe the same clear, increasing trend in the total number of rainless days over each decade (Figure 4.10). This lack of a clear trend could be due to the transitional nature of January and April - the first couple weeks of January may receive extra rainfall as the season transitions from rainy to dry, and the last couple weeks of April mark the transition back into the rainy season and thus additional rainfall may be received, depending on the year. Regardless, the number of rainless days in the dry season in the most recent decade (1027 days) is significantly greater than those in the earlier decades (970-993 days), averaging 44 more rainless days per decade. Closer inspection of the data revealed that the most intensive drought periods were experienced in the recent years of 2019 and 2014 with a total number of dry season rainless days of 114 and 109 , respectively. The data for 2019 is especially shocking as it indicates that over the course of the 120-day dry season, rain was only received on 6 of those days.

The shifts observed in the historical rainfall trends in March and October and over the entire dry season are likely the result of climate change. This claim is supported by the IPCC AR6 WGII regional report for Central America ${ }^{36}$ which states, with high confidence, that climate change is causing changes in the timing and magnitude of precipitation ${ }^{36}$ and an increase in droughts ${ }^{37}$ in the Central American region. This report also states, with medium confidence, that extreme precipitation events, which results in flooding and drought, are projected to intensify in the coming years due to impacts from climate change ${ }^{36}$. With historical rainfall events in the Monteverde Zone intensifying and continuing to grow in intensity as we move into the future, it is vital to include a safety factor in the design of the biogarden basin to ensure it can effectively treat greywater contaminants while receiving additional hydraulic loading from heavy precipitation events.


Figure 4.8.Historical daily rainfall (left) and historical maximum daily rainfall (right) in the Monteverde Zone in October averaged across decades from 1981-2020 (data source: datos Casa LaVal)


Figure 4.9. Historical daily rainfall in the Monteverde Zone in March (left) and historical number of rainless days in the Monteverde Zone in March (right) averaged across decades from 1981-2020 (data source: datos Casa LaVal)


Figure 4.10. Total number of rainless days during dry season (January through April) in the Monteverde Zone summed across decades from 1981-2020 (data source: datos Casa LaVal)

### 4.3.2 Biogarden Treatment System

The biogarden treatment system consists of the following components that are tied into the existing drainage system: grease trap, checkpoint, two settling tanks, HSSF biogarden basin, and a clarifier. Individual component specifications, designs, and intended purposes are discussed in detail below.

The hydraulic and chemical loadings from the CEC kitchen were determined to range from $0.25-1.0 \mathrm{~L} / \mathrm{min}$ and $213-671 \mathrm{mg}$ COD/L, respectively. The upper end of both ranges was used for the system design in order to ensure effective performance during maximum discharge events. Primary filtration was set up in the form of mesh strainers in the kitchen sink drains to prevent food waste and large particles from entering the system. The grease trap was sized to a capacity of $190 \mathrm{~L}(50$ gallons $)$, contains 2 chambers $\left(\mathrm{V}_{1}=154 \mathrm{~L}, \mathrm{~V}_{2}=\right.$ 36 L ) which are separated by a concrete wall, and has a hydraulic retention time of 30 minutes. A large PVC pipe allows passage from the first chamber to the second, but was installed in a way that prevents FOGs from escaping the first chamber and only allows water to pass. The checkpoint was sized to a volume of 19 L ( 5 gallons) and serves as an accessible point for taking water samples and troubleshooting system issues.

Two consecutive 209 L (55-gallon) settling tanks were installed after the checkpoint to ensure sand and gravel particles settle out of the greywater before it flows into the biogarden. Because there is a natural elevation change of 4 m between the checkpoint and settling tanks, greywater will flow into the first settling tank at a high rate, causing temporary turbid conditions that may stir up settled particles. Thus, a second consequent
settling tank was necessary and was installed at the same elevation as the first to prevent turbid flow conditions in the second tank, ensuring particles will settle before water exits the tank. The smallest sand-sized particles ( $d_{\mathrm{p}}=0.05 \mathrm{~mm}, \rho_{\mathrm{p}}=1450 \mathrm{~kg} / \mathrm{m}^{3}$ ) are estimated to settle at a rate of approximately $0.037 \mathrm{~m} / \mathrm{min}$ (in non-turbid conditions) which is quicker than the critical settling velocity ( $v_{\mathrm{c}}=0.0019 \mathrm{~m} / \mathrm{min}$ ), suggesting that particles will effectively settle out of the greywater while in the settling tanks.

Moving on to the biogarden basin, the minimum required hydraulic residence time for degradation of COD to below the legal discharge limit was determined to be 16 hours. With this information, the basin was sized to have a hydraulic retention time of 26 hours which includes the consideration of the 10-year rainfall event and an additional safety factor of 1.6. The safety factor accounts for future increased storm intensities as a result of climate change (see previous section 4.3.1), growth of the student body, reduction in the volume of the biogarden basin (see section 4.3.4.2), and the tightening of discharge laws. The biogarden was sized to a volume of $5,300 \mathrm{~L}$ ( 1,400 gallons) with the following dimensions: $4.6 \mathrm{~m}(180$ ") basin length $(L), 1.3 \mathrm{~m}(50$ ") basin width $(W), 0.9 \mathrm{~m}(36 ")$ basin depth $(D)$, $0.6 \mathrm{~m}(24 ")$ maximum water height $(H)$. The surface area of the biogarden is $5.81 \mathrm{~m}^{2}$ which is greater than the calculated minimum required surface area of $2.95 \mathrm{~m}^{2}$ for effective COD removal. The grade of the basin was set to approximately $2 \%$ to maintain an appropriate hydraulic gradient. $Q_{\text {limit }}$ was calculated to be approximately $6 \mathrm{~m}^{3} / \mathrm{d}$ which exceeds the inflow rate of $0.31 \mathrm{~m}^{3} / \mathrm{d}$, confirming that the pressure head necessary to overcome resistance to flow through the media is available and thus subsurface flow conditions can be maintained. The basin was lined with a double layer flexible plastic sheet and filled with the locally sourced crushed rock ( $\varepsilon=\sim 0.40$ ).

A total of seven native plant species were selected for the biogarden basin: Calathea crotalifera, Heliconia tortuosa, Renealmia cernua, Canna tuerckheimii, Carex donnellsmithii, Ludwigia octovalvis, Costus wilsonii. Along with the criteria mentioned in section 4.2.1.4, these plant species were selected because of their availability in the local cloud forest reserves. The quantity of each species added to the basin was limited by what could be located, accessed, and dug up in the reserves. Figure 4.11 displays photos of three of the seven selected plant species.


Figure 4.11. From left to right: Heliconia tortuosa, Calathea crotalifera, Renealmia сегпиа.

The clarifier, the final component of the treatment train, was installed as a 209 L drum (same as the settling tanks) with the purpose of ensuring any remaining sand- or gravelsized particles settle out before the treated greywater is discharged to the environment. Similar to the settling tanks, $v_{\mathrm{s}}$ is greater than $v_{\mathrm{c}}$, so particles will settle out before water flows out of the clarifier.

### 4.3.3 Contaminant Degradation

Effluent water samples were taken in April of 2022, 1.5 months after the biogarden system construction was complete (Table 4.1). At this time, the biogarden removal efficiencies for COD and $\mathrm{NO}_{3}{ }^{-}$were determined to be $91 \%$ and $86 \%$, respectively. The effluent COD concentration was measured to be $37 \mathrm{mg} / \mathrm{L}$ which falls well below the discharge limit of $150 \mathrm{mg} / \mathrm{L}$. Although $\mathrm{NO}_{3}{ }^{-}$is not regulated by the Costa Rica discharge laws, the biogarden effluent concentration falls well below the U.S. EPA National Primary Drinking Water Regulation ${ }^{38}$ limit of $10 \mathrm{mg} / \mathrm{L}$, suggesting that $\mathrm{NO}_{3}{ }^{-}$levels were treated to a safe level. The other water quality parameters (BOD, DO, conductivity, $\mathrm{pH}, \mathrm{PO}_{4}{ }^{3-}$, TDS, DO , and turbidity) could not be measured at this time due to limited access to lab equipment and resources.

Table 4.1. Effluent water quality results taken at various locations throughout the biogarden system (samples taken by UCR in April of 2022)

| Parameter | Grease Trap | Checkpoint | Settling <br> Tank 1 | Clarifier | Removal <br> $(\mathbf{\%})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{COD}^{(\mathrm{mg} / \mathrm{L})}$ | 213 | 417 | 671 | 37 | $\mathbf{9 5 \%}$ |
| $\mathrm{NO}_{3}{ }^{-}(\mathrm{mg} / \mathrm{L})$ | 1.5 | 2.3 | 7.0 | 1.0 | $\mathbf{8 6 \%}$ |

With promising effluent water quality results, it is important to explore and understand the chemical and biological processes occurring below the surface of the biogarden. Beginning first with COD, this is the amount of oxygen required to oxidize the organic material found in water. As seen in Table 4.1, the concentration of COD triples on its journey from the grease trap $(213 \mathrm{mg} / \mathrm{L})$ to the checkpoint $(417 \mathrm{mg} / \mathrm{L})$ and finally to the first settling tank ( $671 \mathrm{mg} / \mathrm{L}$ ). This suggests that dissolved oxygen is depleted as water moves through the system as a result of food waste breaking down over time into oxidizable organic matter, which increases COD. As the greywater enters the biogarden basin, the microorganism that live around the root structures consume the abundance of oxygen exuded by the plant roots and begin oxidizing the organic matter, leading to its degradation and a significant drop in COD, hence the much lower concentration of COD in the clarifier ( $37 \mathrm{mg} / \mathrm{L}$ ). The consistent abundance of oxygen around the root structures in the biogarden basin is due to aeration by the biogarden plants which deliver oxygen, a natural biproduct of photosynthesis, to the basin via their root structures.

Similar to $\mathrm{COD}, \mathrm{NO}_{3}{ }^{-}$also increases as it moves through the system, tank, coming to a maximum concentration of $7.0 \mathrm{mg} / \mathrm{L}$ in the settling tank. The major source of organic nitrogen in the CEC greywater discharge is food waste. As the greywater moves the food waste through the treatment system, microbial decomposition and hydrolysis take place
which convert the organic nitrogen in the food particles into ammonia $\left(\mathrm{NH}_{3}\right)$ through a process known as ammonification ${ }^{39}$ (equation 9). $\mathrm{NH}_{3}$ is then oxidized into nitrite $\left(\mathrm{NO}_{2}{ }^{-}\right)$ and $\mathrm{NO}_{3}^{-}$by Nitrosomonas and Nitrobacter bacteria, respectively, in a process known as nitrification ${ }^{40}$ (equations 10 and 11).

$$
\begin{array}{ll}
\text { Ammonification: } & \mathrm{R}^{2} \mathrm{NH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{NH}_{3}+\mathrm{R}-\mathrm{OH} \\
\text { Nitrification: } & \mathrm{NH}_{3}+\mathrm{O}_{2} \rightarrow \mathrm{NO}_{2}^{-}+3 \mathrm{H}^{+}+2 \mathrm{e}^{-} \\
& \mathrm{NO}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{NO}_{3}^{-}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \tag{11}
\end{array}
$$

As the nitrate-rich water travels through the biogarden, its concentration is significantly depleted and reaches a final concentration of $1.0 \mathrm{mg} / \mathrm{L}$ in the clarifier. Denitrification occurs in the biogarden basin by microorganisms that convert nitrate into free atmospheric nitrogen $\left(\mathrm{N}_{2}\right)$ that is released as a gas ${ }^{41}$ (equation 12). In order for denitrification to proceed, both a readily available carbon source and anoxic conditions are necessary ${ }^{41}$. As mentioned in the COD paragraph, carbon-feeding microorganisms will consume the dissolved oxygen available around the root structures during degradation of the organic matter. This, in combination with the slow flow of water through the basin and lack of vertical mixing, will create anoxic conditions below the water surface, allowing denitrification to occur. In the absence of dissolved oxygen, the denitrifying bacteria will consume the oxygen in the $\mathrm{NO}_{3}{ }^{-}$ and $\mathrm{NO}_{2}{ }^{-}$ions, effectively reducing them to $\mathrm{N}_{2}$ gas.

$$
\begin{equation*}
\text { Denitrification: } \quad \mathrm{NO}_{3}^{-}+10 \mathrm{e}^{-}+12 \mathrm{H}^{+} \rightarrow \mathrm{N}_{2}+6 \mathrm{H}_{2} \mathrm{O} \tag{12}
\end{equation*}
$$

Another means through which nitrate is removed from the greywater is through uptake by the biogarden plants. Nitrate is essential for plant growth and serves as a primary nutrient that is converted to protein.

In subsurface flow biogardens, it takes approximately 3-6 months after construction for the biofilm and microbial communities to fully establish ${ }^{21}$. Thus, an additional set of water quality measurements were taken in October of 2022 (seven months after construction) and March of 2023 (approximately one year post-construction) by the Escuela de Ingenieria de Biosistemas team at UCR. Table 4.2 shows the results of the water quality tests as performed by others. In October, removal efficiencies for COD and $\mathrm{NO}_{3}{ }^{-}$were $58 \%$ and $85 \%$, respectively, while in March of 2023 the efficiencies were $91 \%$ and $82 \%$, respectively. Beginning first with the October measurements, these are of particular importance because they were taken (1) during peak rainy season and (2) during the 1.5week fall break when the kitchen is not in use. This is the first and only set of data we have to date that was taken during this scenario and thus it provides valuable insight into the performance of the CEC biogarden when there is the input of precipitation in combination wtih little to no chemical or hydraulic loading from the kitchen. Because the school was on break and fresh organic matter was not being discharged, we observe COD influent concentrations ( $60 \mathrm{mg} / \mathrm{L}$ ) that are $75 \%-90 \%$ lower than those observed during times of
normal chemical and hydraulic loading. Even with a low influent concentration, there is still a chemical loading to the basin and the microbial communities will be available for degradation. Although their population will be declining (see section 4.3.5.1.) resulting in a diminished removal efficiency ( $58 \%$ ), the microbial communities still effectively degrade COD to a concentration of $25 \mathrm{mg} / \mathrm{L}$ which falls below the compliance limit. However, this concentration is lower than those observed during the dry season ( $34-40 \mathrm{mg} / \mathrm{L}$ ), suggesting that rainfall is entering the biogarden basin and diluting the chemical loading. The results of the water quality measurements taken in March of 2023 were approximately the same as they were in April of 2022, and the effluent concentrations were still well below the discharge limits, suggesting that the established biofilm is performing as intended.

Table 4.2. Effluent water quality results taken at various locations throughout the biogarden system (samples taken by UCR in October of 2022 and March of 2023)

| Parameter | Grease Trap | Checkpoint | Settling <br> Tank 1 | Clarifier | Removal <br> $(\%)$ |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
|  | October 2022 |  |  |  |  |  |
| $\mathrm{COD}^{(\mathrm{mg} / \mathrm{L})}$ | -- | -- | 60 | 25 | $\mathbf{5 8 \%}$ |  |
| $\mathrm{NO}_{3}{ }^{-}(\mathrm{mg} / \mathrm{L})$ | -- | -- | 4.0 | 0.6 | $\mathbf{8 5 \%}$ |  |
|  | March 2023 |  |  |  |  |  |
| $\mathrm{COD}^{(\mathrm{mg} / \mathrm{L})}$ | 335 | 490 | 380 | 34 | $\mathbf{9 1 \%}$ |  |
| $\mathrm{NO}_{3}{ }^{-}(\mathrm{mg} / \mathrm{L})$ | 6.0 | 5.0 | 5.0 | 0.9 | $\mathbf{8 2 \%}$ |  |

In March of 2023, on-site probe readings of pH , electrical conductivity, temperature, and turbidity were taken in the settling tank (biogarden influent) and the clarifier (biogarden effluent) to determine how these parameters change as water flows through the biogarden basin (Table 4.3). Beginning first with pH , this parameter increases by nearly one order of magnitude between entering and exiting the biogarden basin, effectively making the effluent water more basic. This is likely a result of the Piedra cuatro substrate which is limestone based and may release carbonate ions $\left(\mathrm{CO}_{3}{ }^{2-}\right)$ into the water over time, raising the pH . However, the pH of the biogarden effluent water falls within the compliance range, suggesting that this increase is no cause for alarm. Conductivity decreases slightly ( 0.60 $\mathrm{mS} / \mathrm{cm}$ to $0.33 \mathrm{mS} / \mathrm{cm}$ ) upon exiting the basin, but both the influent and effluent measurements fall within typical background concentration levels for drinking water ${ }^{42}$, suggesting this parameter is not of concern. Temperature also drops slightly from $20.9^{\circ} \mathrm{C}$ to $20.2^{\circ} \mathrm{C}$ but is maintained within the compliance range. This temperature drop is expected because the water will spend approximately 16 hours in the biogarden basin which is located below the surface of the ground and is not exposed to direct sunlight, so some heat loss is expected. Finally, the turbidity decreases from 58.70 NTU to 0.61 NTU can be attributed to filtration through the substrate and particle settlement out of the slow-moving basin water. Although turbidity is not regulated in the Ley de Aguas, the effluent level complies with the World Health Organization suggested limit of 1.0 NTU for drinking water ${ }^{6}$.

Table 4.3. On-site probe readings of various water quality parameters taken in the settling tank and clarifier (samples taken by UCR in March of 2023)

| Parameter | Biogarden <br> Influent | Biogarden <br> Effluent | Compliance <br> Range |
| :---: | :---: | :---: | :---: |
| pH | 6.6 | 7.5 | $5-9$ |
| Conductivity $(\mathrm{mS} / \mathrm{cm})$ | 0.60 | 0.33 | -- |
| Temperature $\left({ }^{\circ} \mathrm{C}\right)$ | 20.9 | 20.2 | $15^{\circ} \mathrm{C}-40^{\circ} \mathrm{C}$ |
| Turbidity $(\mathrm{NTU})$ | 58.70 | 0.61 | -- |

### 4.3.4 Performance Comparison

The biogarden greywater treatment system developed in this study is not the first nor only biogarden in Costa Rica. A handful of various individuals, schools, businesses, and hotels have developed their own biogarden to treat their greywater (and sometimes blackwater) discharge ${ }^{43}$. A total of 77 biogardens, including the biogarden in this study, have been established in Costa Rica and can be found in the central and western regions of the country at a variety of altitudes ranging from sea level to as high as 2,200 meters. Many of the biogardens have a unique design tailored to a specific hydraulic and chemical loading and greatly vary in terms of size, capacity, and flora. The UCR Escuela de Ingeniería de Biosistemas team has been working on a comprehensive study (Project C2451 Sistematización de los Humedales Artificiales Instalados en Costa Rica y Evaluación de Sustratos Alternativos en el Tratamiento de las Aguas Residuales Ordinarias) to document the location, design, and performance of each of these 77 biogardens. According to the UCR team, the CEC biogarden developed in this study is performing in the top $33 \%$ and top $25 \%$ of all biogardens in Costa Rica, in terms of $\mathrm{NO}_{3}{ }^{-}$and COD removal, respectively (full analysis to be published by the UCR Escuela de Ingeniería de Biosistemas team). With these promising results, we hope that the CEC's biogarden design components, layout, and best maintenance practices can be incorporated into lower-performing biogardens to aid in their optimization.

### 4.3.5 Discussion Topics

### 4.3.5.1 Microbial Communities

The microbial communities that reside in the biogarden basin and are responsible for contaminant degradation are arguably the most important component of an effective biogarden system. Microorganisms live on substrate and plant roots, and may also be suspended in water as floc or clusters ${ }^{21}$. Growth and decline of the microbial populations can be calculated using Monod-type kinetics ${ }^{21}$ (equation 13) where $\mu_{S}$ is the specific growth rate of the population, $\mu_{S, \max }$ is the maximum growth rate, $S$ is the concentration of the consumable nutrient (i.e. organic matter as COD, N , etc.), and $K_{S}$ is the Monod constant for the growth rate of microbial populations in a wetland environment.

$$
\begin{equation*}
\mu_{S}=\mu_{S, \max } \frac{S}{K_{S}+S} \tag{13}
\end{equation*}
$$

As mentioned in the methods section of this chapter, the CEC biogarden basin will typically never perform at steady-state due to the kitchen use schedule. Therefore, we expect the microbial population to fluctuate in response to changes in the hydraulic and chemical loading. Populations will grow and die off as nutrients become more readily available and limited, respectively. For example, over the weekend when the CEC kitchen is not in use, we expect a small decline in the microbial population. The population will begin to grow again when school resumes on Monday. We will also observe populations shifts as a result of horizontal transport of microorganisms with the water flow. Studies have shown that horizontal transport has a greater effect on the population than the death rate ${ }^{21}$. This will be especially apparent during the rainy season when large amounts of precipitation enter the biogarden basin, increasing the horizontal flow rate and thus transport, and reducing the HRT. However, even with the aforementioned microbial population fluctuations, biogardens have proven to be resilient, and negligible changes are often observed in the removal efficiencies ${ }^{44}$.

The same is not true during extreme events when microbial communities are deprived of nutrients for much longer periods of time. During these events, the efficiency of the biogarden will significantly decrease as a result of rapidly shrinking microbial populations. During school shut down periods, such as for summer and long holiday breaks, there will be no hydraulic or chemical loading to the biogarden, leading to population decline. The population decline will only be dependent on the death rate at this time as horizontal transport will halt in response to a lack of hydraulic loading ${ }^{21}$. However, once inflow begins again, microbial populations are expected to bounce back to normal sizes in approximately 2-3 weeks, as reported by a study that modeled microbial populations in a tropical biogarden of similar size and loading to the CEC biogarden ${ }^{21}$. The biogarden as a whole should be back to normal removal efficiency in approximately 6-8 weeks which is much quicker than the initial startup (3-6 months).

Although this was not implemented in the CEC due to lack of resources, one way to increase the self-sustainability of a biogarden system is to house specialized microbial communities in the grease trap that are capable of breaking down FOGs. These microbes could be used in place of the periodic manual task of skimming FOGs off of the surface of the grease trap. Investigation of these microorganisms and their impact on the downstream chemical loading will be explored in future work.

### 4.3.5.2 Reduction in Hydraulic Residence Time

Although the biogarden basin was designed to have a porous volume of 1472 liters and a hydraulic retention time of 26 hours, various factors will cause these two parameters to decrease over time. The reduction in biogarden volume and thus the HRT can be attributed to sludge, inorganic materials, and plant growth. Sludge will build up over time as microbial communities develop and settle as floc, effectively taking up pore space in the biogarden. However, this will have a minimal impact and is estimated to only reduce volume by $0.2 \% /$ year $^{21}$. Buildup of inorganic materials, such as silt- and clay-sized particles that effectively pass through the settling tanks, will also reduce the volume of pore space in the basin. It was found that a constructed wetland in the United States had a $2 \%$ -
$6 \%$ reduction in volume over the course of 5 years as a result of accumulation of inorganic matter ${ }^{34}$. However, it is important to note that this constructed wetland was located near a large construction site that had a large surface area of exposed particles (i.e. sand, gravel, clay, silt). Biogardens that are not in proximity to construction sites, such as the CEC, are expected to have significantly less input and accumulation of inorganic particles that will likely reduce volume on the same order of magnitude as sludge (i.e. $0.1 \%-1 \%$ ). Finally, the most significant reduction in basin volume will be due to the growth of plant roots. One study estimates that plant roots will reduce basin volume by $15 \%-30 \%{ }^{45}$, however, this is dependent on many factors, including the type of plant, type of root structure, age of the plant, and the health of the plant. Regardless, out of the three factors discussed in this paragraph, plant root structures will have the most significant impact on HRT and the volume of the basin. Means for reducing this impact include replacing large, mature plants that have long root structures with younger, smaller plants that are still developing. Plants should be replaced strategically and periodically (i.e. replace one plant every 6 months), so as to not disrupt the microbial community populations or shock the biogarden system.

### 4.3.5.3 Plants, Substrate, Liner

Plants, substrate, and the impermeable liner all play a critical role in effective contaminant removal in the biogarden. Beginning first with plants ${ }^{46}$, they transport oxygen throughout the rhizosphere, which is in turn consumed by microbes for degradation of organic matter ${ }^{47,48}$. The roots of these plants provide a large surface area for attachment and growth of microbial communities, allowing the formation of a biofilm ${ }^{47,48}$. The root systems also aid in maintaining hydraulic conductivity, improving sedimentation and filtration, and reducing flow velocity ${ }^{16,48,49}$. As plants naturally die, their leaves and roots provide an additional source of nitrogenous matter to the microbes residing in the basin. Regarding contaminant removal, it is not clear whether or not plants play a role in this process. Some studies suggest that plants are responsible for up to $10 \%$ of contaminant removal ${ }^{48,50-53}$, specifically contaminants containing nitrogen, phosphorus, and heavy metals, while other studies claim that plant uptake is negligible ${ }^{54-57}$. This, of course, is heavily dependent on the plant species, chemical loadings, hydraulic retention time of the basin, and the microclimate around the biogarden. Native, water-loving plants are the ideal choice for biogardens and will be the most likely to survive. Choosing native plants over non-native plants prevents the spread of invasive species, ensures the plants are already adapted to the climate and altitude, and can serve as a resource for pollinators, birds, and other animals.

The purpose of the substrate is four-fold: (1) to serve as a growing medium for biogarden plants ${ }^{46}$, (2) to provide a sufficient surface area for microbial growth, (3) to maintain an appropriate hydraulic conductivity ${ }^{45}$, and (4) to filter particles out of the water. The use of substrate with a high porosity (i.e. gravel) is ideal because it allows greater penetration of plant roots through the media. Whenever possible, substrate should be excavated and crushed locally to ensure affordability. This is especially important in developing countries where the substrate is typically the most expensive system component ${ }^{58,59}$. Furthermore, locally sourced substrate helps the biogarden imitate a natural, native environment which in turn benefits the plants and microbial communities. Foreign substrates could introduce
unfamiliar chemicals to the greywater and cause pH shifts that may negatively impact biogarden efficiency ${ }^{45}$.

The plastic liner serves as an impermeable barrier between the greywater and the groundwater table, creating a semi-closed system for treatment. However, because of its plastic composition, the HDPE liner will not last forever and is susceptible to degradation over time. Degradation can result from oxidation, which is catalyzed when the liner is exposed to direct sunlight and temperatures of $38^{\circ} \mathrm{C}$ and greater ${ }^{60}$. Chemical degradation could also occur, although this is unlikely because liners are manufactured to resist this form of degradation. Significant temperature fluctuations cause liners to shrink and expand which wears out the plastic, leading to inevitable cracks. The CEC liner is covered by substrate and only experiences mild temperature fluctuations $\left(15^{\circ} \mathrm{C}-30^{\circ} \mathrm{C}\right)$ throughout the year, so we expect the liner to function as intended for a very long time. A study ${ }^{61}$ on polyethylene liner degradation in wetland systems reported that covered liners (i.e. those with no exposure to sunlight) will last for hundreds of years, further solidifying this expectation. Another study reported that constructed wetlands effectively filter out microplastics, suggesting that any liner degradation will remain within the biogarden until it can be removed manually. Thus, whenever a biogarden liner is replaced, the substrate should be removed and thoroughly cleaned to remove any microplastics and other inorganic material.

### 4.3.5.4 Biodegradable Soaps and Cleaners

To protect the health of the biofilm and plants in the biogarden basin, it is important to ensure only biodegradable soaps and cleaners are used in the CEC kitchen. Unlike synthetic soaps, which typically originate from petrochemicals, biodegradable soaps are comprised of natural ingredients such as vegetable oils and plant extracts ${ }^{62}$. These ingredients will flow through the biogarden without causing harm to the microbial communities or plants. However, the discharge of the treated greywater containing the biodegradable soap directly to the environment is of concern. In order for a soap to be classified as biodegradable, it must degrade via biological agents to $90 \% \mathrm{H}_{2} \mathrm{O}, \mathrm{CO}_{2}$, and biomass within 6 months ${ }^{63}$. This level and speed of degradation is only achievable if the soap is discharged into soil where the appropriate microorganisms are available for degradation. Greywater containing biodegradable soap that is discharged into or near a body of water will breakdown at a slower pace and will negatively impact the chemical makeup of the body of water and the mucus layer of aquatic organisms ${ }^{64}$. On the CEC campus, the biogarden greywater effluent is discharged into a heavily vegetated area that is greater than 100 meters from any water bodies, ensuring any biodegradable soap remnants will effectively degrade within 6 months and safely return to nature.

### 4.3.5.5 Construction and Education Issues

The startup of the biogarden was not as seamless as anticipated - we ran into a few issues that resulted in damage to the system. One of the first problems occurred in December of 2021, about a month after construction. During a visit to the CEC, we observed many of the biogarden plants looking very dry and some had already died. A quick check on the water meter confirmed that a sufficient volume of water should have discharged from the
kitchen and entered the biogarden basin during the startup period. However, digging down into the basin only revealed dry substrate and the surface of the water could not be located. We suspected this was due to one of two reason: (1) water was leaving the basin through something other than the outflow pipe (such as through holes in the plastic liner), or (2) the kitchen discharge is not entering the basin due to a leak or a clogged pipe in the drainage system. Over the next few days, we performed various trouble shooting tests and narrowed down the cause of the issue to holes in the plastic liner. These holes likely formed as a result of punctures from substrate and age of the liner. To resolve this issue, we, along with volunteers, removed all of the substrate from the basin and laid a new, thicker plastic liner. This time we covered the base of the liner with a layer of sand to minimize the risk of punctures. We then replaced the substrate in the basin and added a new set of plants which were sourced from the surrounding reserves. We returned multiple times over the next few weeks to monitor the basin water level and check on the plant growth.

The second problem was encountered in March of 2022. We again observed many dry and dead plants in the basin which we discovered were a result of a clogged pipe in the grease trap that was prohibiting the greywater from flowing to the rest of the system. The pipe was clogged with what appeared to be beans, bread, and vegetables, rather than grease. This suggested that there may have been some miscommunications with the kitchen staff, perhaps due to the language barrier. To resolve this issue, we unclogged the grease trap pipe, checked downstream system components for additional clogs, re-installed primary filtration in the kitchen sinks, and educated the kitchen staff on best sink practices. We also replanted the biogarden at this time.

These two major issues we encountered demonstrate the self-sustaining, yet delicate nature of a biogarden system. Neglect in one component will negatively impact the others. Therefore, periodic and consistent system maintenance is necessary to ensure the biogarden continues operating in harmony with the surrounding environment. Biogarden system maintenance is discussed in more detail in section 4.3.6.

A final issue was encountered in March of 2023 during my visit to Monteverde. Upon arriving at the CEC to check on the status of the biogarden and take photos, I learned that the principal, maintenance worker, and kitchen staff, who were my main contacts and played a vital role in the establishment of the system, had recently quit their jobs and left the school. I also learned that these staff members did not pass on any of the biogarden education materials (i.e. step-by-step maintenance guide, construction drawings, YouTube educational videos, etc. (see next section)), and thus the new principal and maintenance team were unaware that a working biogarden existed on the CEC campus. The timing of my visit to Monteverde was optimal as I was able to set aside time to introduce the full biogarden system to the new staff and educate them on best practices. However, this situation demonstrates the importance of having a local contact point external to the CEC who can stay abreast of staffing changes and ensure educational resources are passed on to the correct people. Moving forward, MVI will serve as the main contact point for the CEC biogarden, as they are located just down the road and have extensive knowledge on biogarden systems.

### 4.3.6 Community Resources

The goal of this research is not only to build an effective greywater treatment system in the Monteverde Zone, but to also empower community members with the knowledge they need to understand the greywater discharge issue and remediate it with a nature-based solution. To achieve the second piece of this two-fold goal, I created a set of open-access educational resources for the CEC staff and broader community, including a biogarden maintenance guide, kitchen staff education, social media content, biogarden sizing tool, construction plan set, and a plant reference tool, each of which are described in detail below.

### 4.3.6.1 Kitchen Staff Education

One of the most important factors influencing the effectiveness of a biogarden is the actions of the kitchen staff. Failure to educate the kitchen staff on proper sink usage could result in chronic biogarden problems and even permanent damage to the system. Thus, a critical part of this project was educating the CEC kitchen staff on best kitchen practices for optimal biogarden performance. Regarding food waste, the mesh strainers, which serve as primary filtration, should remain over the drains whenever the sink is in use to prevent food scraps from entering the system and potentially clogging pipes. Rather than being discarded in the kitchen sink, FOGs should be collected in a separate container, allowed to cool, and then be disposed of in the garbage. Since bleach and other harsh chemicals can wipe out the microbial community in the biogarden basin and degrade the plastic piping, only natural and environmentally friendly cleaners are recommended for the kitchen sink. Similarly, hand and dish soaps should be certified as biodegradeable and eco-friendly. Figure 4.12 shows the best practices sign that was hung up in the CEC kitchen as a reminder for the staff.


Figure 4.12. CEC kitchen waste and discharge guidelines.

### 4.3.6.2 Biogarden Maintenance Guide

While biogardens are nearly completely self-sustaining, periodic maintenance is necessary to ensure the system continues performing optimally year-round. To assist the CEC staff in meeting these maintenance requirements, a biogarden maintenance guide was created that details out best practices and weekly, monthly, and annual maintenance for each system component. Best practices include, among others, keeping lids on the grease trap, settling tank, and clarifier at all times to prevent debris and runoff from entering the system, and pruning the tree branches above the biogarden to ensure the biogarden is exposed to sunlight for part of the day. Maintenance ranges from checking pipes weekly for clogs to doing a full component cleanout once per year. The guide also includes a section on recommended personal protection equipment that should be worn by individuals working directly with the system (i.e. those taking water samples, cleaning, performing maintenance) to minimize the risk of coming into contact with aquatic bacteria and viruses that may be present in the greywater. Both English and Spanish versions of the maintenance guide were created to maximize useability. The full biogarden maintenance guide (English version) can be found in Appendix C.3.

### 4.3.6.3 Social Media Content

Together with Irene Gonzales, the marketing manager at MVI, we created a 6-part video series titled, "Aprendiendo de Biojardineras con Rose Daily" ("Learning about Biogardens with Rose Daily") in which I walk the viewer through each component of an effective biogarden in detail, including discussing the purpose and importance of each step in the treatment train. A screenshot from one of the videos is shown in Figure 4.13. These videos were posted to the MVI YouTube channel (monteverde institute) as a playlist titled, "Humedales Artificiales" ("Constructed Wetlands") and to the MVI Instagram page (@ monteverde_institute) as reels. These videos were made with English audio and Spanish subtitles, and have collectively received approximately 10,000 views. In addition to this video series, I also worked with Irene to create supplemental Instagram reels that show various aspects of biogarden construction, including sourcing materials from the Cloud Forest Reserve and planting macrophytes in the biogarden basin.


Figure 4.13. Screenshot from part 2 of the "Aprendiendo de biojardineras con Rose Daily" video series that is posted on the Monteverde Institute YouTube channel.

### 4.3.6.4 Construction Plan Set

A detailed yet understandable construction plan set was compiled for the CEC biogarden which includes detailed designs, dimensions, and construction notes for each component of the biogarden system. A screenshot of page 8 from the plan set is shown below in figure 4.14. Although this plan set is specific to the CEC chemical and hydraulic loadings and should not necessarily be used as the exact design for other systems, it is intended to serve as a guide for community members who wish to design and construct their own biogarden. The plan set includes information on crucial design details that otherwise may not be visually obvious, such as adjusting pipe elevations to prevent backwash, grading the bottom of the basin to maintain an appropriate hydraulic gradient, and ensuring the top of the grease trap walls are above grade to prevent runoff from entering the system. In order to maximize the useability of the plan set, the construction and building notes parallel Costa Rican building practices. Additionally, because the Monteverde Zone consists of a bilingual community and many American expats, Spanish and English versions of the plan set were created that include dimensions in metric and imperial units, respectively (English version available in Appendix C.2; Spanish version available upon request).


Figure 4.14. Page 8 of the CEC biogarden construction plan set.

### 4.3.6.5 Plant Reference Table

Selecting appropriate plants for a biogarden is a vital step in ensuring the system's effectiveness for greywater treatment. A one-size fits all approach for biogarden plants in Costa Rica is impractical because of the diverse microclimates and large variety of plants found in this region. Through independent research and collaboration with Willow Zuchowski, a botanist and plant expert in Monteverde, I created a plant reference tool (available upon request) in Excel that can be used to select appropriate plants for a biogarden basin in a specific location with given basic design criteria. All plants included in the spreadsheet are native to Costa Rica and the tool contains specific information on each plant type, including plant height, root length, altitude range in which it grows, growth conditions, and water preferences (example for Heliconia tortuosa shown in Figure 4.15). This specific information makes it easy for a user to select the types of macrophytes that will thrive in a biogarden constructed at their altitude and in their specific microclimate. For example, a biogarden that is built on Costa Rica's Pacific coast (i.e. at sea level) with a depth of 0.3 meters in a partially shaded area will require a different set of plants than a biogarden that is constructed in the Monteverde Cloud Forest (i.e. altitude of 1400 meters) with a depth of 1 meter in a fully shaded area. The tool also contains comments regarding locations where specific plants have proven effective in a biogarden and links to relevant resources that provide further information on the plants.


Figure 4.15. Information on Heliconia tortuosa, found in the biogarden plant reference tool.

### 4.3.6.6 Sizing Tool \& Community Biogarden Program

One of the biggest barriers to local residents implementing a biogarden system on their property for treatment of their greywater is a lack of knowledge on how big the system needs to be and which treatment train components are necessary. In order to obtain this information, both the chemical and hydraulic loading of the greywater need to be known. Regarding hydraulic loading, it is uncommon for Costa Rican homes to have a water meter installed on the greywater discharge pipe and thus there is no feasible method for obtaining an accurate volume or flow rate of greywater. One way to estimate this hydraulic loading is to multiply the amount of water entering the house by the ratio of wastewater that is typically discharged as greywater (i.e. approximately $85 \%$, on average). However, UCR has determined that this method results in significant overestimations of hydraulic loading and therefore it is not an appropriate approach. To overcome this barrier, we (myself, MVI, and UCR) propose to order a set of standard water meters that will live at MVI and can be checked out by local residents for up to one month. These water meters can be easily installed on greywater discharge pipes of homes and have the ability to measure both volume and flowrate of the water passing through them. We determined one month to be a sufficient amount of time to obtain an average hydraulic loading of greywater discharge via the water meter.

Regarding chemical loading, this will vary greatly between homes and will depend on many factors including the number of people living in the home, water use habits, the number and type of meals prepared, the types of water-using appliances (i.e. washing machine, dishwasher, etc.) in the house, and the products used (i.e. cleaning products, personal care products, laundry detergent, etc.). Measuring water quality parameters at each home via probes and lab tests is not feasible due to a lack of resources, prohibitive costs, and limited staff. Instead, chemical loading can be estimated through a two-part process. First, we propose to investigate chemical loadings to the 77 biogardens in the UCR database. These biogardens serve a diverse set of customers throughout Costa Rica such as houses, schools, hotels, and small businesses, and will therefore allow us to establish ranges for typical chemical loading based on each type of customer. Second, we propose to interview each resident who is interested in installing a biogarden so we can better understand their cooking and cleaning habits, and overall water use. The interviews will be given in the form of a standard survey through Google Forms. The combination of the
interview results and the established typical chemical loadings based on the existing biogardens will allow us to accurately predict the greywater's chemical loading.

The set of water meters available for checkout and the two-part process for determining chemical loading will allow residents to overcome the barriers to implementing their own biogarden. One concern with this system is that residents will checkout a water meter without being fully committed to building a biogarden. This monopolization of a water meter for up to one month may delay or prevent a committed resident from beginning the biogarden process for their home. To avoid this potential issue, interested residents will need to show their dedication to implementing a biogarden system by first building a grease trap on their property. Once the grease trap is constructed, the resident will receive a water meter and the chemical loading survey.

Once the survey has been completed and after a month of tracking greywater discharge via the water meter, the chemical and hydraulic loading results will be input into our Biogarden Sizing Tool, created in Microsoft Excel, which will calculate the necessary dimensions for the biogarden system. These dimensions, along with the CEC biogarden construction plan set (see section 4.3.6.4), will be given to the resident so they can begin construction of their system. We will also provide them with the plant reference table (see section 4.3.6.5) so they can select the best plants for their biogarden based on their altitude, basin size, and microclimate. To bridge any final knowledge gaps, we will direct the resident to the series of MVI YouTube videos (see section 4.3.6.3) that explain the purpose of each system component. When construction of the system is complete, the resident will be the proud owner of an appropriately sized nature-based system that effectively treats their greywater discharge.

In order to ensure locally implemented biogardens continue performing optimally, it is vital that the owner of the system performs the required periodic maintenance. All biogarden owners will be provided a copy of our Biogarden Maintenance Guide (see section 4.3.6.2) so they can understand what maintenance entails. To provide incentive for owners to keep up with maintenance tasks, they will be offered Verdes ${ }^{65}$, which is the local Monteverde currency that is used to award residents for environmental action and volunteering. Verdes can be spent at a handful of local businesses and farmers' markets. As we move forward with our community biogarden plan, we hope to develop a full business model around our program that includes forming partnerships with local substrate and plastic suppliers, requesting funding and grants from the government, and hiring locals to serve as the fulltime program coordinators.

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## A Linear Free Energy Relationship Supplemental Information

## A. 1 Tables

Table A.1. Summary of computational method and basis set

| Organic Compounds | Reaction <br> Mechanisms | Optimization and <br> Frequency Calculation | Single Point Energy <br> Calculation (if any) |
| :---: | :---: | :---: | :---: |
| Conventional compounds <br> including fluorinated <br> compounds and selected <br> PFAS for prediction | Associative | M06-2X/cc-pVDZ | M06-2X/Aug-cc- <br> pVTZ |
|  | Concerted and <br> stepwise | M06-2X/Aug-cc-pVTZ | -- |
| Iodinated compounds | Concerted | M06-2X/LANL2DZ | -- |
| Fluorinated compounds <br> and PFASs | Stepwise | M06-2X/cc-pVDZ | -- |

Table A.2. Validation of M06-2X method with various basis sets with experimentally determined one electron reduction potential

|  |  | GIBBS FREE ENERGY (HARTREE) |  |  |  | CHANGE IN FREE ENERGY (KCAL/MOL) |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Gaussian Method/Basis Set | Reaction | Radical (g) | Anion (g) | Radical (aq) | Anion (aq) | $\begin{aligned} & \Delta G \text { Solv, } \\ & \text { Radical } \\ & (g \rightarrow a q) \end{aligned}$ | $\begin{aligned} & \Delta G \text { Red } \\ & (g \rightarrow g-) \end{aligned}$ | $\begin{gathered} \Delta G \text { Solv, } \\ \text { Anion } \\ (g \rightarrow a q) \end{gathered}$ | $\begin{gathered} \Delta G \text { Red } \\ (a q \rightarrow a q-) \end{gathered}$ | $\Delta \Delta G$ Solv | $\Delta \mathrm{G}$ Reduction (aq) kcal/mol | One Electron Reduction Potential (V) |
| $\begin{gathered} \text { Experimental } \\ \text { (Isse et al 2011)a } \end{gathered}$ | $\mathrm{F}^{*}+\mathrm{e}-\cdots \mathrm{F}$ - | -- | -- | -- | -- | -- | -76.63 | -- | -- | -- | -- | 3.66 |
|  | $\mathrm{Cl}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Cl}-$ | -- | -- | -- | - | -- | -81.64 | - | -- | -- | -- | 2.59 |
|  | $\mathrm{Br}^{*}+\mathrm{e}-\cdots>\mathrm{Br}-$ | -- | -- | -- | -- | -- | -75.88 | -- | -- | -- | -- | 2.05 |
|  |  | -- | -- | -- | -- | -- | -68.85 | -- | -- | -- | .- | 1.37 |
| M06-2X/cc-pvdz | $\mathrm{F}^{*}+\mathrm{e}-\cdots>\mathrm{F}-$ | -99.710 | -99.755 | -99.708 | -99.903 | 1.364 | -27.811 | -92.793 | -121.968 | -94.156 | -121.968 | 1.01 |
|  | $\mathrm{Cl}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Cl}-$ | -460.137 | -460.246 | -460.137 | -460.354 | 0.143 | -68.481 | -67.843 | -136.467 | -67.986 | -136.467 | 1.64 |
|  | $\mathrm{Br}^{*}+\mathrm{e}-\cdots>\mathrm{Br}-$ | -2574.148 | -2574.254 | -2574.149 | -2574.341 | -0.762 | -67.057 | -54.098 | -120.392 | -53.335 | -120.392 | 0.94 |
| M06-2X/LANL2DZ | $1^{*}+\mathrm{e}-\ldots>1$ - | -11.323 | -11.436 | -11.328 | -11.538 | -3.004 | -70.985 | -64.119 | -132.101 | -61.116 | -132.101 | 1.45 |
| M06-2X/aug-cc-pvtz | F* + e- --> F- | -99.747 | -99.868 | -99.745 | -100.007 | 1.338 | -75.585 | -87.289 | -164.212 | -88.627 | -164.212 | 2.84 |
|  | $\mathrm{Cl}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Cl}-$ | -460.157 | -460.290 | -460.157 | -460.394 | 0.188 | -83.507 | -65.226 | -148.920 | -65.413 | -148.920 | 2.18 |
|  | $\mathrm{Br}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Br}-$ | -2574.215 | -2574.341 | -2574.217 | -2574.426 | -0.739 | -78.637 | -53.306 | -131.204 | -52.567 | -131.204 | 1.41 |
| M06-2X/LANL2DZ | $1^{*}+\mathrm{e}-\cdots>1-$ | -11.323 | -11.436 | -11.328 | -11.538 | -3.004 | -70.985 | -64.119 | -132.101 | -61.116 | -132.101 | 1.45 |
| B3LYP/cc-pVTZ | $\mathrm{F}^{*}+\mathrm{e}-\cdots>\mathrm{F}-$ | -99.778 | -99.864 | -99.776 | -100.011 | 1.340 | -54.377 | -92.110 | -147.827 | -93.450 | -147.827 | 2.13 |
|  | $\mathrm{Cl}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Cl}-$ | -460.190 | -460.313 | -460.190 | -460.420 | 0.164 | -76.692 | -67.237 | -144.094 | -67.401 | -144.094 | 1.97 |
|  | $\mathrm{Br}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Br}-$ | -2574.204 | -2574.327 | -2574.206 | -2574.413 | -0.747 | -77.039 | -53.949 | -130.242 | -53.203 | -130.242 | 1.37 |
| B3LYP/LANL2DZ | ${ }^{*}+\mathrm{e}-\ldots>1-$ | -11.380 | -11.489 | -11.385 | -11.592 | -2.994 | -68.296 | -64.502 | -129.803 | -61.507 | -129.803 | 1.35 |
| M06-2X/aug-cc-pVDZ | $\mathrm{F}^{*}+\mathrm{e}-\cdots>\mathrm{F}-$ | -99.720 | -99.837 | -99.718 | -99.976 | 1.314 | -73.484 | -86.906 | -161.703 | -88.220 | -161.703 | 2.73 |
|  | Cl* + e- $-\gg \mathrm{Cl}-$ | -460.139 | -460.272 | -460.139 | -460.376 | 0.115 | -83.444 | -65.060 | -148.619 | -65.175 | -148.619 | 2.16 |
|  | $\mathrm{Br}^{*}+\mathrm{e}-\cdots>\mathrm{Br}-$ | -2574.150 | -2574.278 | -2574.151 | -2574.363 | -0.781 | -80.259 | -53.240 | -132.719 | -52.460 | -132.719 | 1.47 |
| M06-2X/LANL2DZ | $1^{*}+\mathrm{e}-\ldots>1-$ | -11.323 | -11.436 | -11.328 | -11.538 | -3.004 | -70.985 | -64.119 | -132.101 | -61.116 | -132.101 | 1.45 |
| M06-2X/cc-pvTZ | $\mathrm{F}^{*}+\mathrm{e}-\cdots \mathrm{P}$ - | -99.745 | -99.832 | -99.743 | -99.979 | 1.344 | -54.784 | -92.118 | -148.246 | -93.462 | -148.246 | 2.15 |
|  | $\mathrm{Cl}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Cl}-$ | -460.156 | -460.280 | -460.156 | -460.387 | 0.166 | -77.391 | -67.251 | -144.808 | -67.417 | -144.808 | 2.00 |
|  | $\mathrm{Br}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Br}-$ | -2574.215 | -2574.335 | -2574.216 | -2574.421 | -0.753 | -75.209 | -53.956 | -128.412 | -53.203 | -128.412 | 1.29 |
| M06-2X/LANL2DZ | $1^{*}+\mathrm{e}-\cdots>1-$ | -11.323 | -11.436 | -11.328 | -11.538 | -3.004 | -70.985 | -64.119 | -132.101 | -61.116 | -132.101 | 1.45 |
| M06-2X/Aug-cc-pVTZ//M06-2X/cc-pVDZ | $\mathrm{F}^{*}+\mathrm{e}-\cdots>\mathrm{F}-$ | -99.747 | -99.868 | -99.745 | -100.007 | 1.338 | -75.586 | -87.289 | -164.213 | -88.627 | -164.213 | 2.84 |
|  | $\mathrm{Cl}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Cl}-$ | -460.157 | -460.290 | -460.157 | -460.394 | 0.188 | -83.506 | -65.223 | -148.918 | -65.412 | -148.918 | 2.18 |
|  | $\mathrm{Br}^{*}+\mathrm{e}-\cdots>\mathrm{Br}-$ | -2574.215 | -2574.341 | -2574.217 | -2574.426 | -0.753 | -78.656 | -53.338 | -131.241 | -52.585 | -131.241 | 1.41 |
| M06-2X/LANL2DZ//M06-2X/LANL2DZ | $\mathrm{l}^{*}+\mathrm{e}-\mathrm{-}>1-$ | -11.323 | -11.436 | -11.328 | -11.538 | -3.005 | -70.984 | -64.120 | -132.100 | -61.116 | -132.100 | 1.45 |
| CCSD(T)/cc-pVTZ//M06-2X/cc-pVTZ | $\mathrm{F}^{*}+\mathrm{e}-\cdots>\mathrm{F}$ - | -99.635 | -99.713 | -99.633 | -99.859 | 1.332 | -48.550 | -92.123 | -142.004 | -93.454 | -142.004 | 1.88 |
|  | $\mathrm{Cl}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Cl}-$ | -459.687 | -459.800 | -459.687 | -459.907 | 0.182 | -70.699 | -67.282 | -138.162 | -67.463 | -138.162 | 1.71 |
|  | $\mathrm{Br}{ }^{*}+\mathrm{e}-\cdots>\mathrm{Br}-$ | -2572.67803 | -2572.792 | -2572.679 | -2572.878 | -0.753 | -71.690 | -53.966 | -124.903 | -53.213 | -124.903 | 1.14 |
| CCSD(T)/LANL2DZ//M06-2X/LANL2DZ | $1^{*}+\mathrm{e}-$ - $>$ + | -11.185 | -11.267 | -11.190 | -11.369 | -3.065 | -51.601 | -63.985 | -112.522 | -60.920 | -112.522 | 0.60 |

Table A.3. Compilation of $k_{\text {exp }}$ values with experimental conditions in the literature






|  | No. | Name | Chemical Formula | Identified Exp. Products | Proposed Mechanism | Arrhenius Parameters | Ionic Strength <br> (M) | Exp. $\mathrm{pH}^{\text {a }}$ | pKa | Adequate Exp. pH? | $\begin{gathered} k_{\text {exp }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Average $\begin{gathered} k_{\text {exp }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 60 |  | Chloromethane | $\mathrm{CH}_{3} \mathrm{Cl}$ | ${ }^{*} \mathrm{CH}_{3}+\mathrm{Cl}^{-}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | -- | -- | -- | $4.70 \mathrm{E}+08$ | $8.06 \mathrm{E}+08$ | 52 |
|  |  | $\begin{gathered} \log (\mathrm{A})=11.163 ; \mathrm{Ea} \\ =14.24 \mathrm{~kJ} / \mathrm{RT}(\text { temp } \\ 276-358 \mathrm{~K}) \end{gathered}$ |  |  |  | -- | -- | -- | -- | $4.60 \mathrm{E}+08$ | 54 |  |
|  |  | -- |  |  |  | -- | -- | -- | -- | $1.20 \mathrm{E}+09$ | 53 |  |
|  |  | -- |  |  |  | -- | -- | -- | -- | $1.10 \mathrm{E}+09$ | 54 |  |
|  |  | -- |  |  |  | -- | 10.00 | -- | Y | $\sim 8.0 \mathrm{E} 8$ | 56 |  |
|  | 61 |  | Dibromomethane | $\mathrm{CH}_{2} \mathrm{Br}_{2}$ | $\mathrm{Br}+{ }^{*} \mathrm{CH}_{2} \mathrm{Br}$ | $\mathrm{Br}^{-}$leaving | -- | -- | 4.00 | -- | Y | $2.00 \mathrm{E}+10$ | $2.00 \mathrm{E}+10$ | 55 |
|  | 62 |  | Bromoform | $\mathrm{CHBr}_{3}$ | -- | -- | -- | -- | 7.00 | 13.70 | Y | $1.00 \mathrm{E}+10$ | $1.00 \mathrm{E}+10$ | 56 |
|  | 63 |  | Bromoethane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Br}$ | $\mathrm{Br}^{-}+{ }^{*} \mathrm{CH}_{2} \mathrm{CH}_{3}$ | $\mathrm{Br}^{-}$leaving | -- | -- | 7.00 | -- | Y | $8.00 \mathrm{E}+09$ | $1.07 \mathrm{E}+10$ | 58 |
|  |  |  |  |  |  |  | -- | -- | 9-10 | -- | Y | $1.20 \mathrm{E}+10$ |  | 57 |
|  |  | -- |  |  |  |  | -- | 7.10 | -- | Y | $1.20 \mathrm{E}+10$ | 58 |  |
|  | 64 | Bromopropane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Br}$ | -- | -- | -- | -- | 7.00 | -- | Y | $1.00 \mathrm{E}+10$ | $9.25 \mathrm{E}+09$ | 58 |
|  |  |  |  | -- | -- | -- | -- | 6.15 | -- | Y | $8.50 \mathrm{E}+09$ |  | 60 |
|  | 65 | Chloropropane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Cl}$ | ${ }^{*} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}+\mathrm{Cl}^{-}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | 7.6-8.5 | -- | Y | $6.20 \mathrm{E}+08$ | $6.67 \mathrm{E}+08$ | 13 |
|  |  |  |  |  |  | -- | -- | 9-10 | -- | Y | $6.90 \mathrm{E}+08$ |  | 59 |
|  |  |  |  |  |  | -- | -- | 6.30 | -- | Y | $6.90 \mathrm{E}+08$ |  | 60 |
|  | 66 | Chloroethane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{Cl}$ | ${ }^{*} \mathrm{CH}_{2} \mathrm{CH}_{3}+\mathrm{Cl}^{-}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | -- | -- |  | $7.00 \mathrm{E}+08$ | $7.00 \mathrm{E}+08$ | 55 |
|  | 67 | 1-Bromo-2-chloroethane | $\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Br}$ | -- | -- | -- | -- | 7.00 | -- | Y | $8.00 \mathrm{E}+09$ | $8.00 \mathrm{E}+09$ | 58 |
|  | 68 | Halothane | $\mathrm{CF}_{3} \mathrm{CHClBr}$ | $\mathrm{CF}_{3} \mathrm{CHCl}+\mathrm{Br}^{-}$ | $\mathrm{Br}^{-}$leaving | -- | -- | 7.00 | -- | Y | $1.40 \mathrm{E}+10$ | $1.40 \mathrm{E}+10$ | 59 |
|  | 69 | 1,1-Dichloroethane | $\mathrm{CH}_{3} \mathrm{CHCl}_{2}$ | $\mathrm{Cl}^{-}+{ }^{*} \mathrm{CH}_{3} \mathrm{CHCl}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | $\sim 7$ | -- | Y | $9.00 \mathrm{E}+09$ | $9.00 \mathrm{E}+09$ | 60 |
|  | 70 | Diiodomethane | $\mathrm{CH}_{2} \mathrm{I}_{2}$ | $\mathrm{I}+{ }^{*} \mathrm{CH}_{2} \mathrm{I}$ | $I^{-}$leaving | -- | -- | 4.00 | -- | Y | $3.40 \mathrm{E}+10$ | $3.40 \mathrm{E}+10$ | 57 |
|  |  |  |  |  |  | -- | -- | -- | -- | -- | $3.40 \mathrm{E}+10$ |  | 61 |


|  | Name | Chemical Formula | Identified Exp. Products | Proposed Mechanism | Arrhenius Parameters | Ionic Strength (M) | Exp. $\mathrm{pH}^{\text {a }}$ | pKa | Adequate Exp. pH ? | $\underset{\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)}{k_{\mathrm{exp}}}$ | Average $k_{\text {exp }}$ $\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 71 | Iodoethane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{I}$ | $\mathrm{I}+{ }^{*} \mathrm{CH}_{2} \mathrm{CH}_{3}$ | I leaving | -- | -- | 9-10 | -- | Y | $1.50 \mathrm{E}+10$ | $1.50 \mathrm{E}+10$ | $\begin{aligned} & 59 \\ & 60 \end{aligned}$ |
|  |  |  |  |  | -- | -- | 6.04-6.75 | -- | Y | $1.50 \mathrm{E}+10$ |  |  |
|  | Dichloromethane | $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ | ${ }^{*} \mathrm{CH}_{2} \mathrm{Cl}+\mathrm{Cl}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | 10 | -- | Y | $6.00 \mathrm{E}+09$ | $6.00 \mathrm{E}+09$ | 62 |
|  | Chloroform | $\mathrm{CHCl}_{3}$ | -- | -- | -- | -- | 7.00 | 15.50 | Y | $3.00 \mathrm{E}+10$ | $3.00 \mathrm{E}+10$ | 12 |
|  | Trichlorofluoromethane | $\mathrm{CCl}_{3} \mathrm{~F}$ | ${ }^{*} \mathrm{CFCl}_{2}+\mathrm{Cl}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | $\sim 6$ | -- | Y | $1.60 \mathrm{E}+10$ | $1.60 \mathrm{E}+10$ | 63 |
|  | ichlorodifluoromethane | $\mathrm{CF}_{2} \mathrm{Cl}_{2}$ | ${ }^{*} \mathrm{CF}_{2} \mathrm{Cl}+\mathrm{Cl}{ }^{-}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | $\sim 6$ | -- | Y | $1.40 \mathrm{E}+10$ | $1.40 \mathrm{E}+10$ | 65 |
|  | Chlorotrifluoromethane | $\mathrm{CClF}_{3}$ | ${ }^{*} \mathrm{CF}_{3}+\mathrm{Cl}^{-}$ | Cl leaving | -- | -- | 9-10 | -- | Y | $4.40 \mathrm{E}+09$ | $4.40 \mathrm{E}+09$ | 59 |
|  | Bromotrifluoromethane | $\mathrm{CF}_{3} \mathrm{Br}$ | $\mathrm{Br}+{ }^{*} \mathrm{CF}_{3}$ | Br leaving | -- | -- | 9-10 | -- | Y | $2.30 \mathrm{E}+10$ | $2.30 \mathrm{E}+10$ | 59 |
| 78 | Carbon Tetrachloride | $\mathrm{CCl}_{4}$ | ${ }^{*} \mathrm{CCl}_{3}+\mathrm{Cl}^{-}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | -- | -- | -- | $1.30 \mathrm{E}+10$ | $1.87 \mathrm{E}+10$ | 46 |
|  |  |  |  |  | $\log (\mathrm{A})=13.010 ; \mathrm{Ea}$ $=15 \mathrm{~kJ} / \mathrm{RT}$ (temp 293-348 K) | -- | -- | -- | -- | $2.40 \mathrm{E}+10$ |  | 64 |
|  |  |  |  |  | -- | -- | -- | -- | -- | $1.90 \mathrm{E}+10$ |  | 65 |
|  | Chlorodifluoromethane | $\mathrm{CHClF}_{2}$ | ${ }^{*} \mathrm{CHF}_{2}+\mathrm{Cl}^{-}$ | Cl leaving | -- | -- | -- | -- |  | $2.90 \mathrm{E}+09$ | $2.90 \mathrm{E}+09$ | 66 |
|  | 1,1,2-Trichloroethane | $\mathrm{ClCH}_{2} \mathrm{CHCl}_{2}$ | $\mathrm{Cl}+{ }^{*} \mathrm{CH}_{2} \mathrm{ClCHCl}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | $\sim 7$ | -- | Y | $8.40 \mathrm{E}+09$ | $8.40 \mathrm{E}+09$ | 62 |
| 81 | 1,1,1-Trichloroethane | $\mathrm{CH}_{3} \mathrm{CCl}_{3}$ | $\mathrm{Cl}+{ }^{*} \mathrm{CH}_{3} \mathrm{CCl}_{2}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | -- | -- | -- | $2.50 \mathrm{E}+10$ | $1.95 \mathrm{E}+10$ | 55 |
|  |  |  |  |  | -- | -- | $\sim 7$ | -- | Y | $1.40 \mathrm{E}+10$ |  | 62 |
|  | Hexachloroethane | $\mathrm{CCl}_{3} \mathrm{CCl}_{3}$ | $\mathrm{Cl}+{ }^{*} \mathrm{CCl}_{3} \mathrm{CCl}_{2}$ | $\mathrm{Cl}^{\text {l }}$ leaving | -- | -- | $\sim 7$ | -- | Y | $3.90 \mathrm{E}+10$ | $3.90 \mathrm{E}+10$ | 62 |
|  | 2-Chlorobutane | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{CH}(\mathrm{Cl}) \mathrm{CH}_{3}$ | -- | -- | -- | -- | 6.64 | -- | Y | $5.10 \mathrm{E}+08$ | $5.10 \mathrm{E}+08$ | 60 |
| 84 | 1,2-Dibromoethane | $\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{Br}$ | $\mathrm{Br}+{ }^{*} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Br}$ | Br leaving | -- | -- | 7.00 | -- | Y | $1.40 \mathrm{E}+10$ | $1.30 \mathrm{E}+10$ | 58 |
|  |  |  |  |  | -- | -- | $\sim 7$ | -- | Y | $1.20 \mathrm{E}+10$ |  | 62 |
|  | 1,2-Dichloroethane | $\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathrm{Cl}$ | $\mathrm{Cl}^{+}{ }^{*} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Cl}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | -- | -- | -- | $6.40 \mathrm{E}+08$ | $1.77 \mathrm{E}+09$ | 67 |
| 85 |  |  |  |  | -- | -- | $\sim 7$ | -- | Y | $2.90 \mathrm{E}+09$ |  | 62 |
|  | 1,1,2-Trichloro-1,2,2trifluoroethane | $\mathrm{ClCF}_{2} \mathrm{CCl}_{2} \mathrm{~F}$ | $\mathrm{Cl}+{ }^{*} \mathrm{CF}_{2} \mathrm{CCl}_{2} \mathrm{~F}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | $\sim 7$ | -- | Y | $1.40 \mathrm{E}+10$ | $1.40 \mathrm{E}+10$ | 62 |


|  | Name | Chemical Formula | Identified Exp. Products | Proposed <br> Mechanism | Arrhenius Parameters | Ionic Strength (M) | Exp. $\mathrm{pH}^{\text {a }}$ | pKa | Adequate Exp. pH ? | $\begin{gathered} k_{\text {exp }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Average $k_{\text {exp }}$ $\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1-Iodopropane | $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{I}$ | -- | I leaving | -- | -- | 6.20 | -- | Y | $1.30 \mathrm{E}+10$ | $1.30 \mathrm{E}+10$ | 60 |
|  | 1-Iodobutane | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{I}$ | -- | -- | -- | -- | 7.60 | -- | Y | $1.20 \mathrm{E}+10$ | $1.20 \mathrm{E}+10$ | 60 |
| 89 | 1-Bromobutane | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}$ | $\begin{gathered} \mathrm{Br}+ \\ { }^{\mathrm{Cr}} \mathrm{CH}_{2}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{3} \end{gathered}$ | $\mathrm{Br}^{-}$leaving | -- | -- | 7.00 | -- | Y | $9.00 \mathrm{E}+09$ |  | 58 |
|  |  |  |  |  | -- | -- | 9-10 | -- | Y | $1.00 \mathrm{E}+10$ | $9.67 \mathrm{E}+09$ | 59 |
|  |  |  |  |  | -- | -- | 6.57 | -- | Y | $1.00 \mathrm{E}+10$ |  | 60 |
|  | 1-Chlorobutane | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Cl}$ | $\begin{gathered} \mathrm{Cl}^{-}+ \\ { }^{*} \mathrm{CH}_{2}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{3} \end{gathered}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | 7.6-8.5 | -- | Y | $4.00 \mathrm{E}+08$ | $3.37 \mathrm{E}+08$ | 13 |
|  |  |  |  |  | -- | -- | -- | -- | -- | $4.80 \mathrm{E}+07$ |  | 28 |
|  |  |  |  |  | -- | -- | 9-10 | -- | Y | $4.50 \mathrm{E}+08$ |  | 59 |
|  |  |  |  |  | -- | -- | 7.28 | -- | Y | $4.50 \mathrm{E}+08$ |  | 60 |
|  | 1-Chloro-2-methylpropane | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}$ | -- | -- | -- | -- | 5.82 | -- | Y | $5.10 \mathrm{E}+08$ | $5.10 \mathrm{E}+08$ | 60 |
|  | 1-Bromopentane | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}$ | -- | -- | -- | -- | 7.00 | -- | Y | $8.00 \mathrm{E}+09$ | $8.00 \mathrm{E}+09$ | 58 |
|  | 2-Bromo-2-methylpropane | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}$ | -- | -- | -- | -- | 7.00 | -- | Y | $7.20 \mathrm{E}+09$ | $7.20 \mathrm{E}+09$ | 58 |
|  | 2-Bromobutane | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{Br}) \mathrm{CH}_{3}$ | -- | -- | -- | -- | 7.00 | -- | Y | $7.20 \mathrm{E}+09$ | 7.20E+09 | 58 |
|  | Trifluoroiodomethane | $\mathrm{CF}_{3} \mathrm{I}$ | ${ }^{*} \mathrm{CF}_{3}+\mathrm{I}$ | I leaving | -- | -- | 9-10 | -- | Y | $1.30 \mathrm{E}+10$ | $1.30 \mathrm{E}+10$ | 59 |
| 96 | Iodomethane | $\mathrm{CH}_{3} \mathrm{I}$ | ${ }^{*} \mathrm{CH}_{3}+\mathrm{I}$ | I' leaving | -- | -- | 9-10 | -- | Y | $1.60 \mathrm{E}+10$ | $1.60 \mathrm{E}+10$ | 59 |
|  |  |  |  |  | -- | -- | -- | -- |  | $1.60 \mathrm{E}+10$ |  |  |
|  | Isoflurane | $\mathrm{CHF}_{2} \mathrm{OCHClCF}_{3}$ | $\mathrm{CHF}_{2} \mathrm{OCHCF}_{3}$ | $\mathrm{Cl}^{-}$leaving | -- | -- | $\sim 7$ | -- | Y | $4.70 \mathrm{E}+09$ | 4.70E+09 | 62 |
|  | 1,1,1-Trifluoroacetone | $\mathrm{CF}_{3} \mathrm{COCH}_{3}$ | -- | -- | -- | -- | 5.19 | -- | Y | $6.60 \mathrm{E}+07$ | $6.60 \mathrm{E}+07$ | 20 |
| 99 | Fluoroacetone | $\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{~F}$ | -- | -- | -- | -- | 6.70 | -- | Y | $1.00 \mathrm{E}+09$ | $9.40 \mathrm{E}+08$ | 20 |
|  |  |  | -- | -- | -- | -- | 11.00 | -- |  | $8.80 \mathrm{E}+08$ |  |  |
|  | Methoxyflurane | $\mathrm{CH}_{3} \mathrm{OCF}_{2} \mathrm{CHCl}_{2}$ | $\begin{gathered} \mathrm{Cl}^{*}+ \\ { }^{\mathrm{CH}} \mathrm{OCF}_{2} \mathrm{CHCl} \end{gathered}$ | -- | -- | -- | $\sim 7$ | -- | Y | 1.40E+10 | $1.40 \mathrm{E}+10$ | 62 |




|  | Name | Chemical Formula | Identified Exp. Products | Proposed <br> Mechanism | Arrhenius Parameters | Ionic Strength (M) | Exp. $\mathrm{pH}^{\text {a }}$ | pKa | Adequate <br> Exp. pH? | $\begin{gathered} k_{\text {exp }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Average $k_{\text {exp }}$ $\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)$ | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 134 | Formamide | $\mathrm{HCONH}_{2}$ | -- | -- | -- | -- | -- | 16.50 | -- | $2.00 \mathrm{E}+07$ | $2.80 \mathrm{E}+07$ | 85 |
|  |  |  | -- | -- | -- | -- | 6.30 |  | Y | $1.80 \mathrm{E}+07$ |  | 73 |
|  |  |  | -- | -- | -- | -- | 9.20 |  | Y | $6.30 \mathrm{E}+07$ |  | 84 |
|  |  |  | -- | -- | -- | -- | -- |  | -- | <1.0E6 |  | 86 |
|  |  |  | -- | -- | $\log (\mathrm{A})=9.898, \mathrm{Ea}=$ $13 \mathrm{~kJ} /$ RT (temp 293$343 \mathrm{~K})$ | -- | $\sim 5.8$ |  | Y | $3.80 \mathrm{E}+07$ |  | 52 |
|  | 3-Chloropropionamide | $\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathrm{CONH}_{2}$ | -- | -- | -- | -- | $\sim 6$ | 15.92 | Y | $1.80 \mathrm{E}+09$ | $1.80 \mathrm{E}+09$ | 85 |
|  | (S)-2-Hydroxypropanamide | $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CONH}_{2}$ | -- | -- | -- | -- | 7.00 | 13.34 | Y | $1.90 \mathrm{E}+08$ | $1.90 \mathrm{E}+08$ | 24 |
| 137 | Aceturate | $\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{COO}^{-}$ | -- | -- | -- | -- | 11.50 | 3.77 |  | $2.60 \mathrm{E}+06$ | $1.13 \mathrm{E}+07$ | 39 |
|  |  |  | -- | -- | -- | -- | 5.95 |  | Y | $2.00 \mathrm{E}+07$ |  | 87 |
|  | Pivalamide | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCONH}_{2}$ | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCONH}_{2}{ }^{*}$ | -- | -- | -- | 9.20 | -- | Y | $1.50 \mathrm{E}+07$ | $1.50 \mathrm{E}+07$ | 84 |
|  | Malonamide | $\mathrm{H}_{2} \mathrm{NCOCH}_{2} \mathrm{CONH}_{2}$ | -- | -- | -- | -- | 7.00 | 15-17 | Y | $1.10 \mathrm{E}+09$ | $1.10 \mathrm{E}+09$ | 88 |
|  | 2-Hydroxyacetamide | $\mathrm{HOCH}_{2} \mathrm{CONH}_{2}$ | -- | -- | -- | -- | 8.50 | 15-17 | Y | $2.90 \mathrm{E}+08$ | $2.90 \mathrm{E}+08$ | 24 |
|  | Biuret | $\mathrm{H}_{2} \mathrm{NCONHCONH}_{2}$ | $\begin{gathered} \mathrm{H}_{2} \mathrm{NC}\left(\mathrm{O}^{-}\right. \\ ) \mathrm{NHCONH}_{2} \end{gathered}$ | -- | -- | -- | 10.30 | 15-17 | Y | $2.50 \mathrm{E}+08$ | $2.50 \mathrm{E}+08$ | 90 |
|  | 2-Chloropropionamide | $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{Cl}) \mathrm{CONH}_{2}$ | -- | -- | -- | -- | $\sim 6$ | $\sim 15$ | Y | $5.80 \mathrm{E}+09$ | $5.80 \mathrm{E}+09$ | 85 |
|  | Iodoacetamide | $\mathrm{ICH}_{2} \mathrm{CONH}_{2}$ | $\mathrm{I}+{ }^{*} \mathrm{CH}_{2} \mathrm{CONH}_{2}$ | I leaving | -- | -- | -- | -- | -- | $5.00 \mathrm{E}+10$ | $5.00 \mathrm{E}+10$ | 89 |
|  | Hydroxyurea | $\mathrm{HONHCONH}_{2}$ | $\left[\mathrm{HONHCONH}_{2}\right]^{*-}$ | -- | -- | -- | 6.80 | 10.60 | Y | $4.80 \mathrm{E}+08$ | $4.80 \mathrm{E}+08$ | 90 |
|  | Oxamate | $\mathrm{H}_{2} \mathrm{NCOCOO}^{-}$ | -- | -- | -- | -- | 9.20 | 2.49 | Y | $5.70 \mathrm{E}+09$ | $5.70 \mathrm{E}+09$ | 90 |
|  | Succinamide | $\mathrm{H}_{2} \mathrm{NCOCH}_{2} \mathrm{CH}_{2} \mathrm{CONH}_{2}$ | -- | -- | -- | -- | 7.10 | 15-17 | Y | $2.00 \mathrm{E}+08$ | $2.00 \mathrm{E}+08$ | 90 |
|  | Asparaginate | $\mathrm{H}_{2} \mathrm{NCOCH}_{2} \mathrm{CH}\left(\mathrm{NH}_{2}\right) \mathrm{COO}^{-}$ | -- | -- | -- | -- | 11.70 | 2-3 | Y | $2.40 \mathrm{E}+07$ | $2.40 \mathrm{E}+07$ | 91 |
| 148 | N,N-Dimethylformamide | $\mathrm{HCON}\left(\mathrm{CH}_{3}\right)_{2}$ | -- | -- | -- | -- | -- | -0.30 | -- | $4.00 \mathrm{E}+08$ |  | 87 |
|  |  |  | -- | -- | -- | -- | 9.20 |  | Y | $4.60 \mathrm{E}+08$ | $3.04 \mathrm{E}+08$ | 84 |
|  |  |  | -- | -- | -- | -- | -- |  | -- | $5.20 \mathrm{E}+07$ |  | 88 |








| No. | Name | Chemical Formula | Identified Exp. <br> Products | Proposed <br> Mechanism | Arrhenius Parameters | Ionic Strength <br> (M) | Exp. $\mathrm{pH}^{\text {a }}$ | pKa | Adequate Exp. pH? | $\begin{gathered} k_{\text {exp }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Average $\begin{gathered} k_{\text {exp }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 250 | Ethyl Acrylate | $\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOC}_{2} \mathrm{H}_{5}$ | -- | C-O bond cleavage | -- | -- | 11 | -- | -- | 8.70E+09 | $8.70 \mathrm{E}+09$ | 119 |
| 251 | Acetone Oxime | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{NOH}$ | -- | -- | -- | -- | 7 | -- | -- | $3.50 \mathrm{E}+08$ | $3.25 \mathrm{E}+08$ | 73 |
|  |  |  | -- | -- |  | -- | 7.75 | -- | -- | $3.00 \mathrm{E}+08$ |  | 20 |

Table A.4. $E_{\text {red,aq }}^{\circ}$ of all possible attacking sites in each aliphatic compound in the dataset


| Class |  | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\mathrm{e}}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{credaq}}^{\circ}}$ |  |  |  |  | $\begin{aligned} & E_{\mathrm{C}_{\mathrm{red}}} \\ & (\mathrm{~V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\underset{\left(\mathrm{k}_{\mathrm{ca} /}^{\mathrm{reded}, \mathrm{~mol}}\right)}{ }$ | $\begin{aligned} & E_{\mathrm{red}}^{\mathrm{o}} \\ & \text { (V vs } \\ & \text { SHE) } \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right) \end{aligned}$ | $\begin{aligned} & E_{E_{\text {red }}}(\mathrm{Vvs} \\ & \text { SHE } \end{aligned}$ |  |
| Carboxylate |  |  | 9 | Malonate | $\mathrm{OOC}_{-} \mathrm{CH}_{2}-\mathrm{COO}^{-}$ |  | $\begin{aligned} & \mathrm{OOCCH}_{2} \mathrm{COO}+\mathrm{e}^{-} \rightarrow \\ & -\mathrm{OOCCH}_{2} \mathrm{CO}(-) \mathrm{O}^{-} \\ & \mathrm{OOCCH}_{2} \mathrm{COO}+\mathrm{e}^{-} \rightarrow \\ & \mathrm{OOCCHCO}^{-}-\mathrm{O}^{-}+\mathrm{H}^{-} \end{aligned}$ | -9.073 | $-3.89^{\text {b }}$ | -- | -- | -- | -- | $1.00 \times 10^{7}$ |
|  |  | -- |  |  |  |  |  | -- | 13.960 | $-4.89{ }^{\text {a }}$ | -- | -- |  |  |
|  |  |  |  |  |  | $\begin{gathered} \mathrm{HOOCCH}_{2} \mathrm{COO}+\mathrm{e}^{-} \rightarrow \\ \mathrm{HOOCCH}_{2} \mathrm{CO}(-) \mathrm{O}^{-} \end{gathered}$ | -35.927 | $-2.72^{\text {b }}$ | -- | -- | -- | -- |  |  |
|  |  |  |  |  |  | $\begin{gathered} \mathrm{HOOCCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\ \mathrm{OC}^{-} \mathrm{CH}_{2} \mathrm{COO}^{-}+\mathrm{OH}^{-} \end{gathered}$ | -- | -- | 5.142 | $-4.50^{a}$ | -- | -- |  |  |
|  |  |  |  |  |  | $\begin{aligned} & \mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\ & \mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2}{ }_{2} \mathrm{CO}(-) \mathrm{O}^{-} \end{aligned}$ | -32.735 | $-2.86^{\text {b }}$ | -- | -- | -- | -- |  |  |
|  |  |  |  |  |  | $\begin{gathered} \mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}+\mathrm{e}-\rightarrow \\ \mathrm{OCC}^{-}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}+\mathrm{OH}^{-} \end{gathered}$ | -- | -- | 7.757 | $-4.62^{a}$ | -- | -- |  |  |
|  |  |  |  |  |  | $\begin{gathered} \mathrm{CH}_{3} \mathrm{CHOHCOO}^{-}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \mathrm{CHOH} \\ \hline \text { CO(-)O} \end{gathered}$ | -5.700 | $-4.03^{\text {b }}$ | -- | -- | -- | -- |  |  |
|  |  |  |  |  | О | $\begin{gathered} \mathrm{CH}_{3} \mathrm{CHOHCOO}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \mathrm{CH}^{-} \mathrm{COO}^{-}+\mathrm{OH}^{-} \end{gathered}$ | -- | -- | -12.063 | $-3.76{ }^{\text {a }}$ | -- | -- |  |  |


| Class |  | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\mathrm{e}}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  | $\begin{aligned} & E_{\mathrm{red}}^{\mathrm{o} \text { ed }} \\ & (\mathrm{V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\mathrm{credaq}}^{\mathrm{r}} \\ & \left(\mathrm{k}_{\mathrm{c} / \mathrm{mol}}^{\mathrm{mol})}\right. \end{aligned}$ | $\begin{aligned} & E_{\mathrm{Cred}}^{\mathrm{o}} \\ & (\mathrm{~V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\mathrm{cal}}^{\circ} \mathrm{o} \text { od,aq } \\ & \left(\mathrm{K}_{\mathrm{cal}} / \mathrm{mol}\right) \end{aligned}$ |  |  |
| Carboxylate |  |  | 13 | Glycolate | $\mathrm{HOCH}_{2} \mathrm{COO}^{-}$ |  | $\begin{gathered} \mathrm{HOCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-\rightarrow} \\ \mathrm{HOCH}_{2} \mathrm{CO}(-) \mathrm{O}^{-} \end{gathered}$ | -6.606 | $-3.99^{\text {b }}$ | -- | -- | -- | -- | $8.20 \times 10^{6}$ |
|  |  | $\begin{gathered} \mathrm{HOCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\ {\left[\mathrm{OCH}_{2} \mathrm{COO}\right]^{2}+\mathrm{H}^{-}} \end{gathered}$ |  |  |  |  | -- | -- | 6.926 | $-4.58{ }^{\text {a }}$ | -- | -- |  |  |
|  |  | $\begin{aligned} & \mathrm{HOCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{HOCHCOO}^{-}+\mathrm{H}^{-}\right.} \end{aligned}$ |  |  |  |  | -- | -- | 28.841 | $-5.53{ }^{\text {a }}$ | -- | -- |  |  |
|  |  | $\begin{gathered} \mathrm{HOCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow{ }^{-} \mathrm{CH}_{2} \mathrm{COO}^{-} \\ +\mathrm{OH}- \end{gathered}$ |  |  |  |  | -- | -- | -10.115 | $-3.84{ }^{\text {a }}$ | -- | -- |  |  |
|  |  |  |  |  | 을 | $\mathrm{CH}_{3} \mathrm{COCOO}^{-}+\mathrm{e}^{-} \rightarrow$ $\left[\mathrm{CH}_{3} \mathrm{COCOO}\right]^{2-}$ | -50.939 | $-2.07^{\text {b }}$ | -- | -- | -- | -- |  |  |
|  |  |  |  |  | - | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{COCOO}^{-}+\mathrm{e}^{-} \rightarrow \vec{~} \\ & {\left[\mathrm{CH}_{2} \mathrm{COCOO}\right]^{-2}+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | -3.486 | $-4.13{ }^{\text {a }}$ | -- | -- |  |  |


| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\mathrm{e}}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\begin{aligned} & \Delta G^{\circ} \mathrm{o} \text { red.aq } \\ & \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{aligned} & E_{\mathrm{red}}^{\mathrm{o}} \\ & \text { (V vs } \\ & \text { SHE) } \end{aligned}$ | $\begin{aligned} & \Delta G^{\text {red.aq }} \\ & \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right) \end{aligned}$ | $\begin{aligned} & E^{E_{\text {red }}^{\circ}} \\ & \text { (V vs } \\ & \text { SHE) } \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\text {red.aq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right) \end{aligned}$ | $\begin{aligned} & E_{\mathrm{Cred}}^{\circ} \\ & (\mathrm{V} \text { vs } \\ & \mathrm{SHE} \\ & \hline \end{aligned}$ |  |
| Carboxylate | 15 | CID_4134252 | $\mathrm{HOCH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}$ |  | $\mathrm{HOCH}_{2}\left(\mathrm{CHOH}_{4} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow\right.$ $\left[\mathrm{HOCH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}\right]^{-}$ | -13.587 | $-3.69^{\text {b }}$ | -- | -- | -- | -- | $1.00 \times 10^{6}$ |
|  |  |  |  |  | $\begin{aligned} & \mathrm{HOCH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\ & { }^{\circ} \mathrm{CH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}+\mathrm{OH}^{-} \end{aligned}$ | -- | -- | -9.684 | $-3.86^{a}$ | -- | -- |  |
|  |  |  |  |  | $\mathrm{HOCH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow$ $\mathrm{HOCH}_{2}{ }^{\circ} \mathrm{CH}(\mathrm{CHOH})_{3} \mathrm{COO}^{-}+$ $\mathrm{OH}^{-}$ | -- | -- | -7.585 | $-3.95{ }^{\text {a }}$ | -- | -- |  |
|  |  |  |  | - OH | $\mathrm{HOCH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow$ $\mathrm{HOCH}_{2} \mathrm{CHOH} \cdot \mathrm{CH}(\mathrm{CHOH})_{2} \mathrm{CO}$ $\mathrm{O}^{-}+\mathrm{OH}^{-}$ | -- | -- | -8.980 | $-3.89^{a}$ | -- | -- |  |
|  |  |  |  |  | $\mathrm{HOCH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow$ $\mathrm{HOCH}_{2} \mathrm{CHOHCHOH}{ }^{\circ} \mathrm{CHCHOH}$ $\mathrm{COO}^{+} \mathrm{OH}^{-}$ | -- | -- | -13.703 | $-3.69^{a}$ | -- | -- |  |
|  |  |  |  |  | $\mathrm{HOCH}_{2}\left(\mathrm{CHOH}_{4} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow\right.$ $\mathrm{HOCH}_{2}(\mathrm{CHOH})_{3}{ }^{\circ} \mathrm{CHCOO}^{-}$ $\mathrm{OH}^{-}$ | -- | -- | -13.307 | $-3.70^{a}$ | -- | -- |  |
|  | 16 | Malate | $\mathrm{OOCCH}_{2} \mathrm{CHOHCOO}^{-}$ |  | $\underset{\left.\mathrm{OOCCH}_{2} \mathrm{CHOHCOO}^{-}\right]^{-}}{\mathrm{OOCCH}_{2} \mathrm{CHOHCOO}^{-}+{ }^{-} \rightarrow\left[{ }^{-}\right.}$ | -11.815 | $-3.77^{\text {b }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{OOCCH}_{2} \mathrm{CHOHCOO}^{-}+\mathrm{e}^{-} \rightarrow \mathrm{OCO}_{2}^{-} \mathrm{O}^{-} \mathrm{OHOCOO}^{-}+\mathrm{H}^{-} \end{aligned}$ | -- | -- | 8.850 | $-4.66^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \left.\mathrm{OOCCH}_{2} \mathrm{CHOHCOO}^{-}+\mathrm{e}^{-} \rightarrow{ }^{-} \mathrm{OOCCH}_{2} \mathrm{COHCOO}^{-}\right]^{-}+\mathrm{H}^{-} \end{aligned}$ | -- | -- | 32.830 | $-5.70^{a}$ | -- | -- | $6.01 \times 10^{7}$ |
|  |  |  |  |  |  | -- | -- | 24.844 | $-5.36^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{OOCCH}_{2} \mathrm{OHOHCOO}^{-}+\mathrm{e}^{-} \rightarrow \\ \mathrm{OOCHO}_{2} \rightarrow \mathrm{COO}^{-}+\mathrm{OH}^{-} \end{gathered}$ | -- | -- | -11.626 | $-3.78^{a}$ | -- | -- |  |

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} \& \multirow[b]{2}{*}{No.} \& \multirow[b]{2}{*}{Name} \& \multirow[b]{2}{*}{Chemical Formula} \& \multirow[b]{2}{*}{2D Chemical Structure ${ }^{\text {c }}$} \& \multirow[b]{2}{*}{Reduction Mechanism} \& \multicolumn{2}{|l|}{Association} \& \multicolumn{2}{|l|}{Concerted} \& \multicolumn{2}{|l|}{Stepwise} \& \multirow[b]{2}{*}{$$
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
$$} <br>
\hline \& \& \& \& \& \& $$
\begin{gathered}
\Delta G_{\mathrm{cred,aq}}^{\circ} \\
\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{gathered}
$$ \& $$
\begin{aligned}
& E_{\mathrm{C}_{\text {red }}} \mathrm{V} \text { vs } \\
& \mathrm{SHE}
\end{aligned}
$$ \& $$
\begin{aligned}
& \Delta G_{c_{\text {red.aq }}^{\circ}}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
$$ \& $$
\begin{aligned}
& E_{\mathrm{red}}^{\mathrm{o}} \\
& \text { (V vs } \\
& \text { SHE) } \\
& \hline
\end{aligned}
$$ \& $$
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ}}
$$ \& $$
\begin{aligned}
& E_{\mathrm{C}_{\text {red }}}^{(\mathrm{V} \text { vs }} \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
$$ \& <br>
\hline \multirow{9}{*}{Carboxylic Acid} \& 17 \& Oxalic Acid \& HOOCCOOH \&  \& $$
\begin{gathered}
\mathrm{HO}_{2} \mathrm{C}_{2} \mathrm{O}_{2} \mathrm{H}+\mathrm{e}^{-} \rightarrow \mathrm{OH} \mathrm{HOOC} \cdot \mathrm{CO}(- \\
\mathrm{OO}_{2} \mathrm{C}_{2} \mathrm{O}_{2} \mathrm{H}+\underset{\mathrm{OH}^{-}}{\mathrm{e}^{-} \rightarrow \mathrm{HOOC}}{ }^{-} \mathrm{CO}+ \\
\hline
\end{gathered}
$$ \& $$
-62.942
$$ \& $$
-1.55^{\mathrm{b}}
$$ \& --
10.378 \& --
$-4.73{ }^{\text {a }}$ \& -- \& -- \& $2.50 \times 10^{10}$ <br>
\hline \& 18 \& Formic Acid \& HCOOH \&  \& $$
\mathrm{HCOOH}+\mathrm{e}^{-} \rightarrow \mathrm{H}^{*} \mathrm{CO}(-) \mathrm{OH}
$$
$$
\mathrm{HCOOH}+\mathrm{e}^{-} \rightarrow \mathrm{H}^{-} \mathrm{CO}+\mathrm{OH}^{-}
$$ \& -39.005
-- \& $-2.59^{\text {b }}$

-- \& --
6.357 \& --
$-4.56{ }^{\text {a }}$ \& -- \& -- \& $1.41 \times 10^{8}$ <br>

\hline \& \& \& \& \& $$
\begin{gathered}
\mathrm{HO}_{2} \mathrm{C}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CO}_{2} \mathrm{H}+\mathrm{e}^{-} \rightarrow \\
\mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2}{ }^{2} \mathrm{CO}(-) \mathrm{OH}
\end{gathered}
$$ \& -35.299 \& $-2.75^{\text {b }}$ \& -- \& -- \& -- \& -- \& <br>

\hline \& 19 \& Succinic Acid \& $\mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}$ \&  \& $$
\begin{aligned}
& \mathrm{HO}_{2} \mathrm{C}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CO}_{2} \mathrm{H}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{HOOO}^{-}\left(\mathrm{CH}_{2}\right) \mathrm{CHCOO}\right]+{ }^{-}}
\end{aligned}
$$ \& -- \& -- \& -2.834 \& $-4.16^{a}$ \& -- \& -- \& $2.30 \times 10^{8}$ <br>

\hline \& \& \& \& \& $$
\begin{aligned}
& \mathrm{HO}_{2} \mathrm{C}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CO}_{2} \mathrm{H}+\mathrm{e}^{-} \rightarrow \\
& \mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CO}+\mathrm{OH}^{-}
\end{aligned}
$$ \& -- \& -- \& 7.496 \& $-4.60{ }^{\text {a }}$ \& -- \& -- \& <br>

\hline \& \multirow{4}{*}{20} \& \multirow{4}{*}{Propionic Acid} \& \multirow{4}{*}{$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}$} \& \& $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow$ $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}(-) \mathrm{OH}$ \& -35.025 \& $-2.76^{\text {b }}$ \& -- \& -- \& -- \& -- \& \multirow{4}{*}{$2.20 \times 10^{7}$} <br>

\hline \& \& \& \&  \& $$
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CHCOOH}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
$$ \& -- \& -- \& 1.168 \& $-4.33{ }^{\text {a }}$ \& -- \& -- \& <br>

\hline \& \& \& \& + \& $$
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COOOH}\right]+} \\
& \hline
\end{aligned}
$$ \& -- \& -- \& 33.426 \& $-5.73{ }^{\text {a }}$ \& -- \& -- \& <br>

\hline \& \& \& \& \& $$
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}+\mathrm{OH}^{-}
\end{gathered}
$$ \& -- \& -- \& 6.418 \& $-4.56{ }^{\text {a }}$ \& -- \& -- \& <br>

\hline
\end{tabular}



| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\mathrm{e}}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol} / \mathrm{mol}\right)}{\mathrm{rem}^{\mathrm{r}}}$ | $\begin{aligned} & E_{\mathrm{E}_{\mathrm{red}}^{\circ}} \mathrm{V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\underset{\left(\mathrm{k}_{\mathrm{cal}} / G_{\mathrm{credoq}}^{\circ} \mathrm{mol}\right)}{\circ}$ | $\begin{aligned} & \hline E_{\text {red }}^{\circ} \\ & \text { (V vs } \\ & \text { SHE } \end{aligned}$ | $\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{crdaq}}^{\circ}}$ | $\begin{aligned} & E^{E_{\text {red }}^{\circ}} \\ & \text { (V vs } \\ & \text { SHE) } \end{aligned}$ |  |
| Carboxylic Acid | 25 | Glycolic acid | $\mathrm{HOCH}_{2} \mathrm{COOH}$ |  | $\begin{gathered} \mathrm{HOCH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow \\ \mathrm{HOCH}_{2}{ }^{2} \mathrm{CO}(-) \mathrm{OH} \end{gathered}$ | -40.415 | $-2.53^{\text {b }}$ | -- | -- | -- | -- | $4.38 \times 10^{8}$ |
|  |  |  |  |  | $\mathrm{HOCH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow$ $[\mathrm{HOCHCOOH}]^{-}+\mathrm{H}^{+}$ | -- | -- | 0.331 | $-4.29^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{HOCH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow \\ {\left[\mathrm{OCH}_{2} \mathrm{COOH}\right]+\mathrm{H}^{-}} \end{gathered}$ | -- | -- | -4.933 | $-4.07{ }^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{HOCH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow \\ & \mathrm{HOCH}_{2}{ }^{-} \mathrm{CO}+\mathrm{OH}^{-} \end{aligned}$ | -- | -- | 6.645 | $-4.57^{a}$ | -- | -- |  |
|  |  |  |  |  | $\xrightarrow{\mathrm{HOCH}_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow} \rightarrow$ | -- | -- | -15.503 | $-3.61{ }^{\text {a }}$ | -- | -- |  |
| Alcohol | 26 | Methanediol | $\mathrm{CH}_{2}(\mathrm{OH})_{2}$ |  | $\mathrm{CH}_{2}(\mathrm{OH})_{2}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CH}_{2}(\mathrm{OH})_{2}\right]^{-}$ | -13.523 | $-3.69^{\text {b }}$ | -- | -- | -- | -- | $1.00 \times 10^{7}$ |
|  |  |  |  |  | $\begin{gathered} \mathrm{CH}_{2}(\mathrm{OH})_{2}+\mathrm{e}^{-} \rightarrow \\ { }^{-\mathrm{CH}_{2} \mathrm{OH}+\mathrm{OH}^{-}} \end{gathered}$ | -- | -- | -6.929 | $-3.98{ }^{\text {a }}$ | -- | -- |  |
|  | 27 | Tert-Butanol | $\left(\mathrm{CH}_{3}\right)_{3}$ - $\mathrm{C}-\mathrm{OH}$ | $\mathrm{OH}$ | $\left(\mathrm{CH}_{3}\right)_{3}-\mathrm{C}-\mathrm{OH}+\mathrm{e}^{-} \rightarrow$ <br> $\left[\left(\mathrm{CH}_{3}\right)_{3}-\mathrm{C}-\mathrm{OH}\right]^{-}$ | -6.326 | $-4.01^{\text {b }}$ | -- | -- | -- | -- | $4.00 \times 10^{5}$ |
|  |  |  |  |  | $\begin{gathered} \left(\mathrm{CH}_{3}\right)_{3}-\mathrm{C}-\mathrm{OH}+\mathrm{e}^{-} \rightarrow \\ \left(\mathrm{CH}_{3}\right)_{3}-\mathrm{C}+\mathrm{OH}^{-} \end{gathered}$ | -- | -- | -10.962 | $-3.80{ }^{\text {a }}$ | -- | -- |  |



| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\text {e }}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\begin{aligned} & \Delta G^{\text {red.aq }} \\ & \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right) \end{aligned}$ | $\begin{aligned} & E_{\text {red }}^{\circ} \mathrm{c} \\ & \text { (V vs } \\ & \text { SHE) } \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\text {red.aq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right) \end{aligned}$ | $\begin{aligned} & \begin{array}{l} E_{\mathrm{red}}^{\circ} \\ (\mathrm{V} \text { vs } \\ \text { SHE) } \\ \hline \end{array} \\ & \hline \end{aligned}$ | $\begin{gathered} \Delta G_{\text {red.aq }}^{\circ} \\ \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right) \end{gathered}$ | $\begin{aligned} & E_{E_{\text {red }}^{\circ}}^{(\mathrm{V} \mathrm{vs}} \\ & (\mathrm{V} \text { SE) } \\ & \hline \end{aligned}$ |  |
| Ester | 31 | Methyl Propionate | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{3}$ |  | $\begin{gathered} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{3}+\mathrm{e}^{-} \rightarrow \mathrm{C}_{2} \mathrm{CH}_{5}{ }^{\circ} \mathrm{CO}(- \\ \mathrm{OCH}_{3} \end{gathered}$ | -33.244 | $-2.84^{\text {b }}$ | -- | -- | -- | -- | $9.03 \times 10^{7}$ |
|  |  |  |  |  | $\begin{aligned} & \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{3}+\mathrm{e}^{-} \vec{~} \\ & {\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{2}\right]+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | 0.704 | $-4.31{ }^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCOHOCH}_{3}+\mathrm{e}^{-} \rightarrow \\ {\left[\mathrm{CH}_{3} .\right.} \end{gathered}$ | -- | -- | 33.583 | $-5.74{ }^{\text {a }}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{3}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COOCH}_{3}\right]+{ }^{-}} \end{aligned}$ | -- | -- | 28.489 | $-5.52^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{3}+\mathrm{e}^{-} \rightarrow \mathrm{C}_{2} \mathrm{H}_{5} \cdot \mathrm{CO}+ \\ \mathrm{OCH}_{3} \end{gathered}$ | -- | -- | -2.429 | $-4.17^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{3}+\mathrm{e}^{-} \rightarrow \\ \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}+{ }^{-\mathrm{CH}_{3}} \end{gathered}$ | -- | -- | -49.257 | $-2.14{ }^{a}$ | -- | -- |  |
|  | 32 | Ethyl Propionate | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOC}_{2} \mathrm{H}_{5}$ |  | $\begin{gathered} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{e}^{-} \rightarrow \\ \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{CO}(-) \mathrm{OC}_{2} \mathrm{H}_{5} \end{gathered}$ | -33.220 | $-2.84{ }^{\text {b }}$ | -- | -- | -- | -- | $7.52 \times 10^{7}$ |
|  |  |  |  |  | $\begin{array}{r} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCO}_{2} \mathrm{H}_{5}+\mathrm{e}^{-} \rightarrow \\ {\left[\mathrm{CH}_{3} \mathrm{CHCOOC}_{2}\right.} \end{array}$ | -- | -- | 0.606 | $-4.31{ }^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{e}-\rightarrow \\ {\left[\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COOCO}_{2} \mathrm{H}_{5}\right]^{-}+\mathrm{H}^{-}} \end{gathered}$ | -- | -- | 33.721 | $-5.74{ }^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{e}^{-} \rightarrow \\ \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}+{ }^{\circ}{ }^{-} \mathrm{C}_{2} \mathrm{H}_{5} \end{gathered}$ | -- | -- | -49.535 | $-2.13{ }^{\text {a }}$ | -- | -- |  |


| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{e}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\begin{aligned} & \Delta G_{\mathrm{cred,aq}}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{aligned} & E_{E_{\text {red }}^{\circ}}(\mathrm{V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\text {red.aq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{ca}} \mathrm{~mol}\right) \end{aligned}$ | $\begin{aligned} & \begin{array}{l} E_{\mathrm{Cred}}^{\circ} \\ (\mathrm{V} v \mathrm{vs} \\ \mathrm{SHE}) \\ \hline \end{array}{ }^{2} \end{aligned}$ | $\underset{\left(\mathrm{k}_{\mathrm{cac} / \mathrm{redaq}}^{\mathrm{omol}}\right)}{\substack{\mathrm{omol}}}$ | $\begin{aligned} & E_{\mathrm{Cred}}^{\mathrm{o}} \\ & (\mathrm{~V} \text { vs } \\ & \mathrm{SHE} \\ & \hline \end{aligned}$ |  |
| Ester | 33 | Dimethyl Oxalate | $\mathrm{CH}_{3} \mathrm{OOCCOOCH}_{3}$ |  | ```CH3OOCCOOCH3+ + - } CH3OOC CH3OOCCOOCH}+3+e- - CH3OOCCOO + ' }\mp@subsup{}{}{+}\mp@subsup{\textrm{CH}}{3}{``` | -59.029 | $-1.72^{\text {b }}$ | -- | -- | -- | -- | $1.04 \times 10^{11}$ |
|  |  |  |  |  |  | -- | -- | -59.324 | $-1.71^{a}$ | -- | -- |  |
|  |  |  |  |  | $\underset{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCOOCH}_{3}+\mathrm{e}^{-} \rightarrow}{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{COO}(-) \mathrm{OCH}_{3}}$ | -30.196 | $-2.97{ }^{\text {b }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCOOCH}_{3}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CCOO}(-) \mathrm{CH}_{3}+{ }^{-}\left(\mathrm{CH}_{3}\right)_{3} \end{gathered}$ | -- | -- | -53.704 | $-1.95{ }^{\text {a }}$ | -- | -- |  |
|  |  | 2-Hydroxyethyl Acetate | $\mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ |  | $\begin{gathered} \mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \cdot \mathrm{CO}(-) \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{OH} \end{gathered}$ | -33.275 | $-2.84^{\text {b }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \mathrm{COO}^{-}+{ }^{-} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH} \end{gathered}$ | -- | -- | -51.150 | $-2.06^{a}$ | -- | -- |  |
|  | 36 | Di-tert-butyl Peroxide | $\left(\mathrm{CH}_{3}\right)_{3}-\mathrm{COOC}\left(\mathrm{CH}_{3}\right)_{3}$ |  | $\begin{gathered} \left(\mathrm{CH}_{3}\right)_{3} \mathrm{COOC}\left(\mathrm{CH}_{3}\right)_{3}+\mathrm{e}^{-} \rightarrow \\ \left(\mathrm{CH}_{3}\right)_{3} \mathrm{CO}(-) \mathrm{OC}\left(\mathrm{CH}_{3}\right)^{3} \end{gathered}$ | -134.702 | $1.56{ }^{\text {a }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \left(\mathrm{CH}_{3}\right)_{3} \mathrm{COOC}\left(\mathrm{CH}_{3}\right)_{3}+\mathrm{e}^{-} \rightarrow \\ \left(\mathrm{CH}_{3}\right)_{3} \mathrm{CO}+{ }^{-} \mathrm{OC}\left(\mathrm{CH}_{3}\right)_{3} \end{gathered}$ | -- | -- | 44.927 | $-6.23{ }^{\text {a }}$ | -- | -- |  |



| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{e}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\begin{gathered} \Delta G_{\mathrm{c} \text { red.aq }}^{\circ} \\ \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{gathered}$ | $\begin{aligned} & E^{\circ} E_{\text {red }}^{\circ} \\ & (\mathrm{V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\mathrm{red.aq}}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{aligned} & E_{\mathrm{E}_{\text {red }}} \\ & \text { (V vs } \\ & \text { SHE) } \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G^{\text {red.aq }} \\ & \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right) \end{aligned}$ | $\begin{aligned} & E_{\text {red }}^{\circ} \\ & (V \text { vs } \\ & \text { SHE) } \end{aligned}$ |  |
| Ester | 39 | Methyl trifluoroacetate | $\mathrm{CF}_{3} \mathrm{COOCH}_{3}$ |  | $\begin{gathered} \mathrm{CF}_{3} \mathrm{COOCH}_{3}+\mathrm{e}^{-} \rightarrow \mathrm{CF}_{3} \cdot \mathrm{CO}(- \\ ) \mathrm{OCH}_{3} \\ \mathrm{CF}_{3} \mathrm{COOCH}_{3}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CF}_{2} \mathrm{COOCH}_{3}+\mathrm{F}^{-} \end{gathered}$ | -55.217 | $-1.89^{\text {b }}$ | -- | -- | -- | -- | $2.06 \times 10^{\text { }}$ |
|  |  |  |  |  |  | -- | -- | 10.892 | $-4.75^{a}$ | 28.138 | $-5.50^{\text {c }}$ |  |
|  | 40 | Ethyl glycinate | $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COOC}_{2} \mathrm{H}_{5}$ |  | $\begin{gathered} \mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{e}^{-} \rightarrow \\ \mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CO}(-) \mathrm{OC}_{2} \mathrm{H}_{5} \end{gathered}$ | -34.863 | $-2.77^{\text {b }}$ | -- | -- | -- | -- | $8.58 \times 10^{8}$ |
|  | 41 | Acetoxymethylamine | $\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{COOCH}_{3}$ |  | $\begin{gathered} \mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{COOCH}_{3}+\mathrm{e}^{-} \rightarrow \\ \mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CO}(-) \mathrm{OCH}_{3} \end{gathered}$ | -32.451 | $-2.87^{\text {b }}$ | -- | -- | -- | -- | $3.14 \times 10^{8}$ |
| Ether | 42 | Diethyl Ether | $\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{O}$ |  | $\underset{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{3}\right]^{-}}{\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{3}+\mathrm{e}^{-}} \rightarrow$ | 23.466 | $-5.30^{\text {a }}$ | -- | -- | -- | -- | $1.00 \times 10^{7}$ |
|  |  |  |  |  | $\begin{gathered} \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \mathrm{CH}_{2}+(-) \mathrm{OCH}_{2} \mathrm{CH}_{3} \end{gathered}$ | -- | -- | -38.953 | $-2.59^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{3}\right]^{-}+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | 30.857 | $-5.62^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{CH}_{3} \mathrm{CHOCH}_{2} \mathrm{CH}_{3}\right]+\mathrm{H}} \end{aligned}$ | -- | -- | 37.511 | $-5.91{ }^{\text {a }}$ | -- | -- |  |
| Ketone | 43 | Acetone | $\mathrm{CH}_{3} \mathrm{COCH}_{3}$ |  | $\begin{gathered} \mathrm{CH}_{3} \mathrm{COCH}_{3}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \mathrm{CO}(-) \mathrm{CH}_{3} \end{gathered}$ | -38.955 | $-2.59^{\text {b }}$ | -- | -- | -- | -- | $8.90 \times 10^{9}$ |
|  |  |  |  |  | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{COCH}_{3}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{CH}_{2} \mathrm{COCH}_{3}\right]^{-}+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | -4.570 | $-4.08^{a}$ | -- | -- |  |


| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\text {e }}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\underset{\left(\mathrm{k}_{\mathrm{cal}} \stackrel{\Delta \mathrm{~mol}}{\mathrm{r}}\right)}{\stackrel{\circ}{\circ} \mathrm{maq}}$ | $\begin{aligned} & E_{\mathrm{E}_{\mathrm{red}}} \\ & (\mathrm{~V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\underset{\left(\mathrm{K}_{\mathrm{cal}} G_{\mathrm{red}, \mathrm{al}}^{\mathrm{omol}}\right)}{ }$ | $\begin{aligned} & E_{\text {}}^{E_{\text {red }}} \\ & \text { (V vs } \\ & \text { SHE) } \\ & \hline \end{aligned}$ | $\begin{gathered} \Delta G_{\text {red.aq }}^{\circ} \\ \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{gathered}$ | $\begin{aligned} & E_{E_{\text {red }}} \\ & (\mathrm{V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ |  |
| Ketone | 44 | Methyl Ethyl Ketone | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}$ |  | $\begin{gathered} \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \mathrm{CH}_{2} \cdot \mathrm{CO}(-) \mathrm{CH}_{3} \end{gathered}$ | -38.719 | $-2.60^{\text {b }}$ | -- | -- | -- | -- | $6.11 \times 10^{9}$ |
|  |  |  |  | $\\|$ | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{2}\right]^{-}+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | -3.653 | $-4.12^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{CH}_{3} \mathrm{CHCOCH}_{3}\right]^{-}+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | 33.035 | $-5.71{ }^{\text {a }}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}+\mathrm{e}^{-} \rightarrow \overrightarrow{ } \\ & {\left[\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COCH}_{3}\right]^{-}+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | -3.304 | $-4.14^{a}$ | -- | -- |  |
|  | 45 | 2,3-Butanedione | $\mathrm{CH}_{3} \mathrm{COCOCH}_{3}$ |  | $\underset{) \mathrm{COCH}_{3}}{\mathrm{CH}_{3} \mathrm{COCOCH}_{3}+\mathrm{e}^{-}} \rightarrow \mathrm{CH}_{3} \cdot \mathrm{CO}(-$ | -69.049 | $-1.29^{\text {b }}$ | -- | -- | -- | -- | $1.67 \times 10^{10}$ |
|  |  |  |  |  | $\begin{gathered} \mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \cdot \mathrm{CO}(-) \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3} \end{gathered}$ | -43.759 | $-2.38{ }^{\text {b }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \overrightarrow{+} \\ & {\left[\mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{2}\right]^{-}+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | 11.615 | $-4.78^{a}$ | -- | -- |  |
|  | 46 | Acetoin | $\mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}$ |  | $\begin{gathered} \mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \\ {\left[\mathrm{CH}_{3} \mathrm{COCH}(\mathrm{O}) \mathrm{CH}_{3}\right]^{-}+\mathrm{H}^{-}} \end{gathered}$ | -- | -- | -1.714 | $-4.21^{a}$ | -- | -- | $7.95 \times 10^{9}$ |
|  |  |  |  | $\left.\right\|_{\mathrm{OH}}$ | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{CH}_{3} \mathrm{COC}(\mathrm{OH}) \mathrm{CH}_{3}\right]+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | -2.584 | $-4.17^{a}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \vec{~} \\ & {\left[\mathrm{CH}_{2} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}\right]^{-}+\mathrm{H}^{-}} \end{aligned}$ | -- | -- | -8.967 | $-3.89{ }^{\text {a }}$ | -- | -- |  |



| Class No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\mathrm{e}}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{credaq}}^{\circ}}$ | $\begin{aligned} & E_{I_{\text {red }}}(\mathrm{Vvs} \\ & \text { SHE } \end{aligned}$ | $\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol} / \mathrm{mol}\right)}{\Delta G_{\mathrm{r}}^{\mathrm{o}} \mathrm{aq}}$ | $\begin{aligned} & E_{\mathrm{Cred}}^{\mathrm{o}} \\ & (\mathrm{~V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\mathrm{cal}}^{\circ} \mathrm{o} \text { od,aq } \\ & \left(\mathrm{K}_{\mathrm{cal}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{aligned} & E_{E_{\text {red }}^{\circ}}(\mathrm{V} \text { vs } \\ & \text { SHE } \\ & \hline \end{aligned}$ |  |
|  |  |  |  | $\begin{gathered} \mathrm{BrCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \mathrm{O}^{-} \end{gathered} \mathrm{BrCH}_{2}{ }^{\circ} \mathrm{CO}(-$ | -67.468 | $-1.35^{\text {c }}$ | -- | -- | -- | -- |  |
|  | Bromoacetate | $\mathrm{BrCH}_{2} \mathrm{COO}^{-}$ |  | $\underset{\mathrm{Br}}{\mathrm{BrCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow} \mathrm{CH}_{2} \mathrm{COO}^{+}+$ | -- | -- | -19.940 | $-3.42^{\text {c }}$ | 11.540 | $-4.78^{\text {c }}$ | $8.03 \times 10^{9}$ |
|  |  |  |  | $\begin{aligned} & \mathrm{BrCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\ & {\left[\mathrm{BrCHCOO}^{-}{ }^{-}+\mathrm{H}^{-}\right.} \end{aligned}$ | -- | -- | 7.739 | $-4.62^{\text {c }}$ | -- | -- |  |
|  |  |  |  | $\begin{gathered} \mathrm{Br}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}+\mathrm{CO}^{-} \\ \mathrm{Br}\left(\mathrm{CH}_{2}\right)_{2}{ }^{-} \mathrm{CO}(-) \mathrm{O}^{-} \end{gathered}$ | -62.640 | $-1.56^{\text {c }}$ | -- | -- | -- | -- |  |
|  |  |  |  | $\underset{\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}+\mathrm{Br}^{-}}{\mathrm{Br}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}+\mathrm{e}^{-}} \rightarrow$ | -- | -- | -14.680 | $-3.64{ }^{\text {c }}$ | 15.242 | $-4.94{ }^{\text {c }}$ |  |
|  |  |  |  | $\underset{\mathrm{O}^{-}}{\mathrm{FCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \mathrm{FCH}_{2}{ }^{\circ} \mathrm{CO}(-}$ | -15.028 | $-3.63{ }^{\text {c }}$ | -- | -- | -- | -- |  |
|  | Fluoroacetate | $\mathrm{FCH}_{2} \mathrm{COO}^{-}$ |  | $\begin{gathered} \mathrm{FCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\ { }^{-} \mathrm{CH}_{2} \mathrm{COO}^{-}+\mathrm{F} \cdot \end{gathered}$ | -- | -- | 4.487 | $-4.47^{\text {c }}$ | 66.820 | $-7.18^{\text {c }}$ | $1.20 \times 10^{6}$ |
|  |  |  |  | $\begin{aligned} \mathrm{FCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\ +\mathrm{H}^{\cdot} \end{aligned} \mathrm{FCHCOO}^{2-}$ | -- | -- | 11.537 | $-4.78^{\text {c }}$ | -- | -- |  |
|  |  |  | $\bigcirc$ | $\begin{gathered} \mathrm{CH}_{3} \mathrm{CHBrCOO}^{-}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \mathrm{CHBr} \\ \hline \end{gathered}$ | -71.420 | $-1.18^{\text {c }}$ | -- | -- | -- | -- |  |
|  | 2-Bromopropanoate |  | $\left.\right\|_{\mathrm{Br}}$ | $\begin{gathered} \mathrm{CH}_{3} \mathrm{CHBrCOO}^{-}+\mathrm{e}^{-} \rightarrow \\ \mathrm{CH}_{3} \mathrm{CHCOO}^{-}+\mathrm{Br}^{-} \end{gathered}$ | -- | -- | -22.907 | $-3.29^{\text {c }}$ | 6.181 | $-4.55^{\text {c }}$ | $5.30 \times 10$ |






| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\mathrm{e}}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\begin{aligned} & \Delta G_{{ }_{\mathrm{recdedaq}}^{\mathrm{r}}}^{\left(\mathrm{k}_{\mathrm{c} /} \mathrm{mol}\right)} \end{aligned}$ | $\begin{aligned} & E_{\mathrm{Cred}}^{\mathrm{r}} \\ & (\mathrm{~V} \text { vs } \\ & \mathrm{SHE} \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\text {red.aq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right) \end{aligned}$ | $\begin{aligned} & E_{\mathrm{Cred}}^{\circ} \\ & (\mathrm{V} v \mathrm{vs} \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\mathrm{credaq}}^{\mathrm{o}} \\ & \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{aligned} & E_{C_{\text {red }}^{\circ}} \\ & \text { (V vs } \\ & \text { SHE) } \end{aligned}$ |  |
| Haloalkane | 74 |  | $\mathrm{CCl}_{3} \mathrm{~F}$ |  | $\mathrm{CCl}_{3} \mathrm{~F}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CCl}_{3} \mathrm{~F}\right]^{-}$ | -79.113 | $-0.85^{\text {c }}$ | -- | -- | -- | -- |  |
|  |  | Trichlorofluoromethane |  |  | $\mathrm{CCl}_{3} \mathrm{~F}+\mathrm{e}^{-} \rightarrow{ }^{\text {C }} \mathrm{Cll}_{2} \mathrm{~F}+\mathrm{Cl}^{-}$ | -- | -- | -82.747 | $-0.69^{\text {c }}$ | -77.563 | $-0.92^{\text {c }}$ | $4.60 \times 10^{10}$ |
|  |  |  |  |  | $\mathrm{CCl}_{3} \mathrm{~F}+\mathrm{e}^{-} \rightarrow \mathrm{CCl}_{3}+\mathrm{F}^{-}$ | -- | -- | -25.048 | $-3.19^{\text {c }}$ | -37.457 | $-2.66^{\text {c }}$ |  |
|  | $75$ | Dichlorodifluoromethane | $\mathrm{CF}_{2} \mathrm{Cl}_{2}$ |  | $\mathrm{CF}_{2} \mathrm{Cl}_{2}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CF}_{2} \mathrm{Cl}_{2}\right]^{-}$ | -74.271 | $-1.06^{\text {c }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\mathrm{CF}_{2} \mathrm{Cl}_{2}+\mathrm{e}^{-} \rightarrow{ }^{\text {' }} \mathrm{FF}_{2} \mathrm{Cl}+\mathrm{Cl}^{-}$ | -- | -- | -77.164 | $-0.93^{\text {c }}$ | -62.436 | $-1.57^{\text {c }}$ | $3.28 \times 10^{10}$ |
|  |  |  |  |  | $\mathrm{CF}_{2} \mathrm{Cl}_{2}+\mathrm{e}^{-} \rightarrow{ }^{\cdot} \mathrm{CFCl}_{2}+\mathrm{F}$ | -- | -- | -15.382 | $-3.61{ }^{\text {c }}$ | -20.224 | $-3.40^{\text {c }}$ |  |
|  | 76 Chlorotrifluoromethane |  | $\mathrm{CCIF}_{3}$ |  | $\mathrm{CCIF}_{3}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CClF}_{3}\right]^{-}$ | -70.255 | $-1.23{ }^{\text {c }}$ | -- | -- | -- | -- |  |
|  |  |  | $\mathrm{CClF}_{3}+\mathrm{e}^{-} \rightarrow{ }^{\circ} \mathrm{CF}_{3}+\mathrm{Cl}^{-}$ |  | -- | -- | -71.187 | $-1.19^{\text {c }}$ | -69.497 | $-1.27^{\text {c }}$ | $5.36 \times 10^{9}$ |  |
|  |  |  | $\mathrm{CClF}_{3}+\mathrm{e}-\rightarrow \mathrm{CClF}_{2}+\mathrm{F}$ |  | -- | -- | -6.059 | $-4.02^{\text {c }}$ | -3.135 | $-4.14^{\text {c }}$ |  |  |


| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\text {c }}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }} \\ \left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\begin{aligned} & \Delta G_{\text {red.aq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{cal}} \mathrm{Imol}\right) \end{aligned}$ | $\begin{aligned} & E_{\mathrm{C} \text { red }}^{\circ} \mathrm{V} \\ & (\mathrm{~V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\begin{gathered} \Delta G_{\text {red.aq }}^{\circ} \\ \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right) \end{gathered}$ | $\begin{aligned} & E^{E_{\text {red }}^{\circ}} \\ & (\mathrm{V} \text { vs } \\ & \text { SHE) } \\ & \hline \end{aligned}$ | $\underset{\left(\mathrm{k}_{\text {cal }}\right.}{\left.\Delta G_{\text {red.aq }}^{\mathrm{o}}\right)}$ | $\begin{aligned} & E_{E_{\text {red }}^{\circ}} \\ & (\mathrm{V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ |  |
| Haloalkane | 77 | Bromotrifluoromethane | $\mathrm{CF}_{3} \mathrm{Br}$ |  | $\mathrm{CF}_{3} \mathrm{Br}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CF}_{3} \mathrm{Br}\right]^{-}$ | -70.849 | $-1.21^{\text {c }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\mathrm{CF}_{3} \mathrm{Br}+\mathrm{e}^{-} \rightarrow{ }^{\text {}} \mathrm{CF}_{3}+\mathrm{Br}{ }^{-}$ | -- | -- | -70.324 | $-1.23{ }^{\text {c }}$ | -70.396 | $-1.23{ }^{\text {c }}$ | $3.93 \times 10^{11}$ |
|  |  |  |  |  | $\mathrm{CF}_{3} \mathrm{Br}+\mathrm{e}^{-} \rightarrow{ }^{\text {C }} \mathrm{CF}_{2} \mathrm{Br}+\mathrm{F}$ | -- | -- | -7.619 | $-3.95{ }^{\text {c }}$ | -6.574 | $-3.99^{\text {c }}$ |  |
|  | 78 | Carbon Tetrachloride | $\mathrm{CCl}_{4}$ |  | $\mathrm{CCl}_{4}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CCl}_{4}\right]^{-}$ | -86.869 | $-0.51{ }^{\text {c }}$ | -- | -- | -- | -- | $7.61 \times 10^{10}$ |
|  |  |  |  |  | $\mathrm{CCl}_{4}+\mathrm{e}^{-} \rightarrow{ }^{\cdot} \mathrm{CCl}_{3}+\mathrm{Cl}^{-}$ | -- | -- | -91.148 | $-0.33^{\text {c }}$ | -89.364 | $-0.41^{\text {c }}$ |  |
|  | 79 | Chlorodifluoromethane | $\mathrm{CHClF}_{2}$ |  | $\mathrm{CHClF}_{2}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CHClF}_{2}\right]^{-}$ | -66.256 | $-1.41^{\text {c }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\mathrm{CHClF}_{2}+\mathrm{e}^{-} \rightarrow{ }^{\text {CHFF}}{ }_{2}+\mathrm{Cl}^{-}$ | -- | -- | -70.221 | $-1.24^{\text {c }}$ | -63.028 | $-1.55^{\text {c }}$ | $3.29 \times 10^{9}$ |
|  |  |  |  |  | $\mathrm{CHClF}_{2}+\mathrm{e}^{-} \rightarrow{ }^{\text {- }} \mathrm{CHClF}+\mathrm{F}^{-}$ | -- | -- | -10.444 | $-3.83{ }^{\text {c }}$ | -18.607 | $-3.47^{\text {c }}$ |  |
|  |  | 1,1,2-Trichloroethane | $\mathrm{ClCH}_{2} \mathrm{CHCl}_{2}$ |  | $\underset{\left[\mathrm{ClCH}_{2} \mathrm{CHCl}_{2}+\mathrm{e}_{2}\right.}{\left[\mathrm{CHCl}_{2}\right]^{-}} \rightarrow$ | -76.948 | $-0.94{ }^{\text {c }}$ | -- | -- | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{ClCH}_{2} \mathrm{CHCl}_{2}+\mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-} \mathrm{CH}_{2} \mathrm{CHCl}_{2} \\ +{ }^{-1} \end{gathered}$ | -- | -- | -75.169 | $-1.02^{\text {c }}$ | -82.211 | $-0.72^{\text {c }}$ | $1.27 \times 10^{10}$ |
|  |  |  |  |  | $\begin{gathered} \mathrm{ClCH}_{2} \mathrm{CHCl}_{2}+\mathrm{e}^{-} \\ \mathrm{ClCH}_{2} \mathrm{CHCHCl}^{+} \mathrm{Cl} \end{gathered}$ | -- | -- | -63.785 | $-1.51^{\text {c }}$ | -- | -- |  |



| Class | No. | Name | Chemical Formula | 2D Chemical Structure ${ }^{\text {e }}$ | Reduction Mechanism | Association |  | Concerted |  | Stepwise |  | $\begin{gathered} k_{\text {chem }}^{\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $\begin{aligned} & \Delta G_{\text {red.aq }}^{\circ} \\ & \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right) \end{aligned}$ | $\begin{aligned} & \hline E_{\text {red }}^{\circ} \\ & \text { (V vs } \\ & \text { SHE } \end{aligned}$ | $\begin{gathered} \Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ} \\ \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right) \end{gathered}$ | $\begin{aligned} & E_{\mathrm{red}}^{\mathrm{r} e d} \\ & (\mathrm{~V} \text { vs } \\ & \mathrm{SHE}) \\ & \hline \end{aligned}$ | $\begin{aligned} & \Delta G_{\text {red.aq }}^{\circ} \\ & \left(\mathrm{k}_{\text {cal }} / \mathrm{mol}\right) \end{aligned}$ | $\begin{aligned} & E^{E^{\circ} \text { red }} \\ & \text { (V vs } \\ & \text { SHE } \end{aligned}$ |  |
| Haloalkane | 86 | 1,1,2-Trichloro-1,2,2trifluoroethane | $\mathrm{ClCF}_{2} \mathrm{CCl}_{2} \mathrm{~F}$ |  | $\underset{\mathrm{ClCF}_{2} \mathrm{CClCl}_{2} \mathrm{~F}+\mathrm{e}^{-} \rightarrow}{\left[\mathrm{ClCF}_{2} \mathrm{CCl}_{2} \mathrm{~F}\right]^{-}}$ | -77.672 |  | -- | -- | -- | -- | $3.17 \times 10^{10}$ |
|  |  |  |  |  | $\begin{aligned} & \mathrm{ClCF}_{2} \mathrm{CCl}_{2} \mathrm{~F}+\mathrm{e}^{-} \rightarrow \mathrm{ClCF}_{2} \cdot \mathrm{CClF}^{-} \\ &+\mathrm{Cl} \end{aligned}$ | -- | -- | -80.517 | $-0.79{ }^{\text {c }}$ | -84.396 | $-0.62^{\text {c }}$ |  |
|  |  |  |  |  | $\underset{\mathrm{Cl}}{\mathrm{ClCF}_{2} \mathrm{CCl}_{2} \mathrm{~F}+\underset{\mathrm{e}^{-}}{\rightarrow} \cdot \mathrm{CF}_{2} \mathrm{CCl}_{2} \mathrm{~F}+}$ | -- | -- | -74.448 | $-1.05^{\text {c }}$ | -- | -- |  |
|  |  |  |  |  | $\begin{aligned} & \mathrm{ClCF}_{2} \mathrm{CCl}_{2} \mathrm{~F}+\mathrm{e}^{-} \rightarrow \mathrm{ClCF}_{2} \cdot \mathrm{CCl}_{2} \\ &+\mathrm{F}^{-} \end{aligned}$ | -- | -- | -26.570 | $-3.13^{\text {c }}$ | -- | -- |  |
|  |  |  |  |  | $\begin{gathered} \mathrm{ClCF}_{2} \mathrm{CCl}_{2} \mathrm{~F}+\mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-} \mathrm{CFCCl}_{2} \mathrm{~F} \\ +\mathrm{F} \end{gathered}$ | -- | -- | -15.564 | $-3.61^{\text {c }}$ | -- | -- |  |
|  | 87 | 1-Iodopropane | $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{I}$ |  | $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{I}+\mathrm{e}^{-} \rightarrow\left[\mathrm{C}_{3} \mathrm{H}_{7}\right]^{-}$$\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{I}+\mathrm{e}^{-} \rightarrow{ }^{\cdot} \mathrm{C}_{3} \mathrm{H}_{7}+\mathrm{I}^{-}$ | -75.555 | $-1.00^{\text {d }}$ | -- | ${ }^{--}$ | ${ }^{--}$ | -- | $2.73 \times 10^{10}$ |
|  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  |  |  |  | -- | -- | -75.555 | $-1.00^{\text {d }}$ | -89.251 | $-0.41^{\text {d }}$ |  |
|  | 88 | 1-Iodobutane | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{I}$ |  | $\begin{gathered} \mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{I}+\mathrm{e}^{-} \rightarrow \\ {\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3}\right]^{-}} \\ \underset{\mathrm{I}}{ } \mathrm{I}^{-} \end{gathered}$ | -75.508 | $-1.01{ }^{\text {d }}$ | ---75.500 | -- | -- | -- | $2.29 \times 10^{10}$ |
|  |  |  |  |  |  | -- | -- |  | $-1.01^{\text {d }}$ | -91.800 | $-0.30{ }^{\text {d }}$ |  |
|  | 89 | 1-Bromobutane | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}$ |  | $\underset{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br}\right]^{-}}{\mathrm{CH}_{3}\left(\mathrm{CH}_{2} \mathrm{Br}+\mathrm{e}^{-} \rightarrow\right.} \rightarrow$ | -54.063 | $-1.94{ }^{\text {c }}$ | -- | -- | -- | -- | $1.59 \times 10^{10}$ |
|  |  |  |  |  | $\begin{aligned} \mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Br} & +\mathrm{e}^{-} \rightarrow \mathrm{CH}_{3} \cdot\left(\mathrm{CH}_{2}\right)_{3} \\ + & \mathrm{Br}^{-} \end{aligned}$ | -- | -- | -67.540 | $-1.35^{\text {c }}$ | -70.843 | $-1.21^{\text {c }}$ |  |

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} \& \multirow[b]{2}{*}{No.} \& \multirow[b]{2}{*}{Name} \& \multirow[b]{2}{*}{Chemical Formula} \& \multirow[b]{2}{*}{2D Chemical Structure ${ }^{\mathrm{e}}$} \& \multirow[b]{2}{*}{Reduction Mechanism} \& \multicolumn{2}{|l|}{Association} \& \multicolumn{2}{|l|}{Concerted} \& \multicolumn{2}{|l|}{Stepwise} \& \multirow[b]{2}{*}{$$
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
$$} <br>
\hline \& \& \& \& \& \& $$
\begin{aligned}
& \Delta G^{\text {red.aq }} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
$$ \&  \& $$
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
$$ \& $$
\begin{aligned}
& \begin{array}{l}
E_{\mathrm{red}}^{\circ} \\
(\mathrm{V} \text { vs } \\
\text { SHE) } \\
\hline
\end{array} \\
& \hline
\end{aligned}
$$ \& $$
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\stackrel{\circ}{\mathrm{redaq}})}
$$ \&  \& <br>
\hline \multirow{10}{*}{Haloalkane} \& \multirow[b]{2}{*}{90} \& \multirow[b]{2}{*}{1-Chlorobutane} \& \multirow[b]{2}{*}{$\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Cl}$} \& \multirow[b]{2}{*}{} \& \multirow[t]{2}{*}{$$
\underset{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Cl}^{-{ }^{-}}\right.}{\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{e}+\mathrm{e}^{-}} \rightarrow
$$
$$
\begin{gathered}
\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Cl}+\mathrm{e}^{-} \rightarrow \mathrm{CH}_{3}{ }^{-}\left(\mathrm{CH}_{2}\right)_{3} \\
+{ }^{-}
\end{gathered}
$$} \& -12.529 \& $-3.74{ }^{\text {c }}$ \& -- \& -- \& -- \& -- \& \multirow[b]{2}{*}{$3.42 \times 10^{8}$} <br>
\hline \& \& \& \& \& \& -- \& -- \& -70.825 \& $-1.21^{\text {c }}$ \& -73.047 \& $-1.11^{\text {c }}$ \& <br>
\hline \& \multirow[b]{2}{*}{91} \& \multirow[b]{2}{*}{1-Chloro-2methylpropane} \& \multirow[b]{2}{*}{$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}$} \& \multirow[b]{2}{*}{} \& \multirow[t]{2}{*}{```
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}+\mathrm{e}^{-} \rightarrow$
$\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}\right]^{-}$
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}+\mathrm{e}^{-} \rightarrow$
$\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CH}^{\cdot} \mathrm{CH}_{2}+\mathrm{Cl}^{-}$

```} & -66.405 & \(-1.40^{\text {c }}\) & -- & -- & -- & -- & \multirow[b]{2}{*}{\(5.21 \times 10^{8}\)} \\
\hline & & & & & & -- & -- & -70.620 & \(-1.22^{\text {c }}\) & -71.911 & \(-1.16^{\text {c }}\) & \\
\hline & \multirow[b]{2}{*}{92} & \multirow[b]{2}{*}{1-Bromopentane} & \multirow[b]{2}{*}{\(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\)} & \multirow[b]{2}{*}{} & \multirow[t]{2}{*}{\(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\right]^{-}\)
\[
\begin{gathered}
\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br} \\
+\mathrm{e}^{-} \rightarrow \mathrm{CH}_{3} \cdot\left(\mathrm{CH}_{2}\right)_{4} \\
+{ }^{-}
\end{gathered}
\]} & -54.106 & \(-1.93{ }^{\text {c }}\) & -- & -- & -- & -- & \multirow[b]{2}{*}{\(1.17 \times 10^{10}\)} \\
\hline & & & & & & -- & -- & -67.451 & \(-1.36^{\text {c }}\) & -72.978 & \(-1.12^{\text {c }}\) & \\
\hline & \multirow[b]{2}{*}{93} & \multirow[b]{2}{*}{2-Bromo-2methylpropane} & \multirow[b]{2}{*}{\(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}\)} & \multirow[t]{2}{*}{} & \multirow[t]{2}{*}{\(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}+\mathrm{e}^{-} \rightarrow\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}\right]^{-}\)

\(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}+\mathrm{e}_{-} \rightarrow\)
\(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}+\mathrm{Br}\)} & -67.447 & \[
-1.36^{\text {c }}
\] & -- & -- & -- & -- & \multirow[b]{2}{*}{\(1.02 \times 10^{10}\)} \\
\hline & & & & & & -- & -- & -70.359 & \(-1.23^{\text {c }}\) & -72.263 & \(-1.15^{\text {c }}\) & \\
\hline & \multirow[t]{2}{*}{94} & \multirow[t]{2}{*}{2-Bromobutane} & \multirow[t]{2}{*}{\(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{Br}) \mathrm{CH}_{3}\)} & \multirow[t]{2}{*}{} & \multirow[t]{2}{*}{\[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{Br}) \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \\
\left.\left[\mathrm{CH}_{3} \mathrm{CH} \mathrm{CH}_{2} \mathrm{BH}\right) \mathrm{CH}_{3}\right]^{-} \\
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}(\mathrm{Br}) \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHCH}_{3}+\mathrm{Br}^{-}
\end{gathered}
\]} & \multirow[t]{2}{*}{-65.083} & \(-1.46^{\text {c }}\) & \multirow[t]{2}{*}{--
-69.183} & -- & -- & -- & \multirow[t]{2}{*}{\(1.01 \times 10^{10}\)} \\
\hline & & & & & & & -- & & \(-1.28^{\text {c }}\) & -71.233 & \(-1.19^{\text {c }}\) & \\
\hline
\end{tabular}


\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{aligned}
& \Delta G^{\text {red.aq }} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] &  & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& \begin{array}{l}
E_{\mathrm{red}}^{\circ} \\
(\mathrm{V} \text { vs } \\
\text { SHE) } \\
\hline
\end{array} \\
& \hline
\end{aligned}
\] &  &  & \\
\hline \multirow{6}{*}{Halooxygen} & & & & \({ }^{\text {OH }}\) & \[
\underset{\left[\mathrm{CCl}_{3} \mathrm{CH}(\mathrm{OH})_{2}\right]^{-c}}{\mathrm{CCl}_{3} \mathrm{CH}(\mathrm{OH})_{2}+\mathrm{e}^{-}} \rightarrow
\] & -84.704 & \(-0.61{ }^{\text {c }}\) & -- & -- & -- & -- & \\
\hline & & & &  & \[
\underset{\substack{\mathrm{CCl}_{3} \mathrm{CH}(\mathrm{OH})_{2}+\mathrm{e}_{2} \mathrm{CH}(\mathrm{OH})_{2}+\mathrm{Cl}^{-} \\ \mathrm{Cl}^{-}}}{\text {an }}
\] & -- & -- & -58.870 & \(-1.73^{\text {c }}\) & -0.786 & \(-4.25^{\text {c }}\) & \\
\hline & \multirow{4}{*}{105} & \multirow{4}{*}{Enflurane} & \multirow{4}{*}{\(\mathrm{CHF}_{2} \mathrm{OCF}_{2} \mathrm{CHClF}\)} & & \(\mathrm{CHF}_{2} \mathrm{OCF}_{2} \mathrm{CHClF}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{CHF}_{2} \mathrm{OCF}_{2} \mathrm{CHClF}^{-}\right.\) & -70.858 & \(-1.21^{\text {c }}\) & -- & -- & -- & -- & \multirow{4}{*}{\(3.03 \times 10^{9}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CHF}_{2} \mathrm{OCF}_{2} \mathrm{CHClF}+\mathrm{e}^{-} \rightarrow \\
& \mathrm{CHF}_{2} \mathrm{OCF}_{2} \cdot \mathrm{CHCl}+\mathrm{F}^{-}
\end{aligned}
\] & -- & -- & 2.174 & \(-4.37^{\text {c }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{CHF}_{2} \mathrm{OCF}_{2} \mathrm{CHClF}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CHF}_{2} \mathrm{OCF}_{2}{ }^{2} \mathrm{CHF}+\mathrm{Cl}^{-}
\end{gathered}
\] & -- & -- & -50.059 & \(-2.11^{\text {c }}\) & 4.142 & \(-4.46^{\text {c }}\) & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{CHF}_{2} \mathrm{OCF}_{2} \mathrm{CHClF}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CHFOCF}_{2} \mathrm{CHClF}+\mathrm{F}
\end{gathered}
\] & -- & -- & 18.080 & \(-5.06{ }^{\text {c }}\) & 16.319 & \(-4.99^{\text {c }}\) & \\
\hline \multirow{6}{*}{Cyanide} & \multirow{3}{*}{106} & \multirow{3}{*}{Acetonitrile} & \multirow{3}{*}{\(\mathrm{CH}_{3} \mathrm{CN}\)} & \multirow{3}{*}{\[
\mathrm{N} \equiv \mathrm{C}
\]} & \multirow[t]{3}{*}{\[
\mathrm{CH}_{3} \mathrm{CN}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CH}_{3} \mathrm{CN}\right]^{-}
\]
\[
\mathrm{CH}_{3} \mathrm{CN}+\mathrm{e}^{-} \rightarrow \mathrm{CH}_{3}+\mathrm{CN}^{-}
\]} & -14.829 & \(-3.64{ }^{\text {a }}\) & -- & -- & -- & -- & \multirow{3}{*}{\(3.74 \times 10^{7}\)} \\
\hline & & & & & & & & & & & & \\
\hline & & & & & & -- & -- & -21.899 & \(-3.33^{\text {a }}\) & 119.687 & \(-9.47^{\text {c }}\) & \\
\hline & \multirow{2}{*}{107} & \multirow{2}{*}{Succinonitrile} & \multirow{2}{*}{\[
\mathrm{NC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CN}
\]} & \multirow[t]{2}{*}{} & \multirow[t]{2}{*}{\[
\begin{gathered}
\mathrm{NC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CN}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{NC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CN}\right]^{-}} \\
\\
\mathrm{NC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CN}+\mathrm{e}^{-} \rightarrow \\
\mathrm{NCCH}_{2}{ }^{\circ} \mathrm{CH}_{2}+\mathrm{CN}^{-}
\end{gathered}
\]} & \(-21.837\) & \(-3.33^{\text {a }}\) & -- & -- & -- & -- & \multirow{2}{*}{\(1.83 \times 10^{9}\)} \\
\hline & & & & & & -- & -- & -28.089 & \(-3.06^{\text {a }}\) & 108.910 & \(-9.00^{\text {c }}\) & \\
\hline & 108 & Trichloroacetonitrile & \(\mathrm{CCl}_{3} \mathrm{CN}\) &  & \[
\begin{aligned}
& \mathrm{CCl}_{3} \mathrm{CN}+\mathrm{e}^{-} \rightarrow \\
& { }^{-\mathrm{CCl}} \mathrm{Cl}_{2} \mathrm{CN}+\mathrm{Cl}^{-}
\end{aligned}
\] & -- & -- & -98.667 & \(0.00^{\text {c }}\) & 35.993 & \(-5.84{ }^{\text {c }}\) & \(3.20 \times 10^{10}\) \\
\hline
\end{tabular}

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\circ} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\circ} \\
& (\mathrm{V} v \mathrm{vs} \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ}{ }_{\left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)}
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\mathrm{o}} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{11}{*}{Amine} & \multirow{4}{*}{112} & \multirow{4}{*}{Propylamine} & \multirow{4}{*}{\(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\)} & \multirow{4}{*}{} & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right]^{-}}
\end{aligned}
\] & 19.795 & \(-5.14{ }^{\text {a }}\) & -- & -- & -- & -- & \multirow{4}{*}{\(1.10 \times 10^{6}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHNH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 43.023 & \(-6.15^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CHCHCH}_{2} \mathrm{NH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 40.090 & \(-6.02^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 38.631 & -5.95 \({ }^{\text {a }}\) & -- & -- & \\
\hline & \multirow{3}{*}{113} & \multirow{3}{*}{Ethylamine} & \multirow{3}{*}{\(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}\)} & \multirow{3}{*}{} & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}\right]^{-}}
\end{gathered}
\] & 20.420 & \(-5.17^{\text {a }}\) & -- & -- & -- & -- & \multirow{3}{*}{\[
1.00 \times 10^{6}
\]} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CHNH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 43.284 & \(-6.16^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \overrightarrow{-} \\
& {\left[\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right]^{-}+{ }^{-}}
\end{aligned}
\] & -- & -- & 35.972 & \(-5.84^{\text {a }}\) & -- & -- & \\
\hline & 114 & Isobutylamine & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{NH}_{2}\) & \(\checkmark\) & \[
\underset{\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{NH}_{2}\right]^{-}}{\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHH}_{2}+\mathrm{e}^{-}} \rightarrow
\] & 18.633 & \(-5.09{ }^{\text {a }}\) & -- & -- & -- & -- & \(1.10 \times 10^{7}\) \\
\hline & 115 & Isoamylamine & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\) &  & \[
\underset{\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right]^{-}}{\left(\mathrm{CH}_{3} \mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-}\right.} \rightarrow
\] & 20.072 & \(-5.15^{\text {a }}\) & -- & -- & -- & -- & \(1.00 \times 10^{6}\) \\
\hline & 116 & 2-Dimethylhydrazine & \(\mathrm{CH}_{3} \mathrm{NHNHCH}_{3}\) &  & \(\mathrm{CH}_{3} \mathrm{NHNHCH}_{3}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{CH}_{3} \mathrm{NHNHCH}_{3}\right]^{-}\) & 27.980 & \(-5.49^{\text {a }}\) & -- & -- & -- & -- & \(6.10 \times 10^{6}\) \\
\hline & 117 & Methylhydrazine & \(\mathrm{CH}_{3} \mathrm{NHNH}_{2}\) &  & \[
\underset{\left[\mathrm{CH}_{3} \mathrm{NHNH}_{2}\right]^{-}}{\mathrm{CH}_{3} \mathrm{NHNH}_{2}+\mathrm{e}^{-}} \rightarrow
\] & 12.204 & \(-4.81{ }^{\text {a }}\) & -- & -- & -- & -- & \(6.50 \times 10^{6}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical
Structure \(^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta G_{\text {redaq }}^{\circ}}
\] &  & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\left.\Delta G_{\mathrm{ced}, \mathrm{aq}}^{\mathrm{o}}\right)}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}}(\mathrm{V} \text { vs } \\
& \text { SHE } \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}^{(\mathrm{V} \text { vs }} \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{11}{*}{Amine} & 118 & Glycinate & \(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}\) &  & \(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COO}\right]^{2-}\) & -9.945 & \(-3.85{ }^{\text {b }}\) & -- & -- & -- & -- & \(1.70 \times 10^{6}\) \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\right]^{-}}
\end{gathered}
\] & -0.269 & \(-4.27^{\text {a }}\) & -- & -- & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{O}\right]^{-}+\mathrm{H}^{-}}
\end{gathered}
\] & -- & -- & -1.157 & \(-4.23{ }^{\text {a }}\) & -- & -- & \\
\hline & 120 & Isopropylamine & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHNH}_{2}\) & \[
\mathrm{NH}_{2}
\] & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHNH}_{2}+\mathrm{e}^{-} \rightarrow\) \(\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHNH}_{2}\right]^{-}\) & 18.203 & \(-5.07^{\text {a }}\) & -- & -- & -- & -- & \(1.50 \times 10^{6}\) \\
\hline & 121 & Tert-Butylamine & \(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{2}\) & & \[
\underset{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{2}+\mathrm{e}^{-}}{\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{2}\right]^{-}} \rightarrow
\] & 18.200 & \(-5.07^{\text {a }}\) & -- & -- & -- & -- & \(1.10 \times 10^{6}\) \\
\hline & 122 & beta-Alaninate & \(\mathrm{NH}_{2}\left(\mathrm{CH}_{2}\right)_{2}-\mathrm{COO}^{-}\) &  & \[
\begin{gathered}
\mathrm{NH}_{2}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{NH}_{2}\left(\mathrm{CH}_{2}\right)_{2}{ }^{-} \mathrm{CO}(-) \mathrm{O}^{-}
\end{gathered}
\] & -9.804 & \(-3.85{ }^{\text {b }}\) & -- & -- & -- & -- & \(4.20 \times 10^{6}\) \\
\hline & 123 & \(\stackrel{\mathrm{N}, \mathrm{N}-}{\text { Diethylhydroxylamine }}\) & \(\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{NOH}\) &  & \begin{tabular}{l}
\[
\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{NOH}+\mathrm{e}^{-} \rightarrow
\] \\
\(\left[\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{NOH}\right]^{-}\)
\end{tabular} & -2.508 & \(-4.17^{\text {a }}\) & -- & -- & -- & -- & \(4.81 \times 10^{7}\) \\
\hline & 124 & N -Methyl-Ntritiohydroxylamine & \(\mathrm{CH}_{3} \mathrm{NHOH}\) &  & \(\mathrm{CH}_{3} \mathrm{NHOH}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CH}_{3} \mathrm{NHOH}\right]^{-}\) & -15.916 & \(-3.59^{\text {a }}\) & -- & -- & -- & -- & \(2.42 \times 10^{8}\) \\
\hline & 125 & Amylamine & \(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{NH}_{2}\) &  & \[
\begin{gathered}
\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{NH}_{2}\right]^{-}}
\end{gathered}
\] & 21.111 & \(-5.20^{\text {a }}\) & -- & -- & -- & -- & \(1.00 \times 10^{6}\) \\
\hline & 126 & Trimethylhydrazine & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N}-\mathrm{NHCH}_{3}\) & \[
<^{N} \backslash_{H^{\prime}}
\] & \[
\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N}-\mathrm{NHCH}_{3}+\mathrm{e}^{-} \rightarrow
\]
\[
\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N}-\mathrm{NHCH}_{3}\right]^{-}
\] & -16.761 & \(-3.55^{\text {a }}\) & -- & -- & -- & -- & \(1.00 \times 10^{8}\) \\
\hline & 127 & 1,1-Dimethylhydrazine & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NNH}_{2}\) &  & \[
\xrightarrow{\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NNH}_{2}+\mathrm{e}^{-}} \rightarrow
\] & 18.277 & \(-5.07^{\text {a }}\) & -- & -- & -- & -- & \(2.40 \times 10^{7}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{K}_{\mathrm{cal}} / G_{\text {red.al }}^{\circ} \mathrm{mol}\right)}{\circ}
\] & \[
\begin{aligned}
& E^{E_{\text {red }}} \\
& \text { (V vs } \\
& \text { SHE }
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ}{ }_{\left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)}
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{E}_{\mathrm{red}}} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE} \text { P } \\
& \hline
\end{aligned}
\] & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}} \mathrm{I} \text { cmol.aq }\right)}{\left.\Delta G_{\mathrm{ol}}^{\mathrm{o}}\right)}
\] & \[
\begin{aligned}
& E^{E_{\text {red }}^{\circ}} \\
& \text { (V vs } \\
& \text { SHE }
\end{aligned}
\] & \\
\hline \multirow{11}{*}{Amide} & & & & & \[
\underset{\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow}{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CONH}_{2}\right]^{-}}
\] & -23.714 & \(-3.25^{\text {b }}\) & -- & -- & -- & -- & \\
\hline & & & & \(\mathrm{NH}_{2}\) & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CHCONH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 9.667 & \(-4.70^{\text {a }}\) & -- & -- & \\
\hline & \multirow{4}{*}{129} & \multirow{4}{*}{N-Ethylacetamide} & \multirow{4}{*}{\(\mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{5}\)} & \multirow{4}{*}{} & \[
\underset{\mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{5}+\mathrm{e}^{-}}{\left[\mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{5}\right]^{-}} \rightarrow
\] & -23.750 & \(-3.25{ }^{\text {b }}\) & -- & -- & -- & -- & \multirow{4}{*}{\(1.40 \times 10^{7}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{5}+\mathrm{e}-\rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{4}\right]+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 33.619 & \(-5.74{ }^{\text {a }}\) & -- & -- & \\
\hline & & & & & \begin{tabular}{l}
\(\mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{5}+\mathrm{e}^{-} \rightarrow\) \\
\(\left[\mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{4}\right]^{-}+\mathrm{H}^{-}\)
\end{tabular} & -- & -- & 31.040 & \(-5.63{ }^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CONHC}_{2} \mathrm{H}_{5}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{2} \mathrm{CONHC}_{2} \mathrm{H}_{5}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 7.925 & \(-4.62^{\text {a }}\) & -- & -- & \\
\hline & \multirow{3}{*}{130} & \multirow{3}{*}{N -Methylacetamide} & \multirow{3}{*}{\(\mathrm{CH}_{3} \mathrm{CONHCH}_{3}\)} & \multirow{3}{*}{} & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CONHCH}_{3}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{CH}_{3} \mathrm{CONHCH}_{3}\right]^{-}}
\end{gathered}
\] & -21.793 & \(-3.34{ }^{\text {b }}\) & -- & -- & -- & -- & \multirow{3}{*}{\(2.30 \times 10^{6}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CONHCH}_{3}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{2} \mathrm{CONHCH}_{3}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 31.293 & \(-5.64{ }^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CONHCH}_{3}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CONHCH}_{2}\right]+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 8.714 & \(-4.66{ }^{\text {a }}\) & -- & -- & \\
\hline & \multirow{2}{*}{131} & \multirow[b]{2}{*}{Acetamide} & \multirow[b]{2}{*}{\(\mathrm{CH}_{3} \mathrm{CONH}_{2}\)} & \multirow[t]{2}{*}{} & \[
\underset{\mathrm{CH}_{3} \mathrm{CONH}_{2}+\mathrm{e}^{-}}{\left.\mathrm{CH}_{3} \mathrm{CONH}_{2}\right]^{-}} \rightarrow
\] & -25.725 & \(-3.16^{\text {b }}\) & -- & -- & -- & -- & \multirow{2}{*}{\(3.84 \times 10^{7}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{2} \mathrm{CONH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 5.776 & \(-4.53{ }^{\text {a }}\) & -- & -- & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta G_{\text {redaq }}^{\circ}}
\] &  & \[
\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{red} . \mathrm{aq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}}(\mathrm{V} \text { vs } \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
\] & \[
\begin{gathered}
\Delta G_{\text {red.aq }}^{\circ} \\
\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E_{\text {red }}^{\circ}{ }^{\circ} \\
& \text { (V vs } \\
& \text { SHE) } \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{11}{*}{Amide} & 132 & Urea & \(\mathrm{H}_{2} \mathrm{NCONH}_{2}\) &  & \(\mathrm{H}_{2} \mathrm{NCONH}_{2}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{H}_{2} \mathrm{NCONH}_{2}\right]^{-}\) & -17.397 & \(-3.53{ }^{\text {b }}\) & -- & -- & -- & -- & \(3.10 \times 10^{5}\) \\
\hline & 133 & Glycinamide & \(\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CONH}_{2}\) &  & \[
\underset{\left[\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CONH}_{2}\right]^{-}}{\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-}} \rightarrow
\] & -27.344 & \(-3.09{ }^{\text {b }}\) & -- & -- & -- & -- & \(2.83 \times 10^{8}\) \\
\hline & 134 & Formamide & \(\mathrm{HCONH}_{2}\) &  & \(\mathrm{HCONH}_{2}+\mathrm{e}^{-} \rightarrow\left[\mathrm{HCONH}_{2}\right]^{-}\) & -28.171 & \(-3.06{ }^{\text {b }}\) & -- & -- & -- & -- & \(2.80 \times 10^{7}\) \\
\hline & & & & & \[
\underset{\left[\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathrm{CONH}_{2}\right]^{-}}{\mathrm{ClCH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-}} \rightarrow
\] & -61.908 & \(-1.60{ }^{\text {a }}\) & -- & -- & -- & -- & \\
\hline & & & & & \[
\underset{{ }^{\mathrm{ClH}_{2} \mathrm{CH}_{2} \mathrm{CONH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow} \rightarrow}{ }
\] & -- & -- & -60.223 & \(-1.67^{\text {a }}\) & 10.524 & \(-4.74^{\text {c }}\) & \\
\hline & & & &  & \(\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CONH}_{2}\right]^{-}\) & -29.161 & \(-3.02^{\text {b }}\) & -- & -- & -- & -- & \\
\hline & & & & \[
1
\] & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{CH}_{3} \mathrm{CH}(\mathrm{O}) \mathrm{CONH}_{2}\right]^{+}+\mathrm{H}^{-}}
\end{gathered}
\] & -- & -- & -11.924 & \(-3.76^{\text {a }}\) & -- & -- & \\
\hline & 137 & Aceturate & \(\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{COO}^{-}\) &  & \[
\underset{\left[\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{COO}^{2-2-}\right.}{\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow}
\] & -25.837 & \(-3.16^{\text {b }}\) & -- & -- & -- & -- & \(1.13 \times 10^{7}\) \\
\hline & 138 & Pivalamide & \(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCONH}_{2}\) &  & \[
\underset{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCONH}_{2}+\mathrm{e}^{-} \rightarrow}{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CO} \mathrm{CO}(-) \mathrm{NH}_{2}}
\] & -27.032 & \(-3.11^{\text {b }}\) & -- & -- & -- & -- & \(1.50 \times 10^{7}\) \\
\hline & 139 & Malonamide & \(\mathrm{H}_{2} \mathrm{NCOCH}_{2} \mathrm{CONH}_{2}\) &  & \(\mathrm{H}_{2} \mathrm{NCOCH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow\) \(\mathrm{H}_{2} \mathrm{~N}^{\cdot} \mathrm{CO}(-) \mathrm{CH}_{2} \mathrm{CONH}_{2}\) & -30.467 & \(-2.96{ }^{\text {b }}\) & -- & -- & -- & -- & \(1.15 \times 10^{9}\) \\
\hline & 140 & 2-Hydroxyacetamide & \(\mathrm{HOCH}_{2} \mathrm{CONH}_{2}\) &  & \[
\underset{\substack{\mathrm{HOCH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-}}}{\mathrm{HOCH}_{2} \mathrm{CO}(-) \mathrm{NH}_{2}}
\] & -29.101 & \(-3.02^{\text {b }}\) & -- & -- & -- & -- & \(2.93 \times 10^{8}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{e}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{aligned}
& \Delta G_{(\mathrm{cred}, \mathrm{aq}}^{\circ} \\
& \left(\mathrm{K}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}(\mathrm{V} \text { vs } \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
\] & \[
\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta \mathrm{o}_{\mathrm{red} . \mathrm{aq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{{ }_{\text {red }}^{\circ}}(\mathrm{Vvs} \\
& \text { (V ve } \\
& \hline
\end{aligned}
\] & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}}^{\Delta \mathrm{Ic} / \mathrm{mol}}\right)}{\left.\Delta G_{\mathrm{ol}}^{\mathrm{o}}\right)}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\circ} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{11}{*}{Amide} & 14 & Biuret & \(\mathrm{H}_{2} \mathrm{NCONHCONH}_{2}\) & \[
{ }_{H}
\] & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{NCONHCONH}_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{~N}^{-\mathrm{CO}}(-) \mathrm{NHCONH}_{2}
\end{gathered}
\] & -26.984 & \(-3.11^{\text {b }}\) & -- & -- & -- & -- & \(2.53 \times 10^{8}\) \\
\hline & \multicolumn{2}{|l|}{142 2-Chloropropionamide} & \(\mathrm{H}_{3} \mathrm{CH}(\mathrm{Cl}) \mathrm{CO}\) & \[
\mathrm{NwH}_{2}
\] & \[
\underset{\mathrm{CH}_{3} \mathrm{CH}(\mathrm{Cl}) \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow}{\mathrm{CH}_{3} \mathrm{CHCONH}_{2}+\mathrm{Cl}^{-}} \rightarrow
\] & -- & -- & -70.689 & \(-1.22^{\text {a }}\) & 0.907 & \(-4.32^{\text {c }}\) & \(7.58 \times 10^{9}\) \\
\hline & \multirow{2}{*}{143} & \multirow{2}{*}{Iodoacetamide} & \multirow{2}{*}{ICH2CONH \({ }_{2}\)} & & \multirow[t]{2}{*}{\[
\begin{gathered}
\mathrm{ICH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow \text { } \rightarrow \text { } \mathrm{CH}_{2} \mathrm{CONH}_{2} \\
+\mathrm{I}^{-} \\
\mathrm{ICH}_{2} \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow \mathrm{ICH}_{2} \cdot \mathrm{CO}(- \\
) \mathrm{NH}_{2}
\end{gathered}
\]} & -81.461 & \(-0.75{ }^{\text {d }}\) & -- & -- & -- & -- & \multirow{2}{*}{\(5.00 \times 10^{10}\)} \\
\hline & & & & & & -- & -- & -35.569 & \(-2.74{ }^{\text {d }}\) & -2.753 & \(-4.16^{\text {d }}\) & \\
\hline & 144 & Hydroxyurea & \(\mathrm{HONHCONH}_{2}\) &  & \[
\underset{\mathrm{HONH} \cdot \mathrm{CO}(-) \mathrm{NH}_{2}}{\mathrm{HONHCONH}_{2}+\mathrm{e}^{-}} \rightarrow
\] & -27.450 & \(-3.09{ }^{\text {b }}\) & -- & -- & -- & -- & \(4.90 \times 10^{8}\) \\
\hline & 14 & Oxamate & \(\mathrm{H}_{2} \mathrm{NCOCOO}^{-}\) &  & \[
\underset{\text { ) } \mathrm{COO}^{-}}{\mathrm{H}_{2} \mathrm{NCOCOO}^{-}+\mathrm{e}^{-} \rightarrow} \mathrm{H}_{2} \mathrm{NCCO}^{-}-
\] & -44.349 & \(-2.36{ }^{\text {b }}\) & -- & -- & -- & -- & \(5.70 \times 10^{9}\) \\
\hline & 146 & Succinamide & \multicolumn{3}{|l|}{} & -26.232 & \(-3.14{ }^{\text {b }}\) & -- & -- & -- & -- & \(2.02 \times 10^{8}\) \\
\hline & 147 & Asparaginate & \multicolumn{3}{|l|}{} & -26.514 & \(-3.13{ }^{\text {b }}\) & -- & -- & -- & -- & \(2.40 \times 10^{7}\) \\
\hline & 148 & \begin{tabular}{l}
\(\mathrm{N}, \mathrm{N}-\) \\
Dimethylformamide
\end{tabular} & \(\mathrm{HCON}\left(\mathrm{CH}_{3}\right)_{2}\) &  & \[
\begin{gathered}
\mathrm{HCON}\left(\mathrm{CH}_{3}\right)_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}^{-} \mathrm{CO}(-) \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}
\end{gathered}
\] & -30.349 & \(-2.96{ }^{\text {b }}\) & -- & -- & -- & -- & \(3.08 \times 10^{8}\) \\
\hline & 149 & Methyl 2acetamidoacetate & \multicolumn{3}{|l|}{} & -38.384 & \(-2.62^{\text {b }}\) & -- & -- & -- & -- & \(3.34 \times 10^{8}\) \\
\hline & 150 & 2-Formamidoacetate & \(\mathrm{HCONHCH}_{2} \mathrm{COO}^{-}\) &  & \[
\underset{\substack{\mathrm{HCONHCH} \\ \hline \\ \mathrm{HCOO}^{-}+\left(-\mathrm{CO}^{-}+\mathrm{e}^{-}\right.}}{ } \rightarrow
\] & -25.927 & \(-3.16^{\text {b }}\) & -- & -- & -- & -- & \(2.90 \times 10^{7}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\substack{\mathrm{red}, \mathrm{aq}}}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}(\mathrm{V} \mathrm{vs} \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\mathrm{ca}}^{\mathrm{r} \text { red.aq }} \\
& \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}}(\mathrm{V} \text { vs } \\
& \text { SHE } \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {cred.aq }}^{\circ} \\
& \left(\mathrm{K}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}^{(\mathrm{V} \text { vs }} \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{6}{*}{Amide} & 151 & N -Methylformamide & \(\mathrm{HCONHCH}_{3}\) &  & \[
\underset{\mathrm{HCONHCH}_{3}+\mathrm{e}^{-} \rightarrow}{\mathrm{HCO}(-) \mathrm{NHCH}_{3}}
\] & -25.681 & \(-3.17^{\text {b }}\) & -- & -- & -- & -- & \(4.31 \times 10^{7}\) \\
\hline & 152 & N -Tert-Butylacetamide & \(\mathrm{CH}_{3} \mathrm{CONHC}\left(\mathrm{CH}_{3}\right)_{3}\) &  & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CONHC}\left(\mathrm{CH}_{3}\right)_{3}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{CO}(-) \mathrm{NHC}^{2}\left(\mathrm{CH}_{3}\right)_{3}
\end{gathered}
\] & -21.692 & \(-3.34{ }^{\text {b }}\) & -- & -- & -- & -- & \(1.20 \times 10^{7}\) \\
\hline & 153 & Diacetamide & \(\left(\mathrm{CH}_{3} \mathrm{CO}\right)_{2} \mathrm{NH}\) &  & \[
\begin{gathered}
\left(\mathrm{CH}_{3} \mathrm{CO}\right)_{2} \mathrm{NH}+\mathrm{e}^{-} \rightarrow \\
\left(\mathrm{CH}_{3} \mathrm{CO}\right) \mathrm{NH}\left(\mathrm{CH}_{3} \cdot \mathrm{CO}(-)\right)
\end{gathered}
\] & -43.290 & \(-2.40^{\text {b }}\) & -- & -- & -- & -- & \(1.98 \times 10^{10}\) \\
\hline & 154 & N,N-Diethylacetamide & \(\mathrm{CH}_{3} \mathrm{CON}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}\) & & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CON}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{CO}(-) \mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2}
\end{gathered}
\] & -23.892 & \(-3.24{ }^{\text {b }}\) & -- & -- & -- & -- & \(8.00 \times 10^{6}\) \\
\hline & 155 N & N,N-Dimethylacetamide & \(\mathrm{CH}_{3} \mathrm{CON}\left(\mathrm{CH}_{3}\right)_{2}\) & & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CON}\left(\mathrm{CH}_{3}\right)_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \cdot \mathrm{CO}(-) \mathrm{N}_{3}\left(\mathrm{CH}_{3}\right)_{2}
\end{gathered}
\] & -27.415 & \(-3.09{ }^{\text {b }}\) & -- & -- & -- & -- & \(1.50 \times 10^{7}\) \\
\hline & 156 & -- & \(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCON}\left(\mathrm{CH}_{3}\right)_{2}\) &  & \[
\underset{\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCON}\left(\mathrm{CH}_{3}\right)_{2}+\mathrm{e}^{-}}{\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCON}\left(\mathrm{CH}_{3}\right)_{2}\right]^{-}} \rightarrow
\] & -29.955 & \(-2.98{ }^{\text {b }}\) & -- & -- & -- & -- & \(1.20 \times 10^{7}\) \\
\hline \multirow{4}{*}{Ammonia} & \multirow{2}{*}{157} & \multirow{2}{*}{Methyl Ammonium Hydride} & \multirow{2}{*}{\(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\)} & \multirow[t]{2}{*}{} & \(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CH}_{3} \mathrm{NH}_{3}\right]^{-}\) & -7.523 & \(-3.95^{\text {a }}\) & -- & -- & -- & -- & \multirow{2}{*}{\(1.85 \times 10^{6}\)} \\
\hline & & & & & \(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{e} \rightarrow{ }^{-} \mathrm{CH}_{3}+\mathrm{NH}_{3}\) & -- & -- & -50.076 & \(-2.11^{\text {a }}\) & -- & -- & \\
\hline & \multirow{2}{*}{158} & \multirow[b]{2}{*}{Ethylammonium} & \multirow[b]{2}{*}{\(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}\)} & \multirow{2}{*}{} & \multirow[t]{2}{*}{\[
\begin{gathered}
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}\right]^{-} \\
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow \\
{ }^{2} \mathrm{C}_{2} \mathrm{H}_{5}+\mathrm{NH}_{3}
\end{gathered}
\]} & -25.234 & \(-3.19^{\text {a }}\) & -- & -- & -- & -- & \multirow{2}{*}{\(2.50 \times 10^{6}\)} \\
\hline & & & & & & -- & -- & -51.524 & \(-2.05^{\text {a }}\) & -- & -- & \\
\hline
\end{tabular}

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{gathered}
\Delta G_{\mathrm{cred,aq}}^{\circ} \\
\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E^{E_{\text {red }}^{\circ}} \\
& \text { (V vs } \\
& \text { SHE }
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ}{ }_{\left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)}
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}(\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\mathrm{red}}^{\circ}}^{(\mathrm{V} \mathrm{vs}} \\
& \mathrm{SHE} \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{10}{*}{Ammonia} & \multirow[b]{2}{*}{163} & \multirow[b]{2}{*}{Tert-butylammonium} & \multirow[b]{2}{*}{\(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{3}{ }^{+}\)} & \multirow[t]{2}{*}{\(\mathrm{NH}_{3}{ }^{+}\)} & \multirow[t]{2}{*}{\[
\begin{gathered}
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow \\
{\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{3}\right]} \\
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CNH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow\left(\mathrm{CH}_{3}\right)_{3} \cdot \mathrm{C}+ \\
\mathrm{NH}_{3}
\end{gathered}
\]} & \multirow[t]{2}{*}{-24.443} & \(-3.22^{\text {a }}\) & -- & -- & -- & -- & \multirow[b]{2}{*}{\(1.10 \times 10^{6}\)} \\
\hline & & & & & & & -- & -53.400 & \(-1.96{ }^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\underset{\left[\mathrm{CH}_{3} \mathrm{NHNH}_{3}\right]^{-}}{\mathrm{CH}_{3} \mathrm{NHNH}^{+}+\mathrm{e}^{-}} \rightarrow
\] & -27.873 & \(-3.07^{\text {a }}\) & -- & -- & -- & -- & \\
\hline & & & & \({ }^{+} \mathrm{H}_{3} \mathrm{~N}\) & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{NHNH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{NH}+\mathrm{NH}_{3}
\end{gathered}
\] & -- & -- & -80.617 & \(-0.78^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\xrightarrow{\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NNH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow} \rightarrow
\] & -29.065 & \(-3.02^{\text {a }}\) & -- & -- & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NNH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N}+ \\
\mathrm{NH}_{3}
\end{gathered}
\] & -- & -- & -85.826 & \(-0.56^{\text {a }}\) & -- & -- & \\
\hline & & & & & \(\left(\mathrm{CH}_{3}\right)_{4} \mathrm{~N}^{+}+\mathrm{e}^{-} \rightarrow\left[\left(\mathrm{CH}_{3}\right)_{4} \mathrm{~N}\right]^{-}\) & 9.144 & \(-4.68^{\text {a }}\) & -- & -- & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \left(\mathrm{CH}_{3}\right)_{4} \mathrm{~N}^{+}+\mathrm{e}^{-} \rightarrow \\
& {\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}+{ }^{\circ} \mathrm{CH}_{3}\right.}
\end{aligned}
\] & -- & -- & -49.224 & \(-2.15^{\text {a }}\) & -- & -- & \\
\hline & & & & & \(\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4} \mathrm{~N}^{+}+\mathrm{e}^{-} \rightarrow\left[\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4} \mathrm{~N}^{+}\right]^{-}\) & 24.703 & \(-5.35^{\text {a }}\) & -- & -- & -- & -- & \\
\hline & & & & , & \[
\begin{aligned}
& \left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{4} \mathrm{~N}^{+}+\mathrm{e}^{-} \rightarrow \\
& \left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{3} \mathrm{~N}+{ }^{-\mathrm{C}_{2} \mathrm{H}_{5}}
\end{aligned}
\] & -- & -- & -52.937 & \(-1.98^{\text {a }}\) & -- & -- & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{e}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{aligned}
& \Delta G_{\mathrm{cred,aq}}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{ca}} \mathrm{~mol}\right.
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\circ} \\
& (\mathrm{V} v \mathrm{va} \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G^{\mathrm{o}} \mathrm{r} \text { od,aq } \\
& \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\circ} \mathrm{V} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{{ }^{\text {red.aq }}}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{C} \text { red }}^{\circ} \\
& \text { (V vs } \\
& \text { SHE }
\end{aligned}
\] & \\
\hline \multirow{4}{*}{Hydrogen Sulfide} & \multirow[b]{2}{*}{168} & \multirow[b]{2}{*}{Cysteaminium} & \multirow[b]{2}{*}{\(\mathrm{HSCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}\)} & \multirow[b]{2}{*}{} & \[
\begin{gathered}
\mathrm{HSCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow \\
\cdot{ }^{-} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}+\mathrm{HS}-
\end{gathered}
\] & -- & -- & -51.154 & \(-2.06^{\text {c }}\) & 35.675 & \(-5.83{ }^{\text {c }}\) & \multirow[b]{2}{*}{\(2.25 \times 10^{10}\)} \\
\hline & & & & & \[
\begin{gathered}
\mathrm{HSCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow \\
\mathrm{HSCH}_{2}{ }^{-} \mathrm{CH}_{2}+\mathrm{NH}_{3}
\end{gathered}
\] & -- & -- & -53.409 & \(-1.96^{\text {a }}\) & -- & -- & \\
\hline & \multirow[t]{2}{*}{} & \multirow{2}{*}{3Sulfanylpropylazanium} & \multirow{2}{*}{\(\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{NH}_{3}{ }^{+}\)} & \multirow{2}{*}{} & \[
\xrightarrow{\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow} \underset{\left(\mathrm{CH}_{2}\right)_{3} \mathrm{NH}_{3}^{+}+\mathrm{HS}^{-}}{ }
\] & -- & -- & -52.077 & \(-2.02^{\text {c }}\) & 33.887 & \(-5.75^{\text {c }}\) & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{NH}_{3}{ }^{+}+\mathrm{e}^{-} \rightarrow \mathrm{HS}\left(\mathrm{CH}_{2}\right)_{3}^{\cdot} \\
+\mathrm{NH}_{3}
\end{gathered}
\] & -- & -- & -53.531 & \(-1.96^{\text {a }}\) & -- & -- & \\
\hline \multirow{2}{*}{Alkyne} & 170 & Acetylene & HC triplet bond CH & \(\mathrm{HC} \equiv \mathrm{CH}\) & \(\mathrm{HC}=\mathrm{CH}+\mathrm{e}^{-} \rightarrow[\mathrm{HC} \equiv \mathrm{CH}]^{-}\) & -21.817 & \(-3.33^{\text {a }}\) & -- & -- & -- & -- & \(2.00 \times 10^{7}\) \\
\hline & 171 & Propargyl alcohol & HC triplet bond \(\mathrm{CCH}_{2} \mathrm{OH}\) &  & \(\mathrm{HC} \equiv \mathrm{CCH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{HC} \equiv \mathrm{CCH}_{2} \mathrm{OH}\right]\) & -24.162 & \(-3.23{ }^{\text {a }}\) & -- & -- & -- & -- & \(2.12 \times 10^{8}\) \\
\hline \multirow{3}{*}{Sulfate} & \multirow{3}{*}{172} & \multirow{3}{*}{Ethanesulfonate} & \multirow{3}{*}{\(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{SO}_{3}{ }^{-}\)} & \multirow{3}{*}{} & \(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{SO}_{3}+\mathrm{e}^{-} \rightarrow\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{SO}_{3}\right]^{2-}\) & 7.650 & \(-4.61{ }^{\text {a }}\) & -- & -- & -- & -- & \multirow{3}{*}{\(3.50 \times 10^{7}\)} \\
\hline & & & & & \[
\begin{aligned}
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{SO}_{3}^{-} & +\mathrm{e}^{-} \rightarrow \\
& \rightarrow \mathrm{H}^{-}
\end{aligned}
\] & -- & -- & 31.977 & \(-5.67^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{SO}_{3}^{-}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CH}_{3} \mathrm{CHSO}_{3}\right]^{2-} \\
+\mathrm{H}^{-}
\end{gathered}
\] & -- & -- & 23.473 & \(-5.30^{\text {a }}\) & -- & -- & \\
\hline \multirow{2}{*}{Sulfoxide} & \multirow{2}{*}{173} & \multirow{2}{*}{Dibutyl sulphoxide} & \multirow{2}{*}{\[
\begin{gathered}
{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{SO}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{C}\right.} \\
\left.\mathrm{H}_{3}\right]
\end{gathered}
\]} & \multirow{2}{*}{} & \[
\xrightarrow[{\rightarrow\left[\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{SO}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CO}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CH}_{3}\right]^{-}\right]^{-}}]{ }
\] & -33.031 & \(-2.85{ }^{\text {a }}\) & -- & -- & -- & -- & \multirow{2}{*}{\(3.60 \times 10^{6}\)} \\
\hline & & & & & \[
\begin{gathered}
{\left[\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{SO}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CH}_{3}\right]+\mathrm{e}^{-}} \\
\rightarrow \mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{~S}(-) \mathrm{O}+ \\
\cdot\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CH}_{3}
\end{gathered}
\] & -- & -- & -35.991 & \(-2.72^{\text {a }}\) & 22.095 & \(-5.24{ }^{\text {c }}\) & \\
\hline
\end{tabular}

\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}}^{\Delta \mathrm{rec} / \mathrm{mol}}\right)}{\Delta G_{\mathrm{ol}}^{\mathrm{o}}}
\] & \[
\begin{aligned}
& E_{\mathrm{E}_{\mathrm{red}}} \\
& \text { (V vs } \\
& \text { SHE) } \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E^{E_{\mathrm{o} \text { red }}} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{gathered}
\Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ} \\
\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E^{E_{\mathrm{red}}^{\circ}} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{7}{*}{Thiol} & \multirow{3}{*}{180} & \multirow{3}{*}{beta-Mercaptoethanol} & \multirow{3}{*}{HS \(\left(\mathrm{CH}_{2}\right)_{2} \mathrm{OH}\)} & \multirow{3}{*}{} & \(\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{OH}\right]^{-}\) & -23.177 & \(-3.28^{\text {a }}\) & -- & -- & \multirow[t]{2}{*}{--} & \multirow[t]{2}{*}{--} & \multirow{3}{*}{\(1.73 \times 10^{10}\)} \\
\hline & & & & & \multirow[t]{2}{*}{\[
\begin{gathered}
\begin{array}{c}
\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
\mathrm{HSCH}_{2} \mathrm{CH}_{2}+\mathrm{OH}^{-} \\
\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \cdot\left(\mathrm{HS}_{2}\right)_{2} \mathrm{OH} \\
+\mathrm{HS}^{-}
\end{array}
\end{gathered}
\]} & -- & -- & -11.456 & \(-3.78^{\text {a }}\) & & & \\
\hline & & & & & & -- & -- & -49.878 & \(-2.12^{\text {c }}\) & 38.682 & \(-5.96{ }^{\text {c }}\) & \\
\hline & 181 & 2-Methyl-2propanethiol & \(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CSH}\) & \[
\stackrel{s+1}{\mid r}
\] & \[
\begin{gathered}
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CSH}+\mathrm{e}^{-} \rightarrow \\
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}+\mathrm{HS}
\end{gathered}
\] & -- & -- & -54.275 & \(-1.93{ }^{\text {c }}\) & 32.693 & \(-5.70^{\text {c }}\) & \(3.41 \times 10^{9}\) \\
\hline & 182 & 3-Mercaptopropionic acid & \(\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}\) &  & \[
\begin{gathered}
\mathrm{HS}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}+\mathrm{e}^{-} \rightarrow \\
\cdot\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}+\mathrm{HS}-
\end{gathered}
\] & -- & -- & -50.098 & \(-2.11^{\text {c }}\) & 34.898 & \(-5.79{ }^{\text {c }}\) & \(6.91 \times 10^{9}\) \\
\hline & 183 & Thioglycolate & \(\mathrm{HSCH}_{2} \mathrm{COO}^{-}\) &  & \[
\begin{gathered}
\mathrm{HSCH}_{2} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow{ }^{-} \mathrm{CH}_{2} \mathrm{COO}^{-} \\
+\mathrm{HS}^{-}
\end{gathered}
\] & -- & -- & -54.298 & \(-1.93{ }^{\text {c }}\) & 33.123 & \(-5.72^{\text {c }}\) & \(3.03 \times 10^{9}\) \\
\hline & 184 & & \[
\underset{{ }_{2} \mathrm{SH}}{\mathrm{H}_{2} \mathrm{NC}(=\mathrm{NH}) \mathrm{NHCH}_{2} \mathrm{CF}}
\] &  & \begin{tabular}{l}
\(\mathrm{H}_{2} \mathrm{NC}(=\mathrm{NH}) \mathrm{NHCH}_{2} \mathrm{CH}_{2} \mathrm{SH}+\mathrm{e}\) \\
\(\left[\mathrm{H}_{2} \mathrm{NC}(=\mathrm{NH}) \xrightarrow[{\left.\mathrm{NHCH}_{2} \mathrm{CH}_{2} \mathrm{SH}\right]^{-}}]{\rightarrow}\right.\) \\
\(\mathrm{H}_{2} \mathrm{NC}(=\mathrm{NH}) \mathrm{NHCH}_{2} \mathrm{CH}_{2} \mathrm{SH}+\mathrm{e}-\) \\
\(\rightarrow \mathrm{H}_{2} \mathrm{NC}(=\mathrm{NH}) \mathrm{NHCH}_{2}{ }^{\circ} \mathrm{CH}_{2}+\) HS
\end{tabular} & 0.881
-- & \(-4.32^{\text {a }}\)

-- & -51.249 & --
\(-2.06{ }^{\text {c }}\) & -- & \(-5.64{ }^{\text {c }}\) & \(1.02 \times 10^{11}\) \\
\hline & & & & & \(\mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CH}_{3} \mathrm{SCH}_{3}\right]^{-}\) & 5.808 & \(-4.53^{\text {a }}\) & -- & -- & -- & -- & \\
\hline Sulfide/ Disulfide & 185 & Dimethylsulfide & \(\mathrm{CH}_{3} \mathrm{SCH}_{3}\) &  & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{2} \mathrm{SCH}_{3}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 24.723 & \(-5.35^{\text {a }}\) & -- & -- & \(2.00 \times 10^{7}\) \\
\hline & & & & & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{SCH}_{3}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{~S}^{-}+{ }^{-\mathrm{CH}_{3}}
\end{gathered}
\] & -- & -- & -38.239 & \(-2.62^{\text {c }}\) & 52.271 & \(-6.55^{\circ}\) & \\
\hline
\end{tabular}


\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mel} / \mathrm{mol}\right)}{\left.\Delta G_{\mathrm{o}}^{\mathrm{o}}\right)}
\] & \[
\begin{aligned}
& E_{\mathrm{C}_{\text {red }}} \mathrm{V} \text { vs } \\
& \mathrm{SHE}
\end{aligned}
\] & \[
\underset{\left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{crdaq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}(\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\mathrm{cal}}^{\mathrm{o} \text { redaq }} \\
& (\mathrm{mol})
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\mathrm{o}} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{3}{*}{CS} & 197 & Thiourea & \(\mathrm{H}_{2} \mathrm{NCSNH}_{2}\) &  & \[
\underset{\mathrm{H}_{2} \mathrm{NCSNH}_{2}+\mathrm{e}^{-}}{\left[\mathrm{H}_{2} \mathrm{NCSNH}_{2}\right]^{-}} \rightarrow
\] & -18.118 & \(-3.49^{\text {a }}\) & -- & -- & -- & -- & \(3.29 \times 10^{9}\) \\
\hline & 198 & Thiosemicarbazide & \(\mathrm{H}_{2} \mathrm{NNHCSNH}_{2}\) & & \(\mathrm{H}_{2} \mathrm{NNHCSNH}_{2}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{H}_{2} \mathrm{NNHCSNH}_{2}\right]^{-}\) & -19.102 & \(-3.45^{\text {a }}\) & -- & -- & -- & -- & \(1.15 \times 10^{9}\) \\
\hline & 199 & N,N'-Diethylthiourea & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NHCSNHCH}_{2} \mathrm{C} \\
\mathrm{H}_{3}
\end{gathered}
\] &  & \begin{tabular}{l}
\(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NHCSNHCH}_{2} \mathrm{CH}_{3}+\mathrm{e}^{-}\) \\
\(\rightarrow\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NHCSNHCH}_{2} \mathrm{CH}_{3}\right]^{-}\)
\end{tabular} & -19.126 & \(-3.45^{\text {a }}\) & -- & -- & -- & -- & \(5.10 \times 10^{8}\) \\
\hline \multirow{7}{*}{Nitro} & \multirow{3}{*}{200} & \multirow{3}{*}{Nitromethane} & \multirow{3}{*}{\(\mathrm{CH}_{3} \mathrm{NO}_{2}\)} & & \(\mathrm{CH}_{3} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow\left[\mathrm{CH}_{3} \mathrm{NO}_{2}\right]^{-}\) & -61.020 & \(-1.63{ }^{\text {a }}\) & -- & -- & -- & -- & \\
\hline & & & &  & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{2} \mathrm{NO}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & -15.324 & \(-3.62^{\text {a }}\) & -- & -- & \(1.80 \times 10^{11}\) \\
\hline & & & & & \(\mathrm{CH}_{3} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow \mathrm{CH}_{3}+\mathrm{NO}_{2}{ }^{-}\) & -- & -- & -46.434 & \(-2.27^{\text {a }}\) & 51.633 & \(-6.52^{\text {c }}\) & \\
\hline & \multirow{4}{*}{201} & \multirow{4}{*}{1-Nitropropane} & \multirow{4}{*}{\(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NO}_{2}\)} & \multirow{4}{*}{} & \[
\underset{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NO}_{2}\right]^{-}}{\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NO}_{2}+\mathrm{e}^{-}} \rightarrow
\] & -60.847 & \(-1.64{ }^{\text {a }}\) & -- & -- & -- & -- & \multirow{4}{*}{\(2.70 \times 10^{10}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHNO}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & -16.349 & \(-3.57^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CHCH}_{2} \mathrm{NO}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 33.614 & \(-5.74{ }^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2}+\mathrm{NO}_{2}^{-}\right.}
\end{gathered}
\] & -- & -- & -46.496 & \(-2.26^{\text {a }}\) & 48.013 & \(-6.36^{\text {c }}\) & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{aligned}
& \Delta G_{\mathrm{cral}}^{\mathrm{o}} \mathrm{molaq} \\
& \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}(\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ}{ }_{\left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)}
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{E}_{\mathrm{red}}} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE} \text { ) }
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\mathrm{r}} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{5}{*}{Nitro} & \multirow{3}{*}{202} & \multirow{3}{*}{Nitroethane} & \multirow{3}{*}{\(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NO}_{2}\)} & \multirow{3}{*}{} & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NO}_{2}\right]^{-}}
\end{gathered}
\] & -60.174 & \(-1.67^{\text {a }}\) & -- & -- & -- & -- & \multirow{3}{*}{\(2.70 \times 10^{10}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CHNO}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & -16.097 & \(-3.58^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NO}_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{CH}_{2}+\mathrm{NO}_{2}^{-}
\end{gathered}
\] & -- & -- & -46.401 & \(-2.27^{\text {a }}\) & 49.591 & \(-6.43{ }^{\text {c }}\) & \\
\hline & \multirow{2}{*}{203} & \multirow{2}{*}{2-Methyl-2nitrosopropane} & \multirow{2}{*}{\(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}(\mathrm{NO})\)} & \multirow[t]{2}{*}{} & \multirow[t]{2}{*}{\(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}(\mathrm{NO})+\mathrm{e}^{-} \rightarrow\) \(\left[\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}(\mathrm{NO})\right]^{-}\)
\[
\begin{gathered}
\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}(\mathrm{NO})+\mathrm{e}^{-} \rightarrow\left(\mathrm{CH}_{3}\right)_{3} \cdot \mathrm{C}+ \\
\mathrm{NO}^{-}
\end{gathered}
\]} & \multirow[t]{2}{*}{\[
-63.457
\]} & \multirow[t]{2}{*}{\[
-1.53^{a}
\]} & \multirow[t]{2}{*}{--
4.387} & -- & -- & -- & \multirow{2}{*}{\(8.26 \times 10^{9}\)} \\
\hline & & & & & & & & & \(-4.47^{\text {a }}\) & 20.961 & \(-5.19^{\text {c }}\) & \\
\hline \multirow{6}{*}{PFAS} & & & & o & \[
\begin{gathered}
\mathrm{CF}_{3} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CF}_{3} \cdot \mathrm{CO}(-) \mathrm{O}^{-}
\end{gathered}
\] & -- & -- & -- & -- & -- & -- & \\
\hline & & & & \[
\left.F^{\prime}\right|_{F}
\] & \[
\begin{aligned}
& \mathrm{CF}_{3} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
& \mathrm{CF}_{2} \mathrm{COO}^{-}+\mathrm{F}
\end{aligned}
\] & -- & -- & -8.995 & \(-3.89^{\text {a }}\) & 88.105 & \(-8.10{ }^{\text {a }}\) & \\
\hline & \multirow{4}{*}{205} & \multirow{4}{*}{Perflurobutanoic Acid} & \multirow{4}{*}{\(\mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{COO}^{-}\)} & \multirow{4}{*}{} & \[
\begin{gathered}
\mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{COCO}_{7}(-) \mathrm{O}^{-}
\end{gathered}
\] & -36.211 & \(-2.71^{\text {b }}\) & -- & -- & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{COO}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CF}_{3} \mathrm{CF}_{2} \mathrm{CFCOO}^{-}+\mathrm{F}^{-}
\end{gathered}
\] & -- & -- & -19.143 & \(-3.45^{\text {a }}\) & 59.505 & \(-6.86{ }^{\text {a }}\) & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CF}_{3}{ }^{-} \mathrm{CFCF}_{2} \mathrm{COO}+\mathrm{F}^{-}
\end{gathered}
\] & -- & -- & -13.608 & \(-3.69^{\text {a }}\) & 65.733 & \(-7.13^{\text {a }}\) & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{C}_{3} \mathrm{~F}_{7} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
& \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{COO}+\mathrm{F}^{-}+{ }^{-}
\end{aligned}
\] & -- & -- & -5.305 & \(-4.05^{\text {a }}\) & 73.344 & \(-7.46{ }^{\text {a }}\) & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline & \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & & \[
\begin{gathered}
\Delta G_{\text {red.aq }}^{\circ} \\
\left(\mathrm{K}_{\mathrm{cal}} \mathrm{~mol} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E_{\text {red }}^{\circ} \mathrm{c} \\
& \text { (V vs } \\
& \text { SHE) } \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& \begin{array}{l}
E_{\mathrm{red}}^{\circ} \\
(\mathrm{V} \text { vs } \\
\text { SHE) } \\
\hline
\end{array} \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\mathrm{red.aq}}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] &  & \\
\hline & \multirow{8}{*}{PFAS} & \multirow{8}{*}{206} & \multirow{8}{*}{Perflurooctanoic Acid} & \multirow{8}{*}{\(\mathrm{C}_{7} \mathrm{~F}_{15} \mathrm{COO}^{-}\)} & & \[
\begin{gathered}
\mathrm{C}_{7} \mathrm{~F}_{15} \mathrm{COO}+\mathrm{e}^{-} \rightarrow \\
\mathrm{C}_{7} \mathrm{~F}_{15} \cdot \mathrm{CO}(-) \mathrm{O}^{-}
\end{gathered}
\] & -32.059 & \(-2.89^{\text {b }}\) & -- & -- & -- & -- & \\
\hline & & & & & & \[
\underset{\substack{\mathrm{C}_{2} \mathrm{~F}_{15} \mathrm{COO}^{-}+\mathrm{e}^{-} \\ \mathrm{CF}_{3} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \cdot \mathrm{CFCOO}^{-} \\+\mathrm{F}^{-}}}{\text {and }}
\] & -- & -- & -18.451 & \(-3.48^{\text {c }}\) & 42.899 & \(-6.14{ }^{\text {c }}\) & \\
\hline & & & & & & \[
\begin{gathered}
\mathrm{C}_{1} \mathrm{~F}_{15} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CF}_{3} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CFCF}_{2} \mathrm{CFOC}_{2} \\
+\mathrm{F}^{-}
\end{gathered}
\] & -- & -- & -15.222 & \(-3.62^{\text {c }}\) & 46.128 & \(-6.28^{\text {c }}\) & \\
\hline & & & & & \[
\lambda 1
\] & \[
\begin{gathered}
\mathrm{C}_{1} \mathrm{~F}_{15} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CF}_{3} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2}{ }^{\circ} \mathrm{CFCF}_{2} \mathrm{CF}_{2} \mathrm{COO} \\
+\mathrm{F}^{-}
\end{gathered}
\] & -- & -- & -16.145 & \(-3.58^{\text {c }}\) & 45.436 & \(-6.25^{\text {c }}\) & \(1.70 \times 10^{7}\) \\
\hline & & & & & & \[
\begin{gathered}
\mathrm{C}_{7} \mathrm{~F}_{15} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CF}_{3} \mathrm{CF}_{2} \mathrm{CF}_{2}{ }^{2} \mathrm{CFCF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{COO}^{-} \\
+\mathrm{F}
\end{gathered}
\] & -- & -- & -16.606 & \(-3.56^{\text {c }}\) & 45.206 & \(-6.24^{\text {c }}\) & \\
\hline & & & & & & \[
\begin{gathered}
\mathrm{C}_{1} \mathrm{~F}_{15} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CF}_{3} \mathrm{CF}_{2} \mathrm{CFFCF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{COO} \\
+\mathrm{F}^{-}
\end{gathered}
\] & -- & -- & -16.837 & \(-3.55^{\text {c }}\) & 46.589 & \(-6.30^{\text {c }}\) & \\
\hline & & & & & & \[
\begin{gathered}
\mathrm{C}_{7} \mathrm{~F}_{15} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CF}_{3} \mathrm{CFCF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{COO} \\
+\mathrm{F}
\end{gathered}
\] & -- & -- & -15.684 & \(-3.60^{\text {c }}\) & 46.589 & \(-6.30^{\text {c }}\) & \\
\hline & & & & & & \[
\begin{gathered}
\mathrm{C}_{7} \mathrm{~F}_{15} \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{CF}_{2} \mathrm{COO} \\
+\mathrm{F}^{-}
\end{gathered}
\] & -- & -- & -6.227 & \(-4.01^{\text {c }}\) & 54.892 & \(-6.66^{\text {c }}\) & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{aligned}
& \Delta G_{\text {cred.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E^{E^{\circ} \text { red }} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red,aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{red}}^{\mathrm{o}} \\
& \text { (V vs } \\
& \text { SHE) } \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\text {red }}^{\circ} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{7}{*}{Alkene} & \multirow{4}{*}{207} & \multirow{4}{*}{Allylamine} & \multirow{4}{*}{\(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{NH}_{2}\)} & \multirow{4}{*}{} & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{NH}_{2}\right]^{-}}
\end{gathered}
\] & -23.127 & \(-3.28^{\text {b }}\) & -- & -- & -- & -- & \multirow{4}{*}{\(1.20 \times 10^{7}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCHNH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 19.091 & \(-5.11^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CCH}_{2} \mathrm{NH}_{2}\right]^{-}+\mathrm{H}^{\cdot}}
\end{gathered}
\] & -- & -- & 26.763 & \(-5.44^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{HC}=\mathrm{CHCH}_{2} \mathrm{NH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 26.076 & \(-5.41^{\text {a }}\) & -- & -- & \\
\hline & \multirow{3}{*}{208} & \multirow{3}{*}{Acrylonitrile} & \multirow{3}{*}{\(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCN}\)} & \multirow{3}{*}{} & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCN}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCN}\right]^{-}}
\end{gathered}
\] & -53.943 & \(-1.94{ }^{\text {b }}\) & -- & -- & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCN} & +\mathrm{e}^{-} \rightarrow\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CCN}\right]^{-} \\
& +\mathrm{H}^{\cdot}
\end{aligned}
\] & -- & -- & 3.716 & \(-4.44^{\text {a }}\) & -- & -- & \(2.78 \times 10^{10}\) \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCN}+\mathrm{e}^{-} \rightarrow \\
& {[\mathrm{HC}=\mathrm{CHCN}]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 14.285 & \(-4.90^{\text {a }}\) & -- & -- & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{\mathrm{red}}^{\mathrm{o} \text { ed }} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\underset{\left(\mathrm{k}_{\mathrm{ca}} / G_{\mathrm{red} ., \mathrm{mol}}^{\circ}\right)}{ }
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\circ} \mathrm{V} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}(\mathrm{V} \text { vs } \\
& \text { SHE } \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{9}{*}{Alkene} & \multirow{5}{*}{209} & \multirow{5}{*}{Allyl alcohol} & \multirow{5}{*}{\(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{OH}\)} & \multirow{5}{*}{} & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{OH}\right]^{-}}
\end{gathered}
\] & -27.368 & \(-3.09^{\text {b }}\) & -- & -- & -- & -- & \multirow{5}{*}{\(3.47 \times 10^{7}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{O}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 0.364 & \(-4.30^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCHOH}^{-}+\mathrm{H}^{-}\right.}
\end{gathered}
\] & -- & -- & 17.836 & \(-5.05^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CCH}_{2} \mathrm{OH}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 23.083 & \(-5.28^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{HC}=\mathrm{CHCH}_{2} \mathrm{OH}\right]^{-}+\mathrm{H}^{+}}
\end{gathered}
\] & -- & -- & 19.174 & \(-5.11^{\text {a }}\) & -- & -- & \\
\hline & \multirow{4}{*}{210} & \multirow{4}{*}{Acrylic acid} & \multirow{4}{*}{\(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOH}\)} & \multirow{4}{*}{} & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOH}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{CH} \cdot \mathrm{CO}(-) \mathrm{OH}
\end{gathered}
\] & -59.268 & \(-1.71^{\text {b }}\) & -- & -- & -- & -- & \multirow{4}{*}{\(1.03 \times 10^{12}\)} \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOH}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}^{\circ} \mathrm{CO}+\mathrm{OH}^{-}
\end{gathered}
\] & -- & -- & 7.683 & \(-4.61{ }^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOH}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CCOOH}\right]^{-}+\mathrm{H}^{-}}
\end{gathered}
\] & -- & -- & 11.370 & \(-4.77^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOH}+\mathrm{e}^{-} \rightarrow \\
& {[\mathrm{HC}=\mathrm{CHCOOH}]+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 17.443 & \(-5.04{ }^{\text {a }}\) & -- & -- & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{e}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\circ} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\mathrm{c} / \mathrm{red.aq}}^{\mathrm{r}} \\
& \left(\mathrm{k}_{\mathrm{c} / \mathrm{mol}} \mathrm{mo}\right.
\end{aligned}
\] & \[
\begin{aligned}
& E^{E^{\circ} \text { red }} \\
& \text { (V vs } \\
& \text { SHE) }
\end{aligned}
\] & \[
\begin{gathered}
\Delta G_{\text {red.aq }}^{\circ} \\
\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}}(\mathrm{V} \text { vs } \\
& \mathrm{SHE}
\end{aligned}
\] & \\
\hline \multirow{11}{*}{Alkene} & \multirow{3}{*}{211} & \multirow{3}{*}{Acrylate} & \multirow{3}{*}{\(\mathrm{CH}_{2}=\mathrm{CHCOO}^{-}\)} & \multirow{3}{*}{} & \[
\begin{gathered}
\mathrm{CH}_{2}=\mathrm{CHCOO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{2}=\mathrm{CH} \\
\hline
\end{gathered}
\] & -40.739 & \(-2.51^{\text {b }}\) & -- & -- & -- & -- & \multirow{3}{*}{\(5.30 \times 10^{9}\)} \\
\hline & & & & & \[
\begin{gathered}
\mathrm{CH}_{2}=\mathrm{CHCOO}^{-}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{CH}_{2}=\mathrm{CCOO}\right]^{-2}+\mathrm{H}^{-}}
\end{gathered}
\] & -- & -- & 28.234 & \(-5.50^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{2}=\mathrm{CHCOO}^{-}+\mathrm{e}^{-} \rightarrow \\
& {[\mathrm{CH}=\mathrm{CHCOO}]^{2-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 27.304 & \(-5.46^{\text {a }}\) & -- & -- & \\
\hline & \multirow{4}{*}{212} & \multirow{4}{*}{Methyl vinyl ketone} & \multirow{4}{*}{\(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOCH}_{3}\)} & \multirow{4}{*}{} & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{CH} \cdot \mathrm{CO}(-) \mathrm{CH}_{3}
\end{gathered}
\] & -63.318 & \(-1.53^{\text {b }}\) & -- & -- & -- & -- & \multirow{4}{*}{\(2.78 \times 10^{9}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOCH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & -8.414 & \(-3.92^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CCOCH}_{3}\right]^{+}+\mathrm{H}^{-}}
\end{gathered}
\] & -- & -- & 8.306 & \(-4.64{ }^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{HC}=\mathrm{CHCOCH}_{3}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 18.815 & \(-5.10^{\text {a }}\) & -- & -- & \\
\hline & \multirow{4}{*}{213} & \multirow{4}{*}{Methyl acrylate} & \multirow{4}{*}{\[
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOCH}_{3}
\]} & \multirow{4}{*}{} & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{CH} \cdot \mathrm{CO}(-) \mathrm{OCH}_{3}
\end{gathered}
\] & -57.171 & \(-1.80^{\text {b }}\) & -- & -- & -- & -- & \multirow{4}{*}{\(1.52 \times 10^{10}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOCH}_{2}\right]^{+}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 26.012 & \(-5.41^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CCOOCH}_{3}\right]^{-}+\mathrm{H}^{-}}
\end{gathered}
\] & -- & -- & 11.779 & \(-4.79^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{HC}=\mathrm{CHCOOCH}_{3}\right]+\mathrm{H}}
\end{aligned}
\] & -- & -- & 17.747 & \(-5.05^{\text {a }}\) & -- & -- & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}(\mathrm{V} \mathrm{vs} \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\mathrm{cred}, \mathrm{aq}}^{\mathrm{o}} \\
& \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{Cred}}^{\circ} \\
& (\mathrm{V} v \mathrm{va} \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {red.aq }}^{\circ}{ }_{\left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)}
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}}(\mathrm{V} \text { vs } \\
& \mathrm{SHE}
\end{aligned}
\] & \\
\hline \multirow{10}{*}{Alkene} & \multirow{3}{*}{21} & \multirow{3}{*}{Senecioic acid amide} & \multirow{3}{*}{\(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCONH}_{2}\)} & \multirow{3}{*}{} & \[
\underset{\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCONH}_{2}\right]^{\circ}}{\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCONH}_{2}+\mathrm{e}^{-}} \rightarrow
\] & -44.000 & \(-2.37^{\text {b }}\) & -- & -- & -- & -- & \\
\hline & & & & & \[
\begin{gathered}
\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCONH}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CCONH}_{2}\right]+\mathrm{H}}
\end{gathered}
\] & -- & -- & 17.846 & \(-5.05^{\text {a }}\) & -- & -- & \(7.23 \times 10^{9}\) \\
\hline & & & & & \[
\begin{aligned}
& \left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCONH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{C}=\mathrm{CHCONH}_{2}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & -1.305 & \(-4.22^{\text {a }}\) & -- & -- & \\
\hline & \multirow{2}{*}{215} & \multirow{2}{*}{Vinyl chloride} & \multirow{2}{*}{\(\mathrm{CH}_{2}=\mathrm{CHCl}\)} & \multirow{2}{*}{} & \[
\underset{\left[\mathrm{CH}_{2}=\mathrm{CHCl}\right]^{-}}{\mathrm{CH}_{2}=\mathrm{CHCl}+\mathrm{e}^{-} \rightarrow}
\] & -58.079 & \(-1.76{ }^{\text {c }}\) & -- & -- & -- & -- & \multirow{2}{*}{\(2.53 \times 10^{8}\)} \\
\hline & & & & & \[
\begin{gathered}
\mathrm{CH}_{2}=\mathrm{CHCl}+\mathrm{e}^{-} \rightarrow \\
{ }^{-} \mathrm{CH}_{2}=\mathrm{CH}+\mathrm{Cl}
\end{gathered}
\] & -- & -- & -62.086 & \(-1.59^{\text {c }}\) & 27.100 & \(-5.45^{\text {c }}\) & \\
\hline & \multirow{2}{*}{216} & \multirow{2}{*}{Ethylene} & \multirow{2}{*}{\(\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}_{2}\)} & \multirow[t]{2}{*}{} & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}_{2}+\mathrm{e}^{-} \rightarrow\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}_{2}\right]^{-}\) & -24.747 & \(-3.21^{\text {b }}\) & -- & -- & -- & -- & \multirow{2}{*}{\(3.00 \times 10^{5}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{H}_{2} \mathrm{C}=\mathrm{CH}_{2}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 27.495 & \(-5.47^{\text {a }}\) & -- & -- & \\
\hline & \multirow{3}{*}{217} & \multirow{3}{*}{Ethenesulfonate} & \multirow{3}{*}{\(\mathrm{CH}_{2}=\mathrm{CHSO}_{3}{ }^{-}\)} & \multirow{3}{*}{} & \[
\begin{gathered}
\mathrm{CH}_{2}=\mathrm{CHSO}_{3}-\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{CH}_{2}=\mathrm{CHSO}_{3}\right]^{2-}}
\end{gathered}
\] & -37.671 & \(-2.65{ }^{\text {b }}\) & -- & -- & -- & -- & \multirow{3}{*}{\(2.30 \times 10^{9}\)} \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{2}=\mathrm{CHSO}_{3}^{-}+\mathrm{e}^{-} \rightarrow \\
& {\left[\mathrm{CH}_{2}=\mathrm{CSO}_{3}\right]^{2-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 13.000 & \(-4.84^{\text {a }}\) & -- & -- & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{CH}_{2}=\mathrm{CHSO}_{3}^{-}+\mathrm{e}^{-} \rightarrow \vec{~} \\
& {\left[\mathrm{CH}=\mathrm{CHSO}_{3}\right]^{-}+\mathrm{H}^{-}}
\end{aligned}
\] & -- & -- & 19.342 & \(-5.12^{\text {a }}\) & -- & -- & \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\mathrm{e}}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\underset{\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)}{\Delta G_{\mathrm{ced}, \mathrm{aq}}^{\circ}}
\] & \[
\begin{aligned}
& E_{\text {Cred }}^{\circ} \\
& (\mathrm{V} \text { vs } \\
& \text { SHE }) \\
& \hline
\end{aligned}
\] & \[
\begin{gathered}
\Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ} \\
\left(\mathrm{k}_{\mathrm{ca}} \mathrm{I} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E_{\text {}}^{E_{\mathrm{red}}} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\text {cred.aq }}^{\circ} \\
& \left(\mathrm{K}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E^{E^{\circ} \mathrm{red}} \\
& (\mathrm{~V} \text { vs } \\
& \text { SHE) } \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{8}{*}{Alkene} & 218 & Tetrachloroethylene & \(\mathrm{Cl}_{2} \mathrm{C}=\mathrm{CCl}_{2}\) &  & \[
\begin{gathered}
\mathrm{Cl}_{2} \mathrm{C}=\mathrm{CCl}_{2}+\mathrm{e}^{-} \rightarrow\left[\mathrm{Cl}_{2} \mathrm{C}=\mathrm{CCl}_{2}\right]^{-} \\
\mathrm{Cl}_{2} \mathrm{C}=\mathrm{CCl}_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{Cl}_{2} \mathrm{C}=\mathrm{CCl}+\mathrm{Cl}^{-}
\end{gathered}
\] & -67.930 & \(-1.33^{\text {c }}\) & -70.102 & \(-1.24^{\text {c }}\) & 15.166 & \[
-4.94^{\text {c }}
\] & \(2.67 \times 10^{10}\) \\
\hline & 219 & Crotonyl Alcohol & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCH}_{2} \mathrm{OH}\) &  & \[
\underset{\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow}{\left[\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCH}_{2} \mathrm{OH}\right]^{-}}
\] & -24.308 & \(-3.23^{\text {b }}\) & -- & -- & -- & -- & \(5.51 \times 10^{7}\) \\
\hline & 220 & Crotonic Acid & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCOOH}\) &  & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCOOH}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CH} \mathrm{CO}(-) \mathrm{OH}
\end{gathered}
\] & -54.359 & \(-1.92^{\text {b }}\) & -- & -- & -- & -- & \(6.62 \times 10^{10}\) \\
\hline & 221 & Dimethyl Fumarate & \(\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOO}\) \(\mathrm{CH}_{3}\) &  & \begin{tabular}{l}
\(\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOOCH}_{3}+\mathrm{e}^{-}\) \\
\(\rightarrow \mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CH} \cdot \mathrm{CO}(-) \mathrm{OCH}_{3}\)
\end{tabular} & -76.951 & \(-0.94{ }^{\text {b }}\) & -- & -- & -- & -- & \(3.30 \times 10^{10}\) \\
\hline & 222 & Divinyl Sulfone & \(\left(\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}\right)_{2} \mathrm{SO}_{2}\) &  & \[
\underset{\left.\left(\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}\right)_{2} \mathrm{SO}_{2}+\mathrm{C}_{2} \mathrm{e}_{2} \mathrm{SO}_{2}\right]^{-}}{\left(\mathrm{H}^{-}\right.}
\] & -55.621 & \(-1.87^{\text {b }}\) & -- & -- & -- & -- & \(1.66 \times 10^{10}\) \\
\hline & 223 & Methacrylic Acid & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COOH}\) &  & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COOH}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right)^{\circ} \mathrm{CO}(-) \mathrm{OH}
\end{gathered}
\] & -56.591 & \(-1.83{ }^{\text {b }}\) & -- & -- & -- & -- & \(8.26 \times 10^{10}\) \\
\hline & 224 & Methyl Methacrylate & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COOCH}_{3}\) &  & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COOCH}_{3}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right)^{\cdot} \mathrm{CO}(-) \mathrm{OCH}_{3}
\end{gathered}
\] & -54.409 & \(-1.92^{\text {b }}\) & -- & -- & -- & -- & \(2.72 \times 10^{10}\) \\
\hline & 225 & \begin{tabular}{l}
trans-1,2- \\
Dichloroethylene
\end{tabular} & \(\mathrm{ClCH}=\mathrm{CHCl}\) &  & \(\mathrm{ClCH}=\mathrm{CHCl}+\mathrm{e}^{-} \rightarrow\) \([\mathrm{ClCH}=\mathrm{CHCl}]^{-}\)
\[
\begin{aligned}
\mathrm{ClCH}=\mathrm{CHCl} & +\mathrm{e}^{-} \rightarrow{ }^{\circ} \mathrm{CH}=\mathrm{CHCl} \\
& +\mathrm{Cl}^{-}
\end{aligned}
\] & -60.299 & \(-1.67^{\text {c }}\) & --
-64.409 & --
\(-1.49^{\text {c }}\) & --
22.702 & \[
-5.26^{c}
\] & \(1.08 \times 10^{10}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{gathered}
\Delta G_{\text {red,aq }}^{\circ} \\
\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E_{\mathrm{E}_{\mathrm{red}}} \\
& (\mathrm{~V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\mathrm{red.aq}}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{ca}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}}(\mathrm{V} \text { vs } \\
& \mathrm{SHE} \\
& \hline
\end{aligned}
\] & \[
\begin{gathered}
\Delta G_{\text {red,aq }}^{\circ} \\
\left(\mathrm{k}_{\text {cal }} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}^{\circ}}(\mathrm{V} \text { vs } \\
& \text { SHE) }
\end{aligned}
\] & \\
\hline \multirow{10}{*}{Alkene} & \multirow{3}{*}{226} & \multirow{3}{*}{Trichloroethylene} & \multirow{3}{*}{\(\mathrm{ClCH}=\mathrm{CCl}_{2}\)} & \multirow{3}{*}{} & \[
\underset{\left[\mathrm{ClCH}=\mathrm{CCl}_{2}\right]^{-}}{\mathrm{ClCH}=\mathrm{CCl}_{2}+\mathrm{e}^{-}} \rightarrow
\] & -60.732 & \(-1.65^{\text {c }}\) & -- & -- & -- & -- & \multirow{3}{*}{\(8.28 \times 10^{10}\)} \\
\hline & & & & & \[
\begin{gathered}
\mathrm{ClCH}=\mathrm{CCl}_{2}+\mathrm{e}^{-} \rightarrow \\
{ }^{\circ} \mathrm{CH}=\mathrm{CCl}_{2}+\mathrm{Cl}^{-}
\end{gathered}
\] & -- & -- & -64.187 & \(-1.50^{\text {c }}\) & 21.118 & \(-5.20^{\text {c }}\) & \\
\hline & & & & & \[
\begin{aligned}
& \mathrm{ClCH}=\mathrm{CCl}_{2}+\mathrm{e}^{-} \rightarrow \mathrm{ClCH}=\mathrm{C}^{-} \mathrm{Cl} \\
&+\mathrm{Cl}^{-}
\end{aligned}
\] & -- & -- & -66.977 & \(-1.38^{\text {c }}\) & 18.451 & \(-5.08^{\text {c }}\) & \\
\hline & & & & \({ }^{C l}\) & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CCl}_{2}+\mathrm{e}^{-} \rightarrow\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CCl}_{2}\right]^{-}\) & -64.626 & \(-1.48^{\text {c }}\) & -- & -- & -- & -- & \\
\hline & & & &  & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CCl}_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{C}^{\cdot} \mathrm{Cl}+\mathrm{Cl}^{-}
\end{gathered}
\] & -- & -- & -67.503 & \(-1.35^{\text {c }}\) & 19.855 & \(-5.14^{\text {c }}\) & \\
\hline & 228 & 1,3-Butadiene & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}=\mathrm{CH}_{2}\) &  & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}=\mathrm{CH}_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}=\mathrm{CH}_{2}\right]^{-}}
\end{gathered}
\] & -42.651 & \(-2.43^{\text {b }}\) & -- & -- & -- & -- & \(1.19 \times 10^{10}\) \\
\hline & 229 & Acetaldehyde Oxime & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{NOH}\) &  & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{NOH}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{CH}_{3} \mathrm{CH}=\mathrm{NOH}\right]^{-}\) & -30.634 & \(-2.95{ }^{\text {b }}\) & -- & -- & -- & -- & \(7.22 \times 10^{7}\) \\
\hline & 230 & \begin{tabular}{l}
\(\mathrm{N}, \mathrm{N}-\) \\
Dimethylacrylamide
\end{tabular} & \(\mathrm{CH}_{2}=\mathrm{CHCON}\left(\mathrm{CH}_{3}\right)_{2}\) & & \[
\begin{gathered}
\mathrm{CH}_{2}=\mathrm{CHCON}\left(\mathrm{CH}_{3}\right)_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{eH}_{2}=\mathrm{CH}
\end{gathered}
\] & -51.043 & \(-2.07^{\text {b }}\) & -- & -- & -- & -- & \(4.51 \times 10^{10}\) \\
\hline & 231 & Methacrylamide & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{CONH}_{2}\) & & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{CONH}_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \cdot \mathrm{CO}(-) \mathrm{NH}_{2}
\end{gathered}
\] & -49.796 & \(-2.12^{\text {b }}\) & -- & -- & -- & -- & \(7.10 \times 10^{11}\) \\
\hline & 232 & Cyanoguanidine & \(\mathrm{NCN}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2}\) &  & \[
\begin{gathered}
\mathrm{NCN}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{NCN}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2}\right]^{-}-}
\end{gathered}
\] & -31.890 & \(-2.90^{\text {b }}\) & -- & -- & -- & -- & \(1.96 \times 10^{10}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No.} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{aligned}
& \Delta G_{\mathrm{cred.aq}}^{\mathrm{o}} \\
& \left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\text {Ered }}^{\circ} \\
& (\mathrm{V} v \mathrm{vs} \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{gathered}
\Delta G_{\text {red.aq }}^{\circ} \\
\left(\mathrm{k}_{\mathrm{cal}} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}}(\mathrm{Vvs} \\
& (\mathrm{V} \text { as } \\
& \hline
\end{aligned}
\] & \[
\begin{gathered}
\Delta G_{\text {red.aq }}^{\circ} \\
\left(\mathrm{k}_{\text {cal }} / \mathrm{mol}\right)
\end{gathered}
\] & \[
\begin{aligned}
& E_{\mathrm{C}_{\text {red }}} \\
& \text { (V vs } \\
& \text { SHE }
\end{aligned}
\] & \\
\hline \multirow{10}{*}{Alkene} & 233 & Tetracyanoethylene & \((\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}(\mathrm{CN})_{2}\) &  & \[
\begin{gathered}
(\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}(\mathrm{CN})_{2}+\mathrm{e}^{-} \rightarrow \\
{\left[(\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}(\mathrm{CN})_{2}\right]^{-}} \\
(\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}(\mathrm{CN})_{2}+\mathrm{e}^{-} \rightarrow \\
(\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}^{-} \mathrm{CN}+\mathrm{CN}^{-}
\end{gathered}
\] & -107.391
-- & \(0.38{ }^{\text {a }}\) & -- & -- & 36.901 & \(-5.88^{\text {c }}\) & \(3.74 \times 10^{10}\) \\
\hline & 234 & Methacrylate & \(\mathrm{CH}_{2}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COO}^{-}\) &  & \[
\begin{gathered}
\mathrm{CH}_{2}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{2}=\mathrm{C}\left(\mathrm{CH}_{3}\right)^{\circ} \mathrm{CO}(-) \mathrm{O}^{-}
\end{gathered}
\] & -49.796 & \(-2.12^{\text {b }}\) & -- & -- & -- & -- & \(4.50 \times 10^{9}\) \\
\hline & 235 & 3-Buten-1-ol & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\) & N & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{e}^{-} \rightarrow \\
{\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\right]^{-}}
\end{gathered}
\] & -22.989 & \(-3.28^{\text {b }}\) & -- & -- & -- & -- & \(2.45 \times 10^{6}\) \\
\hline & 236 & 3-Buten-2-OL & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}(\mathrm{OH}) \mathrm{CH}_{3}\) &  & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}(\mathrm{OH}) \mathrm{CH}_{3}+\mathrm{e}^{-} \rightarrow\) \(\left[\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}(\mathrm{OH}) \mathrm{CH}_{3}\right]^{-}\) & -26.409 & \(-3.13^{\text {b }}\) & -- & -- & -- & -- & \(5.91 \times 10^{7}\) \\
\hline & 237 & 3-Methylbut-2-enoate & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCO}_{2}{ }^{-}\) &  & \[
\begin{gathered}
\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCO}_{2}^{-}+\mathrm{e}^{-} \rightarrow \\
\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CH} \\
\hline
\end{gathered}
\] & -31.707 & \(-2.91^{\text {b }}\) & -- & -- & -- & -- & \(6.40 \times 10^{8}\) \\
\hline & 238 & 3,3-Dimethylacrylic acid & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCOOH}\) &  & \[
\underset{\left.\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCOOH}+\mathrm{e}_{3}-\mathrm{CH}\right)_{2} \mathrm{C}=\mathrm{CH} \mathrm{CO}(-) \mathrm{OH}}{(\rightarrow)}
\] & -50.403 & \(-2.09^{\text {b }}\) & -- & -- & -- & -- & \(2.53 \times 10^{10}\) \\
\hline & 239 & Isocrotonate & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCOO}^{-}\) &  & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCOO}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CH} \\
\hline
\end{gathered}
\] & -35.702 & \(-2.73^{\text {b }}\) & -- & -- & -- & -- & \(1.30 \times 10^{9}\) \\
\hline & 240 & Hydrogen Fumarate & HOOCCH=CHCOO &  & \[
\begin{gathered}
\mathrm{HOOCCH}=\mathrm{CHCOO}^{-}+\mathrm{e}^{-} \rightarrow \\
\mathrm{HO}(-) \mathrm{OC}^{-} \mathrm{CH}=\mathrm{CHCOO}
\end{gathered}
\] & -66.404 & \(-1.40^{\text {b }}\) & -- & -- & -- & -- & \(1.35 \times 10^{10}\) \\
\hline & 241 & Monomethyl Fumarate & \[
\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOO}
\] &  & \[
\underset{\left[\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOO}\right]^{-}}{\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOO}+\mathrm{e}^{-}} \rightarrow
\] & -64.429 & \(-1.49^{\text {b }}\) & -- & -- & -- & -- & \(1.30 \times 10^{10}\) \\
\hline & 242 & \[
\begin{gathered}
\text { 2-Hydroxyethyl } \\
\text { Acrylate }
\end{gathered}
\] & \[
\begin{gathered}
\mathrm{CH}_{2}=\mathrm{CHCOOCH} \\
\mathrm{H} \\
\mathrm{CH} \\
2
\end{gathered} \mathrm{O}
\] &  & \[
\begin{gathered}
\mathrm{CH}_{2}=\mathrm{CHCOOCH} \\
\mathrm{H}_{2} \mathrm{CH}_{2} \mathrm{OH}+\mathrm{e}^{-} \\
\mathrm{CH}_{2}=\mathrm{CH} \cdot \mathrm{CO}(-) \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{OH}
\end{gathered}
\] & -57.853 & \(-1.77^{\text {b }}\) & -- & -- & -- & -- & \(1.08 \times 10^{10}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{No} & \multirow[b]{2}{*}{Name} & \multirow[b]{2}{*}{Chemical Formula} & \multirow[b]{2}{*}{2D Chemical Structure \({ }^{\text {e }}\)} & \multirow[b]{2}{*}{Reduction Mechanism} & \multicolumn{2}{|l|}{Association} & \multicolumn{2}{|l|}{Concerted} & \multicolumn{2}{|l|}{Stepwise} & \multirow[b]{2}{*}{\[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\]} \\
\hline & & & & & & \[
\begin{aligned}
& \Delta G_{\text {red,aq }}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{ca}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\mathrm{E}_{\text {red }}} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G^{\text {red.aq }} \\
& \left(\mathrm{k}_{\text {cal }} \mathrm{mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{\text {}}^{E_{\text {red }}} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \[
\begin{aligned}
& \Delta G_{\mathrm{red}, \mathrm{aq}}^{\circ} \\
& \left(\mathrm{k}_{\mathrm{cal}} \mathrm{~mol}\right)
\end{aligned}
\] & \[
\begin{aligned}
& E_{E_{\text {red }}} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE}) \\
& \hline
\end{aligned}
\] & \\
\hline \multirow{9}{*}{Alkene} & 243 & trans-Aconitate(3-) & \[
\begin{gathered}
\mathrm{OOCCH}=\mathrm{C}(\mathrm{COO} \\
)^{-} \mathrm{CH}_{2} \mathrm{COO}^{-}
\end{gathered}
\] &  & \[
\begin{gathered}
\mathrm{OOCCH}^{\mathrm{OOC}\left(\mathrm{COO}^{-}\right) \mathrm{CH}_{2} \mathrm{COO}^{-}+} \\
\mathrm{e}^{-} \rightarrow \mathrm{OOCCH}=\mathrm{C}\left(\mathrm{COO}^{-}\right. \\
\left.\mathrm{OOH}_{2} \mathrm{COO}^{-}\right]^{-}
\end{gathered}
\] & -45.032 & \(-2.33^{\text {b }}\) & -- & -- & -- & -- & \(1.80 \times 10^{8}\) \\
\hline & 244 & Acrylamide & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCONH}_{2}\) &  & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCONH}_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}^{\circ} \mathrm{CO}(-) \mathrm{NH}_{2}
\end{gathered}
\] & -51.891 & \(-2.03^{\text {b }}\) & -- & -- & -- & -- & \(3.81 \times 10^{11}\) \\
\hline & 245 & Crotonamide & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCONH}_{2}\) &  & \[
\begin{gathered}
\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCONH}_{2}+\mathrm{e}^{-} \rightarrow \\
\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CH} \\
\hline
\end{gathered}
\] & -47.616 & \(-2.22^{\text {b }}\) & -- & -- & -- & -- & \(2.75 \times 10^{10}\) \\
\hline & 246 & 4-(Ethylamino)-4-oxobut-2-enoate & \multicolumn{3}{|l|}{} & -56.866 & \(-1.81{ }^{\text {b }}\) & -- & -- & -- & -- & \(8.50 \times 10^{9}\) \\
\hline & \multicolumn{2}{|l|}{247 cis-Dimethyl Fumarate} & \[
\underset{\mathrm{CH}_{3}}{\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOO}}
\] & & \(\underset{\rightarrow \mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CH}}{\mathrm{CH}} \mathrm{CO}(-) \mathrm{OCH}_{3}\) & -73.513 & \(-1.09^{\text {b }}\) & -- & -- & -- & -- & \(3.20 \times 10^{10}\) \\
\hline & 248 & 4-Penten-2-OL & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{C} \\
\mathrm{H}_{3}
\end{gathered}
\] & \multicolumn{2}{|l|}{} & -21.903 & \(-3.33^{\text {b }}\) & -- & -- & -- & -- & \(5.00 \times 10^{5}\) \\
\hline & 249 & Guanidine & \(\mathrm{H}_{2} \mathrm{NC}(=\mathrm{NH}) \mathrm{NH}_{2}\) &  & \[
\underset{\mathrm{H}_{2} \mathrm{NC}\left(=\mathrm{NH}_{2} \mathrm{NH} \mathrm{NH}_{2}+\mathrm{e}^{-} \rightarrow\right.}{\left.[\mathrm{NH}) \mathrm{NH}_{2}\right]^{\circ}} \rightarrow
\] & -4.978 & \(-4.06^{\text {b }}\) & -- & -- & -- & -- & \(2.02 \times 10^{8}\) \\
\hline & 250 & Ethyl Acrylate & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOC}_{2} \mathrm{H}_{5}\) &  & \[
\begin{gathered}
\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOC}_{2} \mathrm{H}_{5}+\mathrm{e}^{-} \rightarrow \\
\mathrm{H}_{2} \mathrm{C}=\mathrm{CH} \cdot \mathrm{CO}(-) \mathrm{OC}_{2} \mathrm{H}_{5}
\end{gathered}
\] & -57.326 & \(-1.79^{\text {b }}\) & -- & -- & -- & -- & \(1.34 \times 10^{10}\) \\
\hline & 25 & Acetone Oxime & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{NOH}\) &  & \[
\underset{\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{NOH}\right]}{\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{NOH}+\mathrm{e}^{-} \rightarrow}
\] & -25.737 & \(-3.16^{\text {b }}\) & -- & -- & -- & -- & \(3.29 \times 10^{8}\) \\
\hline
\end{tabular}
\({ }^{\text {a }}\) M06-2X/cc-pVDZ
\({ }^{\mathrm{b}}\) structural optimization with M06-2X/cc-pVDZ and single point energy calculation with M06-2X/Aug-cc-pVTZ
'M06-2X/Aug-cc-pVTZ
\({ }^{\text {d}}\) M06-2X/LANL2DZ
\({ }^{\text {e}}\) All 2D chemical structures drawn using ChemDraw Professional 16.0 software

Table A.5. Corrected experimental \(k_{\text {chem }}\) and calculated \(E_{\text {red,aq }}^{\circ}\) overall results for dataset
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline & Class & No. & Name & Chemical Formula & Molar
Volume, \(V_{\mathrm{b}}\)
\(\left(\mathrm{cm}^{3} /\right.\)
\(\mathrm{mol})\) & Diffusion Coefficient, \(D_{1}\) ( \(\mathrm{cm}^{2} / \mathrm{s}\) ) & \[
\begin{gathered}
k_{\mathrm{D}} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \(\ln k_{\text {chem }}\) & \[
\underset{(\mathrm{kcal} / \mathrm{mol})}{\Delta G^{\mathrm{r}}{ }^{\mathrm{of}} \mathrm{maq}}
\] & \[
\begin{aligned}
& E_{\text {red }}^{\circ} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE})
\end{aligned}
\] & \[
\begin{gathered}
\text { Upper Limit } \\
k_{\text {exp }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \[
\begin{gathered}
\text { ower Limit } \\
k_{\text {exp }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] \\
\hline & \multirow{3}{*}{Alkane} & 1 & Methane & \(\mathrm{CH}_{4}\) & 22.8 & \(7.31 \times 10^{-5}\) & \(2.49 \times 10^{10}\) & \(1.00 \times 10^{7}\) & 16.12 & 25.97 & -5.41 & N/A & N/A \\
\hline & & 2 & Propane & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{3}\) & 40.4 & \(6.62 \times 10^{-5}\) & \(2.44 \times 10^{10}\) & \(2.10 \times 10^{6}\) & 14.56 & 23.74 & -5.31 & N/A & N/A \\
\hline & & 3 & Butane & \(\mathrm{C}_{4} \mathrm{H}_{10}\) & 57.3 & \(6.30 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(2.40 \times 10^{6}\) & 14.69 & 22.77 & -5.27 & N/A & N/A \\
\hline & \multirow{13}{*}{Carboxylate} & 4 & Oxalate & \(\mathrm{OOCCOO}^{-}\) & 46.8 & \(7.34 \times 10^{-5}\) & \(2.77 \times 10^{10}\) & \(2.28 \times 10^{7}\) & 16.94 & -29.94 & -2.98 & \(4.60 \times 10^{7}\) & \(1.00 \times 10^{7}\) \\
\hline & & 5 & Formate & \(\mathrm{HCOO}^{-}\) & 38.5 & \(7.41 \times 10^{-5}\) & \(2.72 \times 10^{10}\) & \(5.04 \times 10^{5}\) & 13.13 & -9.93 & -3.85 & \(1.00 \times 10^{6}\) & \(8.00 \times 10^{3}\) \\
\hline & & 6 & Succinate & \(\mathrm{OOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\) & 72.0 & \(6.91 \times 10^{-5}\) & \(2.79 \times 10^{10}\) & \(1.59 \times 10^{7}\) & 16.58 & -8.72 & -3.90 & \(3.10 \times 10^{7}\) & \(7.00 \times 10^{5}\) \\
\hline & & 7 & Acetate & \(\mathrm{CH}_{3} \mathrm{COO}^{-}\) & 45.9 & \(6.85 \times 10^{-5}\) & \(2.58 \times 10^{10}\) & \(1.05 \times 10^{6}\) & 13.86 & -8.07 & -3.93 & \(1.10 \times 10^{6}\) & \(1.00 \times 10^{6}\) \\
\hline & & 8 & Hydrogen Oxalate & \(\mathrm{HOOCCOO}^{-}\) & 46.6 & \(6.82 \times 10^{-5}\) & \(2.57 \times 10^{10}\) & \(3.65 \times 10^{9}\) & 22.02 & -52.21 & -2.02 & N/A & N/A \\
\hline & & 9 & Malonate & OOC- \(\mathrm{CH}_{2}-\mathrm{COO}^{-}\) & 79.6 & \(7.05 \times 10^{-5}\) & \(2.89 \times 10^{10}\) & \(1.00 \times 10^{7}\) & 16.12 & -9.07 & -3.89 & N/A & N/A \\
\hline & & 10 & Malonate(1-) & \(\mathrm{HOOC}-\mathrm{CH}_{2}-\mathrm{COO}^{-}\) & 68.4 & -- & -- \({ }^{\text {a }}\) & \(5.06 \times 10^{8}\) & 20.04 & -35.93 & -2.72 & \(7.00 \times 10^{8}\) & \(4.00 \times 10^{8}\) \\
\hline & & 11 & Succinate(1-) & \(\mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\) & 86.8 & -- & -- \({ }^{a}\) & \(2.05 \times 10^{8}\) & 19.14 & -32.74 & -2.86 & \(3.40 \times 10^{8}\) & \(7.00 \times 10^{7}\) \\
\hline & & 12 & Lactate & \(\mathrm{CH}_{3} \mathrm{CHOHCOO}^{-}\) & 60.8 & \(6.76 \times 10^{-5}\) & \(2.65 \times 10^{10}\) & \(1.00 \times 10^{7}\) & 16.12 & -5.70 & -4.03 & N/A & N/A \\
\hline & & 13 & Glycolate & \(\mathrm{HOCH}_{2} \mathrm{COO}^{-}\) & 47.9 & -- & -- \({ }^{\text {a }}\) & \(8.20 \times 10^{6}\) & 15.92 & -6.61 & -3.99 & N/A & N/A \\
\hline & & 14 & Pyruvate & \(\mathrm{CH}_{3} \mathrm{COCOO}^{-}\) & 61.5 & -- & -- \({ }^{\text {a }}\) & \(6.80 \times 10^{9}\) & 22.64 & -50.94 & -2.07 & N/A & N/A \\
\hline & & 15 & CID_4134252 & \(\mathrm{HOCH}_{2}(\mathrm{CHOH})_{4} \mathrm{COO}^{-}\) & 145.8 & -- & -- \({ }^{a}\) & \(1.00 \times 10^{6}\) & 13.82 & -13.59 & -3.69 & N/A & N/A \\
\hline & & 16 & Malate & \(\mathrm{OOCCH}_{2} \mathrm{CHOHCOO}^{-}\) & 84.1 & \(6.91 \times 10^{-5}\) & \(2.86 \times 10^{10}\) & \(6.01 \times 10^{7}\) & 17.91 & -11.81 & -3.77 & N/A & N/A \\
\hline & \multirow{9}{*}{Carboxylic Acid} & 17 & Oxalic Acid & HOOCCOOH & 57.9 & \(6.29 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(2.50 \times 10^{10}\) & \(23.94{ }^{\text {b }}\) & -62.94 & -1.55 & N/A & N/A \\
\hline & & 18 & Formic Acid & HCOOH & 28.1 & \(7.02 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(1.41 \times 10^{8}\) & 18.76 & -39.00 & -2.59 & N/A & N/A \\
\hline & & 19 & Succinic Acid & \(\mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COOH}\) & 98.0 & \(5.92 \times 10^{-5}\) & \(2.51 \times 10^{10}\) & \(2.30 \times 10^{8}\) & 19.25 & -35.30 & -2.75 & \(3.70 \times 10^{8}\) & \(8.60 \times 10^{7}\) \\
\hline & & 20 & Propionic Acid & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}\) & 64.9 & \(6.20 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(2.20 \times 10^{7}\) & 16.91 & -35.03 & -2.76 & N/A & N/A \\
\hline & & 21 & Acetic Acid & \(\mathrm{CH}_{3} \mathrm{COOH}\) & 50.2 & \(6.41 \times 10^{-5}\) & \(2.44 \times 10^{10}\) & \(2.02 \times 10^{8}\) & 19.12 & -32.16 & -2.89 & \(2.20 \times 10^{8}\) & \(1.80 \times 10^{8}\) \\
\hline & & 22 & Malonic Acid & \(\mathrm{HOOC}-\mathrm{CH}_{2}-\mathrm{COOH}\) & 55.8 & \(6.32 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(3.03 \times 10^{9}\) & 21.83 & -40.83 & -2.51 & \(5.00 \times 10^{9}\) & \(1.50 \times 10^{9}\) \\
\hline & & 23 & Lactic Acid & \(\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{COOH}\) & 60.2 & \(6.26 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(7.36 \times 10^{8}\) & 20.42 & -38.23 & -2.62 & \(8.00 \times 10^{8}\) & \(6.30 \times 10^{8}\) \\
\hline & & 24 & Malic Acid & \(\mathrm{HOOCCH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{COOH}\) & 77.8 & \(6.07 \times 10^{-5}\) & \(2.48 \times 10^{10}\) & \(3.41 \times 10^{9}\) & 21.95 & -41.24 & -2.49 & N/A & N/A \\
\hline & & 25 & Glycolic acid & \(\mathrm{HOCH}_{2} \mathrm{COOH}\) & 48.7 & \(6.44 \times 10^{-5}\) & \(2.44 \times 10^{10}\) & \(4.38 \times 10^{8}\) & 19.90 & -40.42 & -2.53 & N/A & N/A \\
\hline & \multirow{4}{*}{Alcohol} & 26 & Methanediol & \(\mathrm{CH}_{2}(\mathrm{OH})_{2}\) & 32.4 & \(6.86 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(1.00 \times 10^{7}\) & 16.12 & -13.52 & -3.69 & N/A & N/A \\
\hline & & 27 & Tert-Butanol & \(\left(\mathrm{CH}_{3}\right)_{3}-\mathrm{C}-\mathrm{OH}\) & 71.7 & \(6.12 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(4.00 \times 10^{5}\) & 12.90 & -6.33 & -4.01 & N/A & N/A \\
\hline & & 28 & Butane-1,2,3,4 & \(\mathrm{HOCH}_{2}[\mathrm{CH}(\mathrm{OH})]_{2} \mathrm{CH}_{2} \mathrm{OH}\) & 81.5 & \(6.04 \times 10^{-5}\) & \(2.48 \times 10^{10}\) & \(5.00 \times 10^{6}\) & 15.43 & -11.50 & -3.78 & N/A & N/A \\
\hline & & 29 & Mannitol & \(\mathrm{HOCH}_{2}[\mathrm{CH}(\mathrm{OH})]_{4} \mathrm{CH}_{2} \mathrm{OH}\) & 132.4 & \(5.75 \times 10^{-5}\) & \(2.57 \times 10^{10}\) & \(8.50 \times 10^{6}\) & 15.96 & -16.74 & -3.55 & \(1.00 \times 10^{7}\) & \(7.00 \times 10^{6}\) \\
\hline & \multirow{7}{*}{Ester} & 30 & Methyl Acetate & \(\mathrm{CH}_{3} \mathrm{COOCH}_{3}\) & 63.2 & \(6.22 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(8.73 \times 10^{7}\) & 18.28 & -33.56 & -2.82 & N/A & N/A \\
\hline & & 31 & Methyl Propionate & \(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOCH}_{3}\) & 67.5 & \(6.17 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(9.03 \times 10^{7}\) & 18.32 & -33.24 & -2.84 & N/A & N/A \\
\hline & & 32 & Ethyl Propionate & \(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOC}_{2} \mathrm{H}_{5}\) & 97.9 & \(5.92 \times 10^{-5}\) & \(2.51 \times 10^{10}\) & \(7.52 \times 10^{7}\) & 18.14 & -33.22 & -2.84 & N/A & N/A \\
\hline & & 33 & Dimethyl Oxalate & \(\mathrm{CH}_{3} \mathrm{OOCCOOCH}_{3}\) & 76.4 & \(6.08 \times 10^{-5}\) & \(2.48 \times 10^{10}\) & \(1.04 \times 10^{11}\) & 25.37 & -59.03 & -1.72 & N/A & N/A \\
\hline & & 34 & Tert-butyl Acetate & \(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CCOOCH}_{3}\) & 90.5 & \(5.97 \times 10^{-5}\) & \(2.50 \times 10^{10}\) & \(2.30 \times 10^{7}\) & 16.95 & -30.20 & -2.97 & N/A & N/A \\
\hline & & 35 & 2-Hydroxyethyl Acetate & \(\mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\) & 90.4 & \(5.97 \times 10^{-5}\) & \(2.50 \times 10^{10}\) & \(2.60 \times 10^{7}\) & 17.07 & -33.27 & -2.84 & N/A & N/A \\
\hline & & \(\underline{\underline{36}}\) & Di-tert-butyl Peroxide & \(\left(\mathrm{CH}_{3}\right)_{3}-\mathrm{COOC}\left(\mathrm{CH}_{3}\right)_{3}\) & \(\underline{117.4}\) & \(\underline{\underline{5.82 \times 10^{-5}}}\) & \(\underline{\underline{2.55 \times 10^{10}}}\) & \(\underline{1.41 \times 10^{8}}\) & \(\underline{18.76}\) & \(\underline{44.93}\) & \(\underline{-6.23}\) & N/A & N/A \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline & Class & No. & Name & Chemical Formula & Molar
Volume, \(V_{\mathrm{b}}\)
\(\left(\mathrm{cm}^{3} /\right.\)
\(\mathrm{mol})\) & Diffusion
Coefficient, \(D_{1}\)
\(\left(\mathrm{~cm}^{2} / \mathrm{s}\right)\) & \[
\begin{gathered}
k_{\mathrm{D}} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \(\ln k_{\text {chem }}\) & \[
\begin{gathered}
\Delta G^{\circ}{ }_{(\mathrm{red}, \mathrm{aq}} \\
(\mathrm{kcal} / \mathrm{mol})
\end{gathered}
\] & \[
\begin{gathered}
E_{\text {red }}^{\circ} \\
(\mathrm{V} \text { vs } \\
\mathrm{SHE})
\end{gathered}
\] & \[
\begin{gathered}
\text { Upper Limit } \\
k_{\text {exp }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \[
\begin{gathered}
\text { Lower Limit } \\
k_{\text {exp }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] \\
\hline \multicolumn{2}{|r|}{\multirow{5}{*}{Ester}} & 37 & Methylene glycol monoacetate & \(\mathrm{HOCH}_{2} \mathrm{COOCH}_{3}\) & 59.5 & \(6.27 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(4.90 \times 10^{8}\) & 20.01 & -37.37 & -2.66 & N/A & N/A \\
\hline & & 38 & Methyl methoxyacetate & \(\mathrm{CH}_{3} \mathrm{OCH}_{2} \mathrm{COOCH}_{3}\) & 68.3 & \(6.16 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(4.48 \times 10^{8}\) & 19.92 & -38.04 & -2.63 & N/A & N/A \\
\hline & & 39 & Methyl trifluoroacetate & \(\mathrm{CF}_{3} \mathrm{COOCH}_{3}\) & 62.0 & \(6.23 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(2.06 \times 10^{9}\) & 21.45 & -55.22 & -1.89 & N/A & N/A \\
\hline & & 40 & Ethyl glycinate & \(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{COOC}_{2} \mathrm{H}_{5}\) & 93.9 & \(5.94 \times 10^{-5}\) & \(2.51 \times 10^{10}\) & \(8.58 \times 10^{8}\) & 20.57 & -34.86 & -2.77 & N/A & N/A \\
\hline & & 41 & Acetoxymethylamine & \(\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{COOCH}_{3}\) & 60.7 & \(6.25 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(3.14 \times 10^{8}\) & 19.56 & -32.45 & -2.87 & \(3.30 \times 10^{8}\) & \(2.90 \times 10^{8}\) \\
\hline & Ether & 42 & Diethyl Ether & \(\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{O}\) & 74.8 & \(\underline{6.09 \times 10^{-5}}\) & \(2.47 \times 10^{10}\) & \(1.00 \times 10^{7}\) & 16.12 & -38.95 & -2.59 & N/A & N/A \\
\hline \multicolumn{2}{|r|}{\multirow{4}{*}{Ketone}} & 43 & Acetone & \(\mathrm{CH}_{3} \mathrm{COCH}_{3}\) & 49.1 & \(6.43 \times 10^{-5}\) & \(2.44 \times 10^{10}\) & \(8.90 \times 10^{9}\) & 22.91 & -38.95 & -2.59 & \(8.00 \times 10^{9}\) & \(5.20 \times 10^{9}\) \\
\hline & & 44 & Methyl Ethyl Ketone & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COCH}_{3}\) & 72.3 & \(6.12 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(6.11 \times 10^{9}\) & 22.53 & -38.72 & -2.60 & N/A & N/A \\
\hline & & 45 & 2,3-Butanedione & \(\mathrm{CH}_{3} \mathrm{COCOCH}_{3}\) & 60.9 & \(6.25 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(1.67 \times 10^{10}\) & 23.54 & -69.05 & -1.29 & \(1.00 \times 10^{10}\) & \(9.90 \times 10^{9}\) \\
\hline & & 46 & Acetoin & \(\mathrm{CH}_{3} \mathrm{COCH}(\mathrm{OH}) \mathrm{CH}_{3}\) & 57.2 & \(6.30 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(7.95 \times 10^{9}\) & 22.80 & -43.76 & -2.38 & N/A & N/A \\
\hline \multicolumn{2}{|r|}{\multirow[b]{2}{*}{Aldehyde}} & 47 & Acetaldehyde & \[
\mathrm{CH}_{3} \mathrm{CHO}
\] & 26.5 & \(7.10 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(6.11 \times 10^{9}\) & 22.53 & -44.97 & -2.33 & \(5.40 \times 10^{9}\) & \(4.40 \times 10^{9}\) \\
\hline & & 48 & Propionaldehyde & \[
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHO}
\] & 60.7 & \(6.25 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(4.43 \times 10^{9}\) & 22.21 & -44.42 & -2.35 & \(4.10 \times 10^{9}\) & \(3.40 \times 10^{9}\) \\
\hline \multicolumn{2}{|r|}{\multirow{11}{*}{\[
\begin{gathered}
\text { Halocarbox- } \\
\text { ylate }
\end{gathered}
\]}} & 49 & Chloroacetate & \(\mathrm{ClCH}_{2} \mathrm{COO}^{-}\) & 59.3 & \(6.90 \times 10^{-5}\) & \(2.70 \times 10^{10}\) & \(1.09 \times 10^{9}\) & 20.81 & 10.40 & -4.73 & \(1.20 \times 10^{9}\) & \(8.90 \times 10^{8}\) \\
\hline & & 50 & 3-Chloropropanoate & \(\mathrm{Cl}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\) & 63.5 & -- & -- \({ }^{\text {a }}\) & \(4.40 \times 10^{8}\) & 19.90 & 12.92 & -4.84 & N/A & N/A \\
\hline & & 51 & Bromoacetate & \(\mathrm{BrCH}_{2} \mathrm{COO}^{-}\) & 69.2 & \(6.78 \times 10^{-5}\) & \(2.72 \times 10^{10}\) & \(8.03 \times 10^{9}\) & 22.81 & 11.54 & -4.78 & N/A & N/A \\
\hline & & 52 & 3-Bromopropanoate & \(\mathrm{Br}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\) & 93.2 & -- & -- \({ }^{\text {a }}\) & \(2.70 \times 10^{9}\) & 21.72 & 15.24 & -4.94 & N/A & N/A \\
\hline & & 53 & Fluoroacetate & \(\mathrm{FCH}_{2} \mathrm{COO}^{-}\) & 44.7 & \(6.99 \times 10^{-5}\) & \(2.62 \times 10^{10}\) & \(1.20 \times 10^{6}\) & 14.00 & 66.82 & -7.18 & N/A & \(N / A\) \\
\hline & & 54 & 2-Bromopropanoate & \(\mathrm{CH}_{3} \mathrm{CHBrCOO}^{-}\) & 111.3 & -- & -- \({ }^{\text {a }}\) & \(5.30 \times 10^{9}\) & 22.39 & 6.18 & -4.55 & \(N / A\) & \(N / A\) \\
\hline & & 55 & 2-Chloropropanoate & \(\mathrm{CH}_{3} \mathrm{CHClCOO}^{-}\) & 78.6 & -- & -- \({ }^{\text {a }}\) & \(1.40 \times 10^{9}\) & 21.06 & 5.26 & -4.51 & \(N / A\) & \(N / A\) \\
\hline & & 56 & Trichloroacetate & \(\mathrm{Cl}_{3} \mathrm{CCOO}-\) & 98.1 & \(6.59 \times 10^{-5}\) & \(2.80 \times 10^{10}\) & \(1.22 \times 10^{10}\) & 23.23 & 1.91 & -4.36 & \(N / A\) & \(N / A\) \\
\hline & & 57 & 2-Iodoacetate & \(\mathrm{ICH}_{2} \mathrm{COO}-\) & 75.2 & -- & -- \({ }^{\text {a }}\) & \(1.20 \times 10^{10}\) & 23.21 & 5.89 & -4.54 & \(N / A\) & \(N / A\) \\
\hline & & 58 & 2-Iodopropanoate & \(\mathrm{CH}_{3} \mathrm{CHICOO}^{-}\) & 102.0 & -- & -- \({ }^{\text {a }}\) & \(6.60 \times 10^{9}\) & 22.61 & -1.08 & -4.23 & N/A & N/A \\
\hline & & 59 & 3-Iodanylpropanoate & \(\mathrm{ICH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}\) & 76.9 & -- & -- \({ }^{\text {a }}\) & \(5.80 \times 10^{9}\) & 22.48 & 6.46 & -4.56 & N/A & N/A \\
\hline & \multirow{16}{*}{Haloalkane} & 60 & Chloromethane & \(\mathrm{CH}_{3} \mathrm{Cl}\) & 38.0 & \(6.68 \times 10^{-5}\) & \(\underline{2.44 \times 10^{10}}\) & \(8.33 \times 10^{8}\) & 20.54 & -69.84 & -1.25 & \(\underline{1.20 \times 10^{9}}\) & \(4.60 \times 10^{8}\) \\
\hline & & \(\underline{61}\) & Dibromomethane & \(\mathrm{CH}_{2} \mathrm{Br}_{2}\) & 51.1 & \(\underline{6.39 \times 10^{-5}}\) & \(2.44 \times 10^{10}\) & \(\underline{1.10 \times 10^{11}}\) & 25.42 & -73.00 & -1.11 & N/A & N/A \\
\hline & & \(\underline{62}\) & Bromoform & \(\mathrm{CHBr}_{3}\) & \(\underline{84.6}\) & \(\underline{6.01 \times 10^{-5}}\) & \(\underline{2.49 \times 10^{10}}\) & \(\underline{1.67 \times 10^{10}}\) & \(\underline{23.54}\) & -80.06 & -0.81 & N/A & N/A \\
\hline & & 63 & Bromoethane & \(\mathrm{CH}_{3} \mathrm{CH}_{2}-\underline{\mathrm{Br}}\) & \(\underline{51.1}\) & \(\underline{6.40 \times 10^{-5}}\) & \(\underline{2.44 \times 10^{10}}\) & \(\underline{1.89 \times 10^{10}}\) & \(\underline{23.66}\) & -67.93 & -1.33 & \(1.20 \times 10^{10}\) & \(8.00 \times 10^{9}\) \\
\hline & & 64 & Bromopropane & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Br}\) & 86.9 & \(\underline{5.99 \times 10^{-5}}\) & \(\underline{2.49 \times 10^{10}}\) & \(\underline{1.47 \times 10^{10}}\) & 23.41 & -67.55 & -1.35 & \(\underline{1.00 \times 10^{10}}\) & \(8.50 \times 10^{9}\) \\
\hline & & 65 & Chloropropane & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \underline{\mathrm{Cl}}\) & \(\underline{67.3}\) & \(\underline{6.17 \times 10^{-5}}\) & \(\underline{2.46 \times 10^{10}}\) & \(\underline{6.85 \times 10^{8}}\) & \(\underline{20.35}\) & -70.86 & -1.21 & \(\underline{6.90 \times 10^{8}}\) & \(6.20 \times 10^{8}\) \\
\hline & & \(\underline{66}\) & Chloroethane & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \underline{\mathrm{Cl}}\) & \(\underline{61.3}\) & \(\underline{6.24 \times 10^{-5}}\) & \(\underline{2.45 \times 10^{10}}\) & \(\underline{7.21 \times 10^{8}}\) & \(\underline{20.40}\) & -71.03 & -1.20 & N/A & N/A \\
\hline & & \(\underline{67}\) & 1-Bromo-2-chloroethane & \(\mathrm{CH}_{2} \mathrm{ClCH}_{2} \mathrm{Br}\) & 68.8 & \(\underline{6.15 \times 10^{-5}}\) & \(\underline{2.46 \times 10^{10}}\) & \(\underline{1.18 \times 10^{10}}\) & 23.20 & -70.61 & -1.22 & N/A & N/A \\
\hline & & \(\underline{68}\) & Halothane & \(\mathrm{CF}_{3} \mathrm{CHClBr}\) & \(\underline{76.5}\) & \(\underline{6.08 \times 10^{-5}}\) & \(\underline{2.48 \times 10^{10}}\) & \(\underline{3.22 \times 10^{10}}\) & \(\underline{24.20}\) & -79.44 & -0.84 & N/A & N/A \\
\hline & & \(\underline{69}\) & 1,1-Dichloroethane & \(\mathrm{CH}_{3} \underline{\mathrm{CHCl}}_{2}\) & \(\underline{54.4}\) & \(\underline{6.34 \times 10^{-5}}\) & \(\underline{2.45 \times 10^{10}}\) & \(\frac{1.42 \times 10^{10}}{3.40 \times 10^{10}}\) & \(\underline{23.38}\) & -77.00 & -0.94 & N/A & N/A \\
\hline & & 70 & Diiodomethane & \(\mathrm{CH}_{2} \underline{I}_{2}\) & \(\underline{60.8}\) & \(\underline{6.25 \times 10^{-5}}\) & \(2.45 \times 10^{10}\) & \(3.40 \times 10^{10}\) & \(24.25{ }^{\text {b }}\) & \(\underline{-80.13}\) & -0.81 & N/A & N/A \\
\hline & & \(\underline{71}\) & Iodoethane & \(\mathrm{CH}_{3} \mathrm{CH}_{2}\) & \(\underline{64.1}\) & \(\underline{6.21 \times 10^{-5}}\) & \(\underline{2.46 \times 10^{10}}\) & \(3.85 \times 10^{10}\) & \(\underline{24.37}\) & -75.94 & -0.99 & N/A & N/A \\
\hline & & \(\frac{72}{7}\) & Dichloromethane & \(\mathrm{CH}_{2} \mathrm{Cl}_{2}\) & \(\underline{56.8}\) & \(\underline{6.30 \times 10^{-5}}\) & \(\underline{2.45 \times 10^{10}}\) & \(\underline{7.95 \times 10^{9}}\) & \(\underline{22.80}\) & -75.69 & -1.00 & N/A & N/A \\
\hline & & 73 & Chloroform & \(\mathrm{CHCl}_{3}\) & \(\underline{83.6}\) & \(\underline{6.02 \times 10^{-5}}\) & \(\underline{2.49 \times 10^{10}}\) & \(3.00 \times 10^{10}\) & \(24.12^{\text {b }}\) & \(\underline{-81.97}\) & -0.73 & N/A & N/A \\
\hline & & \(\underline{74}\) & Trichlorofluoromethane & \(\mathrm{CCl}_{3} \mathrm{~F}\) & \(\underline{60.5}\) & \(\underline{6.25 \times 10^{-5}}\) & \(\underline{2.45 \times 10^{10}}\) & \(\underline{4.60 \times 10^{10}}\) & \(\underline{24.55}\) & \(\underline{-82.75}\) & -0.69 & N/A & N/A \\
\hline & & 75 & Dichlorodifluoromethane & \(\mathrm{CF}_{2} \mathrm{Cl}_{2}\) & 42.2 & \(\underline{6.57 \times 10^{-5}}\) & \(\underline{2.44 \times 10^{10}}\) & \(\underline{3.28 \times 10^{10}}\) & \(\underline{24.21}\) & \(\underline{-77.16}\) & \(\underline{-0.93}\) & N/A & N/A \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline & Class & No. & Name & Chemical Formula & Molar
Volume, \(V_{\mathrm{b}}\)
\(\left(\mathrm{cm}^{3} /\right.\)
\(\mathrm{mol})\) & \[
\begin{aligned}
& \text { Diffusion } \\
& \text { Coefficient, } D_{1} \\
& \left(\mathrm{~cm}^{2} / \mathrm{s}\right)
\end{aligned}
\] & \[
\begin{gathered}
k_{\mathrm{D}} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \(\ln k_{\text {chem }}\) & \[
\begin{gathered}
\Delta G_{\mathrm{redaq}}^{\circ} \\
(\mathrm{kcal} / \mathrm{mol})
\end{gathered}
\] & \[
\begin{aligned}
& E_{\text {red }}^{\circ} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE})
\end{aligned}
\] & \[
\begin{gathered}
\text { Upper Limit } \\
k_{\text {exp }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \[
\begin{gathered}
\text { Lower Limit } \\
k_{\text {exp }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] \\
\hline & \multirow{21}{*}{Haloalkane} & 76 & Chlorotrifluoromethane & \(\mathrm{CClF}_{3}\) & 55.7 & \(6.32 \times 10^{-5}\) & \(\underline{2.45 \times 10^{10}}\) & \(5.36 \times 10^{9}\) & \(\underline{22.40}\) & -71.19 & -1.19 & N/A & N/A \\
\hline & & \(\underline{77}\) & Bromotrifluoromethane & \(\mathrm{CF}_{3} \underline{\underline{B r}}\) & 39.7 & \(\underline{6.63 \times 10^{-5}}\) & \(\underline{2.44 \times 10^{10}}\) & \(3.93 \times 10^{11}\) & \(\underline{26.70}\) & -70.32 & -1.23 & N/A & N/A \\
\hline & & \(\underline{78}\) & Carbon Tetrachloride & \(\mathrm{CCl}_{4}\) & 74.4 & \(\underline{6.10 \times 10^{-5}}\) & \(\underline{2.47 \times 10^{10}}\) & \(\underline{7.61 \times 10^{10}}\) & \(\underline{25.06}\) & -91.15 & -0.33 & \(\underline{2.40 \times 10^{10}}\) & \(\underline{1.30 \times 10^{10}}\) \\
\hline & & \(\underline{79}\) & Chlorodifluoromethane & \(\mathrm{CHClF}_{2}\) & 48.9 & \(\underline{6.43 \times 10^{-5}}\) & \(\underline{2.44 \times 10^{10}}\) & \(3.29 \times 10^{9}\) & \(\underline{21.91}\) & -70.22 & -1.24 & N/A & N/A \\
\hline & & \(\underline{80}\) & 1,1,2-Trichloroethane & \(\mathrm{ClCH}_{2} \mathrm{CHCl}_{2}\) & 78.6 & \(\underline{6.06 \times 10^{-5}}\) & \(\underline{2.48 \times 10^{10}}\) & \(\underline{1.27 \times 10^{10}}\) & \(\underline{23.27}\) & -75.17 & -1.02 & N/A & N/A \\
\hline & & \(\underline{81}\) & 1,1,1-Trichloroethane & \(\mathrm{CH}_{3} \mathrm{CCl}_{3}\) & \(\underline{73.7}\) & \(\underline{6.10 \times 10^{-5}}\) & \(\underline{2.47 \times 10^{10}}\) & \(\underline{9.24 \times 10^{10}}\) & \(\underline{25.25}\) & \(\underline{-84.09}\) & \(\underline{-0.63}\) & \(\underline{2.50 \times 10^{10}}\) & \(\underline{1.40 \times 10^{10}}\) \\
\hline & & \(\underline{82}\) & Hexachloroethane & \(\mathrm{CCl}_{3} \mathrm{CCl}_{3}\) & \(\underline{115.4}\) & \(\underline{5.82 \times 10^{-5}}\) & \(\underline{2.54 \times 10^{10}}\) & \(3.90 \times 10^{10}\) & \(\underline{24.39}^{\text {b }}\) & \(\underline{-89.80}\) & \(\underline{-0.39}\) & N/A & N/A \\
\hline & & \(\underline{83}\) & 2-Chlorobutane & \(\mathrm{C}_{2} \underline{H}_{5} \mathrm{CH}(\mathrm{Cl}) \mathrm{CH}_{3}\) & 65.7 & \(\underline{6.19 \times 10^{-5}}\) & \(\underline{2.46 \times 10^{10}}\) & \(5.21 \times 10^{8}\) & \(\underline{20.07}\) & -71.79 & -1.17 & N/A & N/A \\
\hline & & \(\underline{84}\) & 1,2-Dibromoethane & \(\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{Br}\) & \(\underline{76.2}\) & \(\underline{6.08 \times 10^{-5}}\) & \(\underline{2.48 \times 10^{10}}\) & \(\underline{2.74 \times 10^{10}}\) & \(\underline{24.03}\) & -72.81 & -1.12 & \(1.40 \times 10^{10}\) & \(\underline{1.20 \times 10^{10}}\) \\
\hline & & \(\underline{85}\) & 1,2-Dichloroethane & \(\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathrm{Cl}\) & 66.3 & \(\underline{6.18 \times 10^{-5}}\) & \(\underline{2.46 \times 10^{10}}\) & \(\underline{1.91 \times 10^{9}}\) & \(\underline{21.37}\) & -74.11 & -1.07 & \(\underline{2.90 \times 10^{9}}\) & \(6.40 \times 10^{8}\) \\
\hline & & \(\underline{86}\) & \[
\frac{1,1,2 \text {-Trichloro-1,2,2- }}{\text { trifluoroethane }}
\] & \(\mathrm{ClCF}_{2} \mathrm{CCl}_{2} \underline{\mathrm{~F}}\) & 94.5 & \(5.94 \times 10^{-5}\) & \(\underline{2.51 \times 10^{10}}\) & \(3.17 \times 10^{10}\) & \(\underline{24.18}\) & -80.52 & \(\underline{-0.79}\) & N/A & N/A \\
\hline & & \(\underline{87}\) & 1-Iodopropane & \(\mathrm{C}_{3} \underline{H}_{2} \underline{\underline{I}}\) & 81.8 & \(6.03 \times 10^{-5}\) & \(2.48 \times 10^{10}\) & \(\underline{2.73 \times 10^{10}}\) & \(\underline{24.03}\) & -75.56 & -1.00 & N/A & N/A \\
\hline & & \(\underline{88}\) & 1-Iodobutane & \(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{I}\) & 102.4 & \(\underline{5.89 \times 10^{-5}}\) & \(\underline{2.52 \times 10^{10}}\) & \(\underline{2.29 \times 10^{10}}\) & \(\underline{23.85}\) & -75.50 & -1.01 & N/A & N/A \\
\hline & & \(\underline{89}\) & 1-Bromobutane & \(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{Br}\) & \(\underline{64.8}\) & \(\underline{6.20 \times 10^{-5}}\) & \(\underline{2.46 \times 10^{10}}\) & \(\underline{1.59 \times 10^{10}}\) & \(\underline{23.49}\) & -67.54 & -1.35 & \(1.00 \times 10^{10}\) & \(\underline{9.00 \times 10^{9}}\) \\
\hline & & \(\underline{90}\) & 1-Chlorobutane & \(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{Cl}\) & 81.5 & \(\underline{6.04 \times 10^{-5}}\) & \(\underline{2.48 \times 10^{10}}\) & \(3.42 \times 10^{8}\) & \(\underline{19.65}\) & -70.83 & -1.21 & \(\underline{4.50 \times 10^{8}}\) & \(\underline{4.80 \times 10^{7}}\) \\
\hline & & \(\underline{91}\) & 1-Chloro-2-methylpropane & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}\) & \(\underline{80.4}\) & \(\underline{6.04 \times 10^{-5}}\) & \(\underline{2.48 \times 10^{10}}\) & \(\underline{5.21 \times 10^{8}}\) & \(\underline{20.07}\) & -70.62 & -1.22 & N/A & N/A \\
\hline & & \(\underline{92}\) & 1-Bromopentane & \(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{Br}\) & \(\underline{115.5}\) & \(\underline{5.82 \times 10^{-5}}\) & \(\underline{2.54 \times 10^{10}}\) & \(\underline{1.17 \times 10^{10}}\) & \(\underline{23.18}\) & -67.45 & -1.36 & N/A & N/A \\
\hline & & \(\underline{93}\) & 2-Bromo-2-methylpropane & \(\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}\) & \(\underline{67.9}\) & \(\underline{6.16 \times 10^{-5}}\) & \(\underline{2.46 \times 10^{10}}\) & \(\underline{1.02 \times 10^{10}}\) & \(\underline{23.04}\) & -70.36 & -1.23 & N/A & N/A \\
\hline & & \(\underline{94}\) & 2-Bromobutane & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathbf{C H} \mathrm{CH}(\mathrm{Br}) \mathrm{CH}_{3}\) & \(\underline{81.9}\) & \(\underline{6.03 \times 10^{-5}}\) & \(\underline{2.49 \times 10^{10}}\) & \(1.01 \times 10^{10}\) & \(\underline{23.04}\) & -69.18 & -1.28 & N/A & N/A \\
\hline & & \(\underline{95}\) & Trifluoroiodomethane & \(\mathrm{CF}_{3} \mathrm{I}\) & \(\underline{53.4}\) & \(\underline{6.36 \times 10^{-5}}\) & \(\underline{2.45 \times 10^{10}}\) & \(\underline{2.77 \times 10^{10}}\) & \(\underline{24.05}\) & -77.06 & \(\underline{-0.94}\) & N/A & N/A \\
\hline & & \(\underline{96}\) & Iodomethane & \(\mathrm{CH}_{3} \mathrm{I}\) & 48.8 & \(\underline{6.44 \times 10^{-5}}\) & \(\underline{2.44 \times 10^{10}}\) & \(\underline{4.64 \times 10^{10}}\) & \(\underline{24.56}\) & -73.39 & \(\underline{-1.10}\) & N/A & N/A \\
\hline & \multirow{9}{*}{Halooxygen} & 97 & Isoflurane & \(\mathrm{CHF}_{2} \mathrm{OCHClCF}_{3}\) & 77.7 & \(6.07 \times 10^{-5}\) & \(2.48 \times 10^{10}\) & \(5.80 \times 10^{9}\) & 22.48 & 0.87 & -4.32 & N/A & N/A \\
\hline & & 98 & 1,1,1-Trifluoroacetone & \(\mathrm{CF}_{3} \mathrm{COCH}_{3}\) & 40.8 & \(6.61 \times 10^{-5}\) & \(2.44 \times 10^{10}\) & \(6.62 \times 10^{7}\) & 18.01 & 24.93 & -5.36 & N/A & N/A \\
\hline & & 99 & Fluoroacetone & \(\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{~F}\) & 64.0 & \(6.21 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(9.77 \times 10^{8}\) & 20.70 & 19.34 & -5.12 & \(1.00 \times 10^{9}\) & \(8.80 \times 10^{8}\) \\
\hline & & 100 & Methoxyflurane & \(\mathrm{CH}_{3} \mathrm{OCF}_{2} \mathrm{CHCl}_{2}\) & 99.9 & \(5.91 \times 10^{-5}\) & \(2.52 \times 10^{10}\) & \(3.16 \times 10^{10}\) & 24.18 & 1.31 & -4.34 & N/A & N/A \\
\hline & & 101 & 2-Chloroethanol & \(\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\) & 49.5 & \(6.42 \times 10^{-5}\) & \(2.44 \times 10^{10}\) & \(5.34 \times 10^{8}\) & 20.10 & 15.25 & -4.94 & \(7.00 \times 10^{8}\) & \(3.30 \times 10^{8}\) \\
\hline & & 102 & 2-Bromoethanol & \(\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\) & 74.8 & \(6.09 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(1.71 \times 10^{9}\) & 21.26 & 18.64 & -5.09 & N/A & N/A \\
\hline & & 103 & Chloroacetic acid & \(\mathrm{ClCH}_{2} \mathrm{COOH}\) & 62.0 & \(6.23 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(9.60 \times 10^{9}\) & 22.98 & 5.40 & -4.51 & N/A & \(N / A\) \\
\hline & & 104 & Chloral hydrate & \(\mathrm{CCl}_{3} \mathrm{CH}(\mathrm{OH})_{2}\) & 87.4 & \(5.99 \times 10^{-5}\) & \(2.49 \times 10^{10}\) & \(2.31 \times 10^{10}\) & 23.86 & -0.79 & -4.25 & N/A & N/A \\
\hline & & 105 & Enflurane & \(\mathrm{CHF}_{2} \mathrm{OCF}_{2} \mathrm{CHClF}\) & 86.1 & \(6.00 \times 10^{-5}\) & \(2.49 \times 10^{10}\) & \(3.03 \times 10^{9}\) & 21.83 & 4.14 & -4.46 & N/A & N/A \\
\hline & \multirow{4}{*}{Cyanide} & 106 & Acetonitrile & \(\mathrm{CH}_{3} \mathrm{CN}\) & 44.3 & \(6.53 \times 10^{-5}\) & \(2.44 \times 10^{10}\) & \(3.74 \times 10^{7}\) & 17.44 & -14.83 & -3.64 & \(4.40 \times 10^{7}\) & \(3.00 \times 10^{7}\) \\
\hline & & 107 & Succinonitrile & \(\mathrm{NC}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CN}\) & 64.6 & \(6.20 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(1.83 \times 10^{9}\) & 21.33 & -21.84 & -3.33 & N/A & N/A \\
\hline & & \(\underline{108}\) & Trichloroacetonitrile & \(\mathrm{CCl}_{3} \mathrm{CN}\) & \(\underline{86.2}\) & \(\underline{6.00 \times 10^{-5}}\) & \(\underline{2.49 \times 10^{10}}\) & \(\underline{3.20 \times 10^{10}}\) & \(\underline{24.19}{ }^{\text {b }}\) & -98.67 & \(\underline{0.00}\) & N/A & N/A \\
\hline & & 109 & Cyanamide & \(\mathrm{H}_{2} \mathrm{NCN}\) & 36.9 & \(6.71 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(1.60 \times 10^{9}\) & 21.19 & -21.23 & -3.36 & N/A & N/A \\
\hline & \multirow{5}{*}{Amine} & 110 & Methylamine & \(\mathrm{CH}_{3} \mathrm{NH}_{2}\) & 31.3 & \(6.89 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(9.00 \times 10^{5}\) & 13.71 & 19.28 & -5.12 & N/A & N/A \\
\hline & & 111 & Butylamine & \(\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{NH}_{2}\) & 70.1 & \(6.14 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(1.10 \times 10^{6}\) & 13.91 & 17.07 & -5.02 & N/A & N/A \\
\hline & & 112 & Propylamine & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\) & 73.5 & \(6.11 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(1.10 \times 10^{6}\) & 13.91 & 19.79 & -5.14 & N/A & N/A \\
\hline & & 113 & Ethylamine & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}\) & 60.5 & \(6.25 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(1.00 \times 10^{6}\) & 13.82 & 20.42 & -5.17 & N/A & N/A \\
\hline & & 114 & Isobutylamine & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{NH}_{2}\) & 58.8 & \(6.28 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(1.10 \times 10^{7}\) & 16.21 & 18.63 & -5.09 & N/A & N/A \\
\hline
\end{tabular}



\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline & Class & No. & Name & Chemical Formula & \begin{tabular}{c} 
Molar \\
Volume,, \\
\(\left(\mathrm{cm}^{3} /\right.\) \\
\(\mathrm{mol})\) \\
\hline
\end{tabular} & Diffusion Coefficient, \(D_{1}\) ( \(\mathrm{cm}^{2} / \mathrm{s}\) ) & \[
\begin{gathered}
k_{\mathrm{D}} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \[
\begin{gathered}
k_{\text {chem }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \(\ln k_{\text {chem }}\) & \[
\begin{gathered}
\Delta G^{\circ}{ }_{(\mathrm{red}, \mathrm{aq}} \\
(\mathrm{kcal} / \mathrm{mol})
\end{gathered}
\] & \[
\begin{aligned}
& E_{\text {red }}^{\circ} \\
& (\mathrm{V} \text { vs } \\
& \mathrm{SHE})
\end{aligned}
\] & \[
\begin{gathered}
\text { Upper Lim } \\
k_{\text {exp }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] & \[
\begin{gathered}
\text { ower Limit } \\
k_{\text {exp }} \\
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\end{gathered}
\] \\
\hline & \multirow{19}{*}{Alkene} & 233 & Tetracyanoethylene & \((\mathrm{NC})_{2} \mathrm{C}=\mathrm{C}(\mathrm{CN})_{2}\) & 94.0 & \(5.94 \times 10^{-5}\) & \(2.51 \times 10^{10}\) & \(3.74 \times 10^{10}\) & 24.34 & 36.90 & -5.88 & N/A & N/A \\
\hline & & 234 & Methacrylate & \(\mathrm{CH}_{2}=\mathrm{C}\left(\mathrm{CH}_{3}\right) \mathrm{COO}^{-}\) & 60.1 & -- & -- \({ }^{\text {a }}\) & \(4.50 \times 10^{9}\) & 22.23 & -36.63 & -2.69 & N/A & N/A \\
\hline & & 235 & 3-Buten-1-ol & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\) & 74.5 & \(6.10 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(2.45 \times 10^{6}\) & 14.71 & -22.99 & -3.28 & \(4.10 \times 10^{6}\) & \(8.00 \times 10^{5}\) \\
\hline & & 236 & 3-Buten-2-OL & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}(\mathrm{OH}) \mathrm{CH}_{3}\) & 72.5 & \(6.12 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(5.91 \times 10^{7}\) & 17.90 & -26.41 & -3.13 & N/A & N/A \\
\hline & & 237 & 3-Methylbut-2-enoate & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCO}_{2}{ }^{-}\) & 104.6 & -- & -- \({ }^{\text {a }}\) & \(6.40 \times 10^{8}\) & 20.28 & -31.71 & -2.91 & N/A & N/A \\
\hline & & 238 & 3,3-Dimethylacrylic acid & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CHCOOH}\) & 73.4 & \(6.11 \times 10^{-5}\) & \(2.47 \times 10^{10}\) & \(2.53 \times 10^{10}\) & \(23.95{ }^{\text {b }}\) & -50.40 & -2.09 & \(1.50 \times 10^{10}\) & \(1.00 \times 10^{10}\) \\
\hline & & 239 & Isocrotonate & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCOO}^{-}\) & 71.6 & -- & -- \({ }^{\text {a }}\) & \(1.30 \times 10^{9}\) & 20.99 & -35.70 & -2.73 & N/A & N/A \\
\hline & & 240 & Hydrogen Fumarate & \(\mathrm{HOOCCH}=\mathrm{CHCOO}^{-}\) & 64.8 & -- & -- \({ }^{\text {a }}\) & \(1.35 \times 10^{10}\) & \(23.33{ }^{\text {b }}\) & -66.40 & -1.40 & \(1.80 \times 10^{10}\) & \(9.00 \times 10^{9}\) \\
\hline & & 241 & Monomethyl Fumarate & \(\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOO}^{-}\) & 86.1 & -- & - \({ }^{\text {a }}\) & \(1.30 \times 10^{10}\) & \(23.29{ }^{\text {b }}\) & -64.43 & -1.49 & N/A & N/A \\
\hline & & 242 & 2-Hydroxyethyl Acrylate & \(\mathrm{CH}_{2}=\mathrm{CHCOOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\) & 65.9 & \(6.19 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(1.08 \times 10^{10}\) & \(23.10^{\text {b }}\) & -57.85 & -1.77 & N/A & N/A \\
\hline & & 243 & trans-Aconitate(3-) & \({ }^{-} \mathrm{OOCCH}=\mathrm{C}\left(\mathrm{COO}^{-}\right) \mathrm{CH}_{2} \mathrm{COO}^{-}\) & 119.2 & -- & -- \({ }^{\text {a }}\) & \(1.80 \times 10^{8}\) & 19.01 & -45.03 & -2.33 & N/A & N/A \\
\hline & & 244 & Acrylamide & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCONH}_{2}\) & 54.7 & \(6.34 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(3.81 \times 10^{11}\) & \(26.67{ }^{\text {b }}\) & -51.89 & -2.03 & \(3.30 \times 10^{10}\) & \(1.50 \times 10^{10}\) \\
\hline & & 245 & Crotonamide & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CHCONH}_{2}\) & 67.6 & \(6.17 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(2.75 \times 10^{10}\) & \(24.04{ }^{\text {b }}\) & -47.62 & -2.22 & N/A & N/A \\
\hline & & 246 & \[
\begin{aligned}
& \text { 4-(Ethylamino)-4-oxobut-2- } \\
& \text { enoate }
\end{aligned}
\] & \(\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{NHCOCH}=\mathrm{CHCOO}^{-}\) & 119.2 & -- & -- \({ }^{a}\) & \(8.50 \times 10^{9}\) & \(22.86{ }^{\text {b }}\) & -56.87 & -1.81 & N/A & N/A \\
\hline & & 247 & cis-Dimethyl Fumarate & \(\mathrm{CH}_{3} \mathrm{OOCCH}=\mathrm{CHCOOCH}_{3}\) & 95.4 & \(5.93 \times 10^{-5}\) & \(2.51 \times 10^{10}\) & \(3.20 \times 10^{10}\) & \(24.19^{\text {b }}\) & -73.51 & -1.09 & N/A & N/A \\
\hline & & 248 & 4-Penten-2-OL & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCH}_{2} \mathrm{CH}(\mathrm{OH}) \mathrm{CH}_{3}\) & 97.0 & \(5.92 \times 10^{-5}\) & \(2.51 \times 10^{10}\) & \(5.00 \times 10^{5}\) & 13.12 & -21.90 & -3.33 & N/A & N/A \\
\hline \multirow[b]{3}{*}{\[
0
\]} & & 249 & Guanidine & \(\mathrm{H}_{2} \mathrm{NC}(=\mathrm{NH}) \mathrm{NH}_{2}\) & 57.9 & \(6.29 \times 10^{-5}\) & \(2.45 \times 10^{10}\) & \(2.02 \times 10^{8}\) & 19.12 & -4.98 & -4.06 & \(2.50 \times 10^{8}\) & \(1.60 \times 10^{8}\) \\
\hline & & 250 & Ethyl Acrylate & \(\mathrm{H}_{2} \mathrm{C}=\mathrm{CHCOOC}_{2} \mathrm{H}_{5}\) & 89.2 & \(5.98 \times 10^{-5}\) & \(2.50 \times 10^{10}\) & \(1.34 \times 10^{10}\) & \(23.31{ }^{\text {b }}\) & -57.33 & -1.79 & N/A & N/A \\
\hline & & 251 & Acetone Oxime & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{NOH}\) & 64.5 & \(6.20 \times 10^{-5}\) & \(2.46 \times 10^{10}\) & \(3.29 \times 10^{8}\) & 19.61 & -25.74 & -3.16 & \(3.50 \times 10^{8}\) & \(3.00 \times 10^{8}\) \\
\hline
\end{tabular}
\({ }^{a} D_{\mathrm{I}}\) data not available in literature. Assumed \(k_{\text {exp }} \ll k_{\mathrm{D}}\).
\({ }^{b}\) Reaction determined to be diffusion limited.
Association mechanism
Concerted mechanism
Stepwise mechanism

Table A.6. Comparison of \(E_{\text {red,aq }}^{\circ}\) values of representative PFASs calculated at M06\(2 \mathrm{X} / \mathrm{cc}-\mathrm{pVDZ}\) and single point energy calculation at M06-2X/Aug-cc-pVTZ based on the optimized structure at M06-2X/cc-pVDZ
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline \multirow[b]{2}{*}{Class} & \multirow[b]{2}{*}{Compound} & \multirow[b]{2}{*}{Attacking Site} & \multirow[b]{2}{*}{Chemical Structure} & \multicolumn{3}{|c|}{Stepwise Ered} \\
\hline & & & & \[
\begin{gathered}
\text { opt }+ \text { freq } \\
\text { M06- } 2 \mathrm{X} / \mathrm{cc}- \\
\text { pVDZ }
\end{gathered}
\] & \[
\begin{gathered}
\text { single pt } \\
\text { M06- } \\
\text { 2X/aug-cc- } \\
\text { pVTZ }
\end{gathered}
\] & \[
\begin{gathered}
\text { opt }+ \text { freq } \\
\text { M06- } \\
\text { 2X/aug-cc- } \\
\text { pVTZ }
\end{gathered}
\] \\
\hline \multirow{10}{*}{PFCA} & \multirow{3}{*}{Perfluorobutanoic acid (PFBA)} & alpha & \multirow[t]{3}{*}{} & -6.79 & -4.94 & -5.61 \\
\hline & & beta & & -7.06 & -5.22 & -5.61 \\
\hline & & terminal & & -7.39 & -5.54 & -5.61 \\
\hline & \multirow{7}{*}{Perfluorooctanoic acid (PFOA)} & alpha & \multirow{7}{*}{} & -6.14 & -4.30 & -3.33 \\
\hline & & beta & & -6.28 & -4.36 & -3.33 \\
\hline & & gamma & & -6.25 & -4.42 & -3.33 \\
\hline & & delta & & -6.24 & -4.40 & -3.33 \\
\hline & & epsilon & & -6.30 & -4.49 & -3.33 \\
\hline & & zeta & & -6.30 & -4.47 & -3.33 \\
\hline & & terminal & & -6.66 & -4.82 & -3.33 \\
\hline \multirow{4}{*}{PFSA} & \multirow{4}{*}{Perfluorobutanesulfoni c acid} & alpha & \multirow[t]{4}{*}{} & -6.69 & -4.88 & -3.33 \\
\hline & & beta & & -6.71 & -4.87 & -3.33 \\
\hline & & gamma & & -6.60 & -4.67 & -3.33 \\
\hline & & terminal & & -7.04 & -5.08 & -3.33 \\
\hline \multirow{3}{*}{FTOH} & \multirow{3}{*}{Heptafluorobutanol} & alpha & \multirow[t]{3}{*}{} & -7.11 & -5.58 & 25253.07 \\
\hline & & beta & & -7.10 & -5.27 & 25253.06 \\
\hline & & terminal & & -7.40 & -5.90 & 2710.40 \\
\hline
\end{tabular}

\section*{A. 2 Figures}


Axis 2

Figure A.1. Sample box and whisker plot with defined labels. The upper and lower whiskers represent the maximum and minimum datapoints, respectively. The "x" represents the mean of the dataset. The lower edge and upper edge of the box represent the lower quartile (Q1) and upper quartile (Q3) of the data, respectively. The middle horizontal line within the box represents the median (Q2) of the data. The box covers the interquartile interval where \(50 \%\) of the data is found.


Figure A.2. Potential energy surface of reactant and radical anion of methyl trifluoroacetate (no. 39) as a function of dihedral angle with the corrected energy for radical anion.


Figure A.3. LUMO of trifluoroacetate


Figure A.4. Charge distribution of oxalate, dimethylester, and acetamide


Figure A.5. LFER for ester via association and concerted C-O cleavage


Figure A.6. Spin density distribution of nitropropane


Figure A.7. Spin density distribution of 2-chloropropanoate, 3-chloropropanoate, chloroacetate, and trichloroacetate


Figure A.8. Spin density distribution of bromoacetate, 2-bromopropanoate, and 3bromopropanoate


Figure A.9. Spin density distribution of 2-iodoacetate, 2-iodopropanoate, and 3iodanylpropanoate


Figure A.10. LFERs for concerted and association mechanisms of \(\mathrm{C}-\mathrm{NH}_{4}{ }^{+}\)bond of ammonium compounds


Figure A.11. Spin density distribution of cyanide


Figure A.12. Linear free energy relationships for thiols undergoing stepwise (red dot) and concerted (blue dot) mechanisms


Figure A.13. Spin density distribution of fluoroacetate


Figure A.14. LUMO of fluoroacetate


Figure A.15. SOMO of fluoroacetate radical anion


Figure A.16. Potential energy surface of fluoroacetone as a function of C-F bond


Figure A.17. Distribution of charge and spin density of fluoroacetone (No. 99): C-F bond from \(1.279 \AA\) (optimized) (Top), \(1.484 \AA, 1.589 \AA\), and \(1.694 \AA\) (Bottom).


Figure A.18. Potential energy surface of 1,1,1-trifluoroacetone as a function of C-F bond length


Figure A.19. Distribution of charge and spin density of 1,1,1-trifluoroacetone (No. 98). CF bond from \(1.338 \AA\) (optimized) (top), \(1.444 \AA, 1.551 \AA\), and \(1.657 \AA\) (bottom).


Figure A.20. LUMO of 1,1,1-trifluoroacetone (No. 98) and fluoroacetone (No. 99)


Figure A.21. Linear free energy relationships for sulfides and disulfides undergoing stepwise (red dot) and concerted (blue dot) mechanisms


Figure A.22. LFER for fluorinated compounds based on M06-2X/cc-pVDZ

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\section*{B Group Contribution Method Supplemental Information}
B. \(1 \quad\) Group rate constants and group contribution factors

Table B.1. Group rate constants and group contribution factors for compounds undergoing association with \(\mathrm{C}=\mathrm{O} / \mathrm{O}\)
\begin{tabular}{|c|c|}
\hline \multicolumn{2}{|l|}{\(\mathrm{C}=\mathrm{O}\) Association} \\
\hline \multicolumn{2}{|l|}{Group Rate Constant ( \(\times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}\) )} \\
\hline \(k_{\text {C=O }}\) & 1.64 \\
\hline \(k_{\text {C=O(II) }}\) & 400.10 \\
\hline \(k_{\mathrm{O}}\) & 0.03 \\
\hline \multicolumn{2}{|l|}{Group Contribution Factor, \(X\)} \\
\hline - \({ }^{-}\) & 0.04 \\
\hline \(-\mathrm{COO}^{-},-\mathrm{CH}_{2} \mathrm{COO}^{-},-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}\) & 0.99 \\
\hline \(-\mathrm{CH}_{2},-\mathrm{CH}_{3},-\mathrm{CH}_{2} \mathrm{CH}_{2},-\mathrm{CH}_{2} \mathrm{CH}_{3},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\) & 0.17 \\
\hline - OH & 0.81 \\
\hline - COOH & 100.00 \\
\hline \(-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COOH}\) & 1.00 \\
\hline \(-\mathrm{CH}_{2} \mathrm{COOH}\) & 11.42 \\
\hline - \(\mathrm{CHOH},-\mathrm{CH}_{2} \mathrm{OH}\) & 1.00 \\
\hline \(-\mathrm{OCH}_{3},-\mathrm{OCH}_{2} \mathrm{CH}_{3},-\mathrm{OC}\left(\mathrm{CH}_{3}\right)_{3}\) & 1.00 \\
\hline \(-\mathrm{NH}_{2},-\mathrm{NH}\) & 0.30 \\
\hline \(-\mathrm{NHCH}_{2},-\mathrm{NHCH}_{3}\) & 0.11 \\
\hline - \(\mathrm{CH}_{2} \mathrm{NH}_{2}\) & 1.00 \\
\hline \(-\mathrm{NHC}=\mathrm{O},-\mathrm{CH}_{2} \mathrm{C}=\mathrm{O},-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{C}=\mathrm{O}\) & 1.00 \\
\hline \(-\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\) & 0.52 \\
\hline - \(\mathrm{NHC}\left(\mathrm{CH}_{3}\right)_{3}\) & 0.43 \\
\hline -N( \(\left.\mathrm{CH}_{2} \mathrm{CH}_{3}\right)_{2}\) & 0.30 \\
\hline
\end{tabular}

Table B.2. Group rate constants and group contribution factors for compounds undergoing concerted or stepwise cleavage of C-X
\begin{tabular}{|cc|}
\hline \multicolumn{2}{|c|}{ Cleavage of a C-X bond } \\
\hline \hline \multicolumn{2}{|c|}{ Group Rate Constant \(\left(\times 10^{8} \mathrm{M}^{-1} \mathrm{~s}^{-1}\right)\)} \\
\hline\(k_{\mathrm{C}-\mathrm{Br}}\) & 63.00 \\
\(k_{\mathrm{C}-\mathrm{I}}\) & 135.31 \\
\(k_{\mathrm{C}-\mathrm{Cl}}\) & 14.54 \\
\(k_{\mathrm{C}-\mathrm{FI})}\) & 1.80 \\
\(k_{\mathrm{C}-\mathrm{FII})}\) & 0.00 \\
\hline \multicolumn{2}{|c|}{\(\mathrm{Group} \mathrm{Contribution} \mathrm{Factor}, \mathrm{Y}^{-\mathrm{CH},-\mathrm{CH}_{2},-\mathrm{CH}_{2} \mathrm{CH}_{3}}\)} \\
\(-\mathrm{CH}_{3}\) & 0.38 \\
\(-\mathrm{CH}_{2} \mathrm{CH}_{2}\) & 0.72 \\
-Cl & 0.23 \\
-COOH & 2.21 \\
\(-\mathrm{COO}^{-}\) & 6.59 \\
\(-\mathrm{C}=\mathrm{O}\) & 0.79 \\
-F & 5.40 \\
\(-\mathrm{CF}_{2},-\mathrm{CF}_{3}\) & 2.10 \\
\(-\mathrm{CF}_{2}{ }^{*}\) & 2.49 \\
\hline
\end{tabular}
\({ }^{\text {a }}-\mathrm{CF}_{2} *\) is only used in the association component ( \(\mathrm{C}=\mathrm{O}\) or O ) of the overall rate equations for PFAS compounds.

Table B.3. Group rate constants and group contribution factors for compounds undergoing association with \(\mathrm{C}=\mathrm{C}\)
\begin{tabular}{|c|c|}
\hline \multicolumn{2}{|l|}{\(\mathrm{C}=\mathrm{C}\) Association} \\
\hline \multicolumn{2}{|l|}{Group Rate Constant ( \(\times 10^{9} \mathrm{M}^{-1} \mathrm{~s}^{-1}\) )} \\
\hline \(k_{\text {HH>C=C<HH }}\) & 0.00 \\
\hline \(k_{\text {HH>C=C }<\mathrm{H}}\) & 0.28 \\
\hline \(k_{>\mathrm{C}=\mathrm{C}<\mathrm{HH}}, k_{\mathrm{H}>\mathrm{C}=\mathrm{C}<\mathrm{H}(\text { trans })}\) & 4.89 \\
\hline \(k_{\mathrm{H}>\mathrm{C}=\mathrm{C}<\mathrm{H}(\mathrm{cis})}\) & 14.08 \\
\hline \(k_{>\mathrm{C}=\mathrm{C}<\mathrm{H}}\) & 82.49 \\
\hline \(k_{\text {SO3- }}\) & 1.72 \\
\hline \multicolumn{2}{|l|}{Group Contribution Factor, \(X\)} \\
\hline -C=O & 9.92 \\
\hline \(-\mathrm{COO}^{-}\) & 0.99 \\
\hline \(-\mathrm{CH}_{3}\) & 0.09 \\
\hline --Cl & 1.02 \\
\hline \(-\mathrm{CH}_{2},-\mathrm{CH}_{2} \mathrm{CH}_{2},-\mathrm{CH}_{2} \mathrm{NH}_{2}\) & 0.04 \\
\hline \(-\mathrm{SO}_{3}{ }^{-}\) & 2.19 \\
\hline \(-\mathrm{CH}_{2} \mathrm{OH},-\mathrm{CHOH}\) & 0.13 \\
\hline \(-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH},-\mathrm{CH}_{2} \mathrm{CHOH}\) & 0.00 \\
\hline - \(\mathrm{CONH}_{2}\) & 10.00 \\
\hline
\end{tabular}

Table B.4. Group rate constants and group contribution factors for compounds undergoing association with S - or N -containing functional groups or cleavage of \(\mathrm{C}-\mathrm{S}\) or \(\mathrm{C}-\mathrm{N}\) during reduction
\begin{tabular}{|c|c|}
\hline \multicolumn{2}{|l|}{S \& N Interaction} \\
\hline \multicolumn{2}{|l|}{Group Rate Constant ( \(\times 10^{7} \mathrm{M}^{-1} \mathrm{~s}^{-1}\) )} \\
\hline \(k_{\text {C=N }}\) & 3.74 \\
\hline \(k_{\text {NH3+ }}\) & 3.92 \\
\hline \(k_{\text {SO3- }}\) & 3.50 \\
\hline \(k_{\text {S }=0}\) & 0.42 \\
\hline \(k_{\text {-S }}\) & 2.00 \\
\hline \(k_{\text {-S.S. }}\) & 434.87 \\
\hline \(k_{\text {SH }}\) & 408.02 \\
\hline \(k_{\text {S }}\) & 95.51 \\
\hline \(k_{\text {C=S }}\) & 138.00 \\
\hline \(k_{\text {NO2 }}\) & 2699.59 \\
\hline \(k_{\text {N=O }}\) & 826.24 \\
\hline \(k_{\text {C=N }}\) & 20.20 \\
\hline \multicolumn{2}{|l|}{Group Contribution Factor} \\
\hline \(-\mathrm{CH}_{3},-\mathrm{CH}_{2} \mathrm{CH}_{3},-\mathrm{CH}_{2} \mathrm{CH}_{2},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\) & 0.04 \\
\hline
\end{tabular}
\({ }^{\text {a }}\) due to limited data, these group contribution factors are only used in the overall rate equations involving the \(-\mathrm{NH}_{3}{ }^{+}\)reactive site.

Table B.5. Group rate constants and group contribution factors for compounds undergoing addition to an aromatic compound
\begin{tabular}{|c|c|}
\hline \multicolumn{2}{|c|}{Addition to Aromatic} \\
\hline \multicolumn{2}{|l|}{Group Rate Constant ( \(\times 10^{9} \mathrm{M}^{-1} \mathrm{~s}^{-1}\) )} \\
\hline \(k_{\text {C=0 }}\) & 15.00 \\
\hline \(k_{\text {C-Br }}\) & 6.00 \\
\hline \(k_{\text {C-Cl }}\) & 0.64 \\
\hline \(k_{\text {C-F }}\) & 0.30 \\
\hline \(k_{\text {O }}\) & 0.02 \\
\hline \(k_{\text {s }}\) & 0.05 \\
\hline \(k_{\text {C=N }}\) & 18.00 \\
\hline \(k_{\text {NO2 }}\) & 36.60 \\
\hline \(k_{\text {N=0 }}\) & 43.00 \\
\hline \(k_{\text {SO3 }}\) & 2.60 \\
\hline \(k_{\text {C-I }}\) & 0.47 \\
\hline \multicolumn{2}{|l|}{Group Contribution Factor, \(Z\) - Mono-Substituted} \\
\hline -OH & 0.77 \\
\hline - \({ }^{-}\) & 0.23 \\
\hline --Cl & 2.09 \\
\hline -F & 1.42 \\
\hline \(-\mathrm{NH}_{2}\) & 1.00 \\
\hline \multicolumn{2}{|l|}{Group Contribution Factor, \(Z\) - Di \& Tri-Substituted} \\
\hline \multicolumn{2}{|l|}{\(-\mathrm{CH}_{3}(\mathrm{o}) \quad 1.00\)} \\
\hline \multicolumn{2}{|c|}{\(-\mathrm{CH}_{3}(\mathrm{~m}) \quad 0.90\)} \\
\hline \multicolumn{2}{|c|}{\(-\mathrm{CH}_{3}(\mathrm{p}) \quad 0.80\)} \\
\hline \multicolumn{2}{|c|}{\(-\mathrm{Cl}(\mathrm{o}) \quad 1.01\)} \\
\hline \multicolumn{2}{|c|}{-Cl(m) 1.36} \\
\hline \multicolumn{2}{|c|}{-Cl(p) 1.66} \\
\hline \multicolumn{2}{|c|}{-OH(o) 1.00} \\
\hline \multicolumn{2}{|c|}{-OH(m) 1.00} \\
\hline \multicolumn{2}{|c|}{\(-\mathrm{OH}(\mathrm{p}) \quad 0.80\)} \\
\hline \multicolumn{2}{|c|}{- \(\mathrm{NH}_{2}(\mathrm{o}) \quad 0.64\)} \\
\hline \multicolumn{2}{|c|}{\(-\mathrm{NH}_{2}(\mathrm{~m}) \quad 1.00\)} \\
\hline \multicolumn{2}{|c|}{\(-\mathrm{NH}_{2}(\mathrm{p}) \quad 0.69\)} \\
\hline \multicolumn{2}{|c|}{- \({ }^{-}(\mathrm{o}) \quad 0.44\)} \\
\hline \multicolumn{2}{|c|}{-O-(m) 0.42} \\
\hline \multicolumn{2}{|c|}{-O(p) 0.15} \\
\hline \multicolumn{2}{|c|}{-COO \({ }^{(\mathrm{o})} 00.38\)} \\
\hline \multicolumn{2}{|c|}{\(-\mathrm{COO}^{-(\mathrm{m})} 00.06\)} \\
\hline \multicolumn{2}{|c|}{- \(\mathrm{COO}^{-(\mathrm{p})} 1\)} \\
\hline \multicolumn{2}{|c|}{\(-\operatorname{Br}(\mathrm{o}) \quad 1.17\)} \\
\hline \multicolumn{2}{|c|}{- \(\operatorname{Br}(\mathrm{m}\) ) 2.00} \\
\hline \multicolumn{2}{|c|}{\(-\operatorname{Br}(\mathrm{p}) \quad 2.30\)} \\
\hline \multicolumn{2}{|c|}{-F(o) 0.88} \\
\hline \multicolumn{2}{|c|}{-F(m) 1.00} \\
\hline \multicolumn{2}{|c|}{-F(p) 1.26} \\
\hline \multicolumn{2}{|c|}{-I(o) 1.29} \\
\hline \multicolumn{2}{|c|}{-I(m) 3.80} \\
\hline \multicolumn{2}{|c|}{\(-\mathrm{I}(\mathrm{p}) \quad 2.52\)} \\
\hline & \\
\hline
\end{tabular}

\section*{B. 2 Taft Constant Supplemental Information}


Figure B.1. Relationship between calibrated group contribution factors and the Taft constant for the \(\mathrm{C}-\mathrm{X}\) cleavage mechanism.

\section*{B. 3 Calibration and Validation Results}

Table B.6. Summary of experimental data and GCMe predicted results for the calibration compounds.





\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline & 53 & 1-Chloro-2-methylpropane & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCH}_{2} \mathrm{Cl}\) & & \(5.21 \times 10^{8}\) & \(5.53 \times 10^{8}\) & 0.00 & 45 \\
\hline \multirow{5}{*}{Halooxygen} & 54 & Fluoroacetone & \(\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{~F}\) & & \(9.77 \times 10^{8}\) & \(9.77 \times 10^{8}\) & 0.00 & 7 \\
\hline & 55 & 2-Chloroethanol & \(\mathrm{ClCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\) & \[
\mathrm{Cl}_{\mathrm{Cl}}
\] & \(5.34 \times 10^{8}\) & \(5.53 \times 10^{8}\) & 0.00 & \[
\begin{gathered}
49,50,33 \\
51
\end{gathered}
\] \\
\hline & 56 & 2-Bromoethanol & \(\mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\) & & \(1.71 \times 10^{9}\) & \(2.39 \times 10^{9}\) & 0.16 & 19 \\
\hline & 57 & Chloroacetic acid & \(\mathrm{ClCH}_{2} \mathrm{COOH}\) & & \(9.60 \times 10^{9}\) & \(9.60 \times 10^{9}\) & 0.00 & 52 \\
\hline & 58 & Chloral hydrate & \(\mathrm{CCl}_{3} \mathrm{CH}(\mathrm{OH})_{2}\) & & \(2.31 \times 10^{10}\) & \(8.10 \times 10^{9}\) & 0.42 & 53 \\
\hline \multirow{5}{*}{Halocarboxylate} & 59 & Chloroacetate & \(\mathrm{ClCH}_{2} \mathrm{COO}^{-}\) & & \(1.09 \times 10^{9}\) & \(1.15 \times 10^{9}\) & 0.00 & \[
\begin{gathered}
21,51,34 \\
19
\end{gathered}
\] \\
\hline & 60 & 3-Chloropropanoate & \(\mathrm{Cl}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\) & & \(4.40 \times 10^{8}\) & \(5.54 \times 10^{8}\) & 0.07 & 51 \\
\hline & 61 & Bromoacetate & \(\mathrm{BrCH}_{2} \mathrm{COO}^{-}\) & & \(8.03 \times 10^{9}\) & \(4.98 \times 10^{9}\) & 0.14 & 19 \\
\hline & 62 & 3-Bromopropanoate & \(\mathrm{Br}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{COO}^{-}\) & & \(2.70 \times 10^{9}\) & \(2.40 \times 10^{9}\) & 0.01 & 19 \\
\hline & 63 & Fluoroacetate & \(\mathrm{FCH}_{2} \mathrm{COO}^{-}\) & & \(1.20 \times 10^{6}\) & \(1.20 \times 10^{6}\) & 0.00 & 19 \\
\hline
\end{tabular}












\({ }^{\text {a }}\) All 2D chemical structures drawn using ChemDraw Professional 16.0 software.

Table B.7. Summary of experimental data and GCMe predicted results for the validation compounds






\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline & 251 & 2,2'-Sulfanediyldiacetate & \(\mathrm{S}\left(\mathrm{CH}_{2} \mathrm{COO}^{-}\right)_{2}\) & & \(8.30 \times 10^{7}\) & \(2.22 \times 10^{7}\) & 0.54 & 71 \\
\hline & 252 & N-Acetylcysteamine & \(\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{CH}_{2} \mathrm{SH}\) & & \(1.43 \times 10^{10}\) & \(4.09 \times 10^{9}\) & 0.51 & 71 \\
\hline & 253 & Cystamine & \(\mathrm{S}_{2}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)_{2}\) & \(\mathrm{NH}_{2}\) & \(5.85 \times 10^{10}\) & \(4.35 \times 10^{9}\) & 0.86 & 70 \\
\hline & 254 & L-Cystine anion & \(\mathrm{S}_{2}\left[\mathrm{CH}_{2} \mathrm{CH}\left(\mathrm{NH}_{2}\right) \mathrm{COO}^{-}\right]_{2}\) & & \(3.53 \times 10^{9}\) & \(4.35 \times 10^{9}\) & 0.04 & \[
\begin{gathered}
129,27, \\
70,73
\end{gathered}
\] \\
\hline & 255 & 3,3'-Thiodipropanoate & \(\mathrm{S}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COO}^{-}\right)_{2}\) & & \(5.80 \times 10^{7}\) & \(2.22 \times 10^{7}\) & 0.38 & 71 \\
\hline \multirow{2}{*}{S-} & 256 & 2-Hydroxyethanethiolate & \(\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{~S}\) & & \(1.80 \times 10^{7}\) & \(9.56 \times 10^{8}\) & 0.96 & 27 \\
\hline & 257 & 2-Acetamidoethanethiolate & \(\mathrm{CH}_{3} \mathrm{CONHCH}_{2} \mathrm{CH}_{2} \mathrm{~S}\) & & \(1.90 \times 10^{9}\) & \(9.63 \times 10^{8}\) & 0.24 & 71 \\
\hline \multirow{2}{*}{CS} & 258 & Carbon Disulfide & \(\mathrm{CS}_{2}\) & = S & \(3.10 \times 10^{10}\) & \(2.76 \times 10^{9}\) & 0.83 & 130, 5 \\
\hline & 259 & \(\mathrm{N}, \mathrm{N}\)--Diethylthiourea & \(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NHCSNHCH}_{2} \mathrm{CH}_{3}\) & & \(5.10 \times 10^{8}\) & \(1.38 \times 10^{9}\) & 0.40 & 74 \\
\hline \multirow{2}{*}{Imines} & 260 & Cyanoguanidine & \(\mathrm{NCN}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2}\) & & \(1.96 \times 10^{10}\) & \(2.39 \times 10^{8}\) & 0.98 & 131 \\
\hline & 261 & Acetaldehyde Oxime & \(\mathrm{CH}_{3} \mathrm{CH}=\mathrm{NOH}\) & & \(7.22 \times 10^{7}\) & \(2.03 \times 10^{8}\) & 0.42 & 7 \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline 262 & Acetone Oxime & \(\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{NOH}\) & & \(3.29 \times 10^{8}\) & \(2.03 \times 10^{8}\) & 0.15 & 33, 7 \\
\hline
\end{tabular}
\({ }^{\text {a }}\) All 2 D chemical structures drawn using ChemDraw Professional 16.0 software.

Table B.8. Summary of GCMe predicted second-order rate constants for PFAS compounds undergoing reduction via \(\mathrm{e}^{-}\)aq
\begin{tabular}{|c|c|c|c|c|}
\hline Class & Compound Name & 2D Structure \({ }^{\text {a }}\) & \begin{tabular}{l}
Stepwise \\
\(k_{\text {pred(GCMe) }}\)
\[
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\]
\end{tabular} & Stepwise + Association \(k_{\text {pred(GCMe) }}\) ( \(\mathrm{M}^{-1} \mathrm{~s}^{-1}\) ) \\
\hline \multirow{8}{*}{Perfluoroalkyl Carboxylic Acids (PFCA)} & Trifluoroacetate &  & \(9.97 \times 10^{5}\) & \(1.66 \times 10^{6}\) \\
\hline & Perfluorobutanoic acid (PFBA) &  & \(5.11 \times 10^{6}\) & \(5.77 \times 10^{6}\) \\
\hline & Perfluorooctanoic acid (PFOA) &  & \(1.50 \times 10^{7}\) & \(1.57 \times 10^{7}\) \\
\hline & Perfluorohexanoic acid &  & \(1.01 \times 10^{7}\) & \(1.07 \times 10^{7}\) \\
\hline & Perfluorononanoic acid &  & \(1.75 \times 10^{7}\) & \(1.82 \times 10^{7}\) \\
\hline & Ammonium perfluorooctanoate &  & \(1.50 \times 10^{7}\) & \(1.57 \times 10^{7}\) \\
\hline & Methyl heptafluorobutyrate &  & \(9.71 \times 10^{6}\) & \(2.61 \times 10^{7}\) \\
\hline & Methyl perfluorohexanoate &  & \(1.47 \times 10^{7}\) & \(3.11 \times 10^{7}\) \\
\hline \multirow[b]{2}{*}{Perfluoro-alkane Sulfonic Acids (PFSA)} & Perfluorobutanesulfonic acid &  & \(1.31 \times 10^{7}\) & \(4.81 \times 10^{7}\) \\
\hline & Perfluorooctanesulfonic acid &  & \(2.30 \times 10^{7}\) & \(5.80 \times 10^{7}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|}
\hline Class & Compound Name & 2D Structure \({ }^{\text {a }}\) & \begin{tabular}{l}
Stepwise \\
\(k_{\text {pred(GCMe) }}\) \\
( \(\mathrm{M}^{-1} \mathrm{~s}^{-1}\) )
\end{tabular} & Stepwise + Association \(k_{\text {pred(GCMe) }}\) \(\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)\) \\
\hline \multirow{3}{*}{Perfluoro-alkane Sulfonic Acids (PFSA)} & Potassium perfluorooctanesulfonate &  & \(2.30 \times 10^{7}\) & \(5.80 \times 10^{7}\) \\
\hline & Potassium perfluorobutanesulfonate & 
\[
\mathrm{K}^{+}
\] & \(1.31 \times 10^{7}\) & \(4.81 \times 10^{7}\) \\
\hline & Potassium perfluorohexanesulfonate &  & \(1.81 \times 10^{7}\) & \(5.30 \times 10^{7}\) \\
\hline \multirow{8}{*}{Fluorotelomer Alcohols (FTOH)} & 4:2 Fluorotelomer alcohol &  & \(8.49 \times 10^{6}\) & \(9.03 \times 10^{6}\) \\
\hline & 6:2 Fluorotelomer alcohol &  & \(1.35 \times 10^{7}\) & \(1.40 \times 10^{7}\) \\
\hline & 4:4 Fluorotelomer alcohol &  & \(8.49 \times 10^{6}\) & \(9.03 \times 10^{6}\) \\
\hline & 8:2 Fluorotelomer alcohol &  & \(1.84 \times 10^{7}\) & \(1.90 \times 10^{7}\) \\
\hline & 11:1 Fluorotelomer alcohol &  & \(2.59 \times 10^{7}\) & \(2.64 \times 10^{7}\) \\
\hline & Heptafluorobutanol &  & \(6.00 \times 10^{6}\) & \(6.54 \times 10^{6}\) \\
\hline & 3-(Perfluoropropyl)propanol &  & \(6.00 \times 10^{6}\) & \(6.54 \times 10^{6}\) \\
\hline & \[
\begin{gathered}
\text { 3-(Perfluoro-2-butyl)propane-1,2- } \\
\text { diol }
\end{gathered}
\] &  & \(1.10 \times 10^{7}\) & \(1.20 \times 10^{7}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|}
\hline Class & Compound Name & 2D Structure \({ }^{\text {a }}\) & \begin{tabular}{l}
Stepwise \\
\(k_{\text {pred(GCMe) }}\) \\
( \(\mathrm{M}^{-1} \mathrm{~s}^{-1}\) )
\end{tabular} & Stepwise + Association \(k_{\text {pred(GCMe) }}\) \(\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)\) \\
\hline \multirow[b]{2}{*}{Fluorotelomer Acrylates (FTACs)} & 6:2 Fluorotelomer acrylate &  & \(1.21 \times 10^{7}\) & \(2.93 \times 10^{9}\) \\
\hline & 6:2 Fluorotelomer methacrylate &  & \(1.21 \times 10^{7}\) & \(4.59 \times 10^{9}\) \\
\hline \multirow{3}{*}{\begin{tabular}{l}
Perfluoroalkyl Ether \\
Carboxylates (PFECAs)
\end{tabular}} & Perfluoro-2-methyl-3-oxahexanoic acid &  & \(9.95 \times 10^{6}\) & \(1.06 \times 10^{7}\) \\
\hline & Perfluoro(4-methoxybutanoic) acid &  & \(5.12 \times 10^{6}\) & \(5.77 \times 10^{6}\) \\
\hline & Perfluoro-3,6-dioxaoctane-1,8dioic acid &  & \(2.63 \times 10^{6}\) & \(3.94 \times 10^{6}\) \\
\hline \multirow{3}{*}{Perfluoro-alkane Sulfonamides (FASA)} & Perfluorooctanesulfonamide &  & \(2.30 \times 10^{7}\) & \(3.15 \times 10^{7}\) \\
\hline & \begin{tabular}{l}
N - \\
Ethylperfluorooctanesulfonamide
\end{tabular} &  & \(2.30 \times 10^{7}\) & \(3.15 \times 10^{7}\) \\
\hline & N-Methylperfluorooctanesulfonamide &  & \(2.30 \times 10^{7}\) & \(3.15 \times 10^{7}\) \\
\hline \begin{tabular}{l}
Perfluoro-alkane \\
Sulfonyl \\
Fluorides \\
(PASFs)
\end{tabular} & Perfluorobutanesulfonyl fluoride &  & \(1.31 \times 10^{7}\) & \(2.15 \times 10^{7}\) \\
\hline Perfluoro-alkane Sulfonyl Chloride (PASCs) & Perfluoro-1-butanesulfonyl chloride &  & \(1.31 \times 10^{7}\) & \(2.15 \times 10^{7}\) \\
\hline Perfluoroalkyl Acyl Fluorides (PAAFs) & Perfluoroglutaryl difluoride &  & \(4.48 \times 10^{6}\) & \(3.32 \times 10^{8}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|}
\hline Class & Compound Name & 2D Structure \({ }^{\text {a }}\) & \begin{tabular}{l}
Stepwise \\
\(k_{\text {pred(GCMe) }}\)
\[
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\]
\end{tabular} & Stepwise + Association \(k_{\text {pred(GCMe) }}\) \(\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)\) \\
\hline \multirow[b]{2}{*}{Fluorotelomer Amines} & 1H,1H-Perfluoropentylamine &  & \(8.49 \times 10^{6}\) & \(8.49 \times 10^{6}\) \\
\hline & Bis(1H,1H-perfluoropropyl)amine &  & \(8.49 \times 10^{6}\) & \(8.49 \times 10^{6}\) \\
\hline \multirow{3}{*}{Perfluoroalkyl amides} & Octafluoroadipamide &  & \(1.57 \times 10^{7}\) & \(2.56 \times 10^{7}\) \\
\hline & Nonafluoropentanamide &  & \(1.35 \times 10^{7}\) & \(1.84 \times 10^{7}\) \\
\hline & Heptafluorobutyramide &  & \(1.10 \times 10^{7}\) & \(1.59 \times 10^{7}\) \\
\hline Perfluoroalkyl Anhydrides & Pentafluoropropanoic anhydride &  & \(1.39 \times 10^{7}\) & \(4.67 \times 10^{7}\) \\
\hline Polyfluoroalkyl Acyl Fluorides & 5H-Octafluoropentanoyl fluoride &  & \(9.05 \times 10^{6}\) & \(2.54 \times 10^{7}\) \\
\hline Polyfluoroalkyl Aldehydes & 5H-Perfluoropentanal &  & \(9.05 \times 10^{6}\) & \(2.54 \times 10^{7}\) \\
\hline \multirow{3}{*}{Polyfluoroalkyl Ethers} & Sevoflurane &  & \(2.62 \times 10^{6}\) & \(2.62 \times 10^{6}\) \\
\hline & Flurothyl &  & \(9.60 \times 10^{5}\) & \(9.60 \times 10^{5}\) \\
\hline & Perfluoroisobutyl methyl ether &  & \(4.40 \times 10^{6}\) & \(4.40 \times 10^{6}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|}
\hline Class & Compound Name & 2D Structure \({ }^{\text {a }}\) & \begin{tabular}{l}
Stepwise \\
\(k_{\text {pred(GCMe) }}\) \\
. \(\mathrm{M}^{-1} \mathrm{~s}^{-1}\) )
\end{tabular} & \begin{tabular}{l}
Stepwise + \\
Association \\
\(k_{\text {pred(GCMe) }}\) \\
( \(\mathrm{M}^{-1} \mathrm{~s}^{-1}\) )
\end{tabular} \\
\hline \multirow{3}{*}{\[
\begin{aligned}
& \text { Polyfluoroalkyl } \\
& \text { Etherr }
\end{aligned}
\]
Ethers} & tris(Trifluoroethoxy)methane &  & \(1.44 \times 10^{6}\) & \(1.44 \times 10^{6}\) \\
\hline & Difluoromethyl 1H,1Hperfluoropropyl &  & \(3.92 \times 10^{6}\) & \(3.92 \times 10^{6}\) \\
\hline & Allyl perfluoroisopropyl ether &  & \(3.12 \times 10^{6}\) & \(1.50 \times 10^{7}\) \\
\hline \multirow{4}{*}{Semifluorinated Alkenes (SFAenes)} & 1H,1H,2H-Perfluoro-1-hexene &  & \(9.10 \times 10^{6}\) & \(5.64 \times 10^{8}\) \\
\hline & 6H-Perfluorohex-1-ene &  & \(6.96 \times 10^{6}\) & \(6.60 \times 10^{11}\) \\
\hline & 2-Vinylperfluorobutane &  & \(7.48 \times 10^{6}\) & \(5.63 \times 10^{8}\) \\
\hline & 1-Propenylperfluoropropane &  & \(6.62 \times 10^{6}\) & \(8.97 \times 10^{8}\) \\
\hline Perfluoroalkyl Alkyl Ethers (PFAEs) & Ethyl perfluorobutyl ether &  & \(9.10 \times 10^{6}\) & \(9.10 \times 10^{6}\) \\
\hline \multirow{3}{*}{Polyfluorinated Alcohols} & 1H,1H,5H-Perfluoropentanol &  & \(6.34 \times 10^{6}\) & \(6.88 \times 10^{6}\) \\
\hline & Dodecafluoroheptanol &  & \(1.13 \times 10^{7}\) & \(1.18 \times 10^{7}\) \\
\hline & Hexafluoroamylene glycol &  & \(3.24 \times 10^{6}\) & \(4.32 \times 10^{6}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|}
\hline Class & Compound Name & 2D Structure \({ }^{\text {a }}\) & \begin{tabular}{l}
Stepwise \\
\(k_{\text {pred(GCMe) }}\)
\[
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\]
\end{tabular} & Stepwise + Association \(k_{\text {pred(GCMe) }}\) \(\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)\) \\
\hline \multirow[t]{2}{*}{Polyfluorinated Alcohols} & 3H-Perfluoro-2,2,4,4tetrahydroxypentane &  & \(2.62 \times 10^{6}\) & \(1.53 \times 10^{7}\) \\
\hline & 1-Pentafluoroethylethanol &  & \(3.52 \times 10^{6}\) & \(3.61 \times 10^{6}\) \\
\hline \multirow{3}{*}{Polyfluoroalkyl Carboxylates} & 4H-Perfluorobutanoic acid &  & \(4.27 \times 10^{6}\) & \(4.93 \times 10^{6}\) \\
\hline & 3,3-Bis(trifluoromethyl)-2propenoic acid &  & \(2.53 \times 10^{6}\) & \(8.25 \times 10^{10}\) \\
\hline & 3-(Perfluoroisopropyl)-2propenoic acid &  & \(6.88 \times 10^{6}\) & \(4.90 \times 10^{9}\) \\
\hline \multirow[b]{2}{*}{Fluorotelomer Carboxylates (FTCAs)} & \(2 \mathrm{H}, 2 \mathrm{H}, 3 \mathrm{H}, 3 \mathrm{H}\)-Perfluorooctanoic acid &  & \(1.10 \times 10^{7}\) & \(1.21 \times 10^{7}\) \\
\hline & Methyl 2H,2H,3H,3Hperfluoroheptanoate &  & \(8.49 \times 10^{6}\) & \(3.64 \times 10^{7}\) \\
\hline Fluorotelomer Sulfonates (FTSAs) & 4:2 Fluorotelomer sulfonic acid &  & \(8.49 \times 10^{6}\) & \(4.35 \times 10^{7}\) \\
\hline \begin{tabular}{l}
N -alkyl \\
Perfluoro-alkane Sulfonamidoethanols
\end{tabular} & N-Ethyl-N-(2hydroxyethyl)perfluorooctanesulf onamide &  & \(2.30 \times 10^{7}\) & \(3.20 \times 10^{7}\) \\
\hline \multirow[b]{2}{*}{\begin{tabular}{l}
Perfluoroalkyl \\
Polyether \\
Carboxylates \\
(PFPECAs)
\end{tabular}} & Perfluoro-3,6,9-trioxatridecanoic acid &  & \(1.14 \times 10^{7}\) & \(1.21 \times 10^{7}\) \\
\hline & Perfluoro-3,6-dioxaheptanoic acid &  & \(3.57 \times 10^{6}\) & \(4.23 \times 10^{6}\) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|}
\hline Class & Compound Name & 2D Structure \({ }^{\text {a }}\) & \begin{tabular}{l}
Stepwise \\
\(k_{\text {pred(GCMe) }}\)
\[
\left(\mathrm{M}^{-1} \mathrm{~s}^{-1}\right)
\]
\end{tabular} & \begin{tabular}{l}
Stepwise + Association \\
\(k_{\text {pred(GCMe) }}\) ( \(\mathrm{M}^{-1} \mathrm{~s}^{-1}\) )
\end{tabular} \\
\hline Perfluoroalkyl Aldehydes (PFALs) & Perfluorobutyraldehyde &  & \(1.10 \times 10^{7}\) & \(2.74 \times 10^{7}\) \\
\hline Perfluoroalkyl Amino Alcohols & 2-Aminohexafluoropropan-2-ol &  & \(2.53 \times 10^{6}\) & \(5.70 \times 10^{6}\) \\
\hline Perfluoroalkyl Ketones & Methyl perfluoroethyl ketone &  & \(8.53 \times 10^{6}\) & \(1.13 \times 10^{7}\) \\
\hline Perfluoroalkyl Polyether Alcohols & 1H,1H,8H,8H-Perfluoro-3,6-dioxaoctane-1,8-diol &  & \(2.30 \times 10^{6}\) & \(3.38 \times 10^{6}\) \\
\hline Perfluoroalkyl Vinyl Ethers & Heptafluoropropyl trifluorovinyl ether &  & \(6.62 \times 10^{6}\) & \(6.60 \times 10^{11}\) \\
\hline \begin{tabular}{l}
Polyfluoro- \\
alkane \\
Sulfonates
\end{tabular} & 2,2-Difluoroethyl triflate &  & \(6.46 \times 10^{6}\) & \(1.49 \times 10^{7}\) \\
\hline Polyfluoroalkyl Amides & Perfluoropentanamide &  & \(1.13 \times 10^{7}\) & \(1.63 \times 10^{7}\) \\
\hline Polyfluoroalkyl Amines & 2-Amino-2H-perfluoropropane &  & \(2.53 \times 10^{6}\) & \(2.53 \times 10^{6}\) \\
\hline Polyfluoroalkyl Ketones & 3H-Perfluoro-4-hydroxy-3-penten-2-one &  & \(2.53 \times 10^{6}\) & \(6.56 \times 10^{9}\) \\
\hline \begin{tabular}{l}
Polyfluoroalkyl \\
Trifluoro-methane- \\
Sulfonates
\end{tabular} & 2-(Trifluoromethoxy)ethyl trifluoromethanesulfonate &  & \(7.58 \times 10^{6}\) & \(1.60 \times 10^{7}\) \\
\hline \begin{tabular}{l}
Semi- \\
fluorinated Alkanes (SFAs)
\end{tabular} & 1,1,1,3,3-Pentafluorobutane &  & \(5.38 \times 10^{5}\) & \(5.38 \times 10^{5}\) \\
\hline
\end{tabular}
\({ }^{\text {a }}\) All 2D chemical structures drawn using ChemDraw Professional 16.0 software.

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\section*{C Monteverde Zone Biogarden Supplemental Information}

\section*{C. 1 Monteverde Zone Rainwater Data Tables}

Table C.1. Summary of monthly and daily rainfall data in the Monteverde Zone from 2010-2021. Data collected from the MVI micro weather station.
\begin{tabular}{ccccccc}
\hline Month & \begin{tabular}{c} 
Monthly \\
avg \\
rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Avg \\
rainfall/day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} & \begin{tabular}{c} 
Max \\
monthly \\
rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Min \\
monthly \\
rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Max \\
rainfall/day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} & \begin{tabular}{c} 
Mainfall/day \\
\((\mathbf{m m} /\) day \()\)
\end{tabular} \\
\hline JAN & 3.33 & 0.61 & 17.20 & 0.04 & 3.44 & 0.00 \\
\hline FEB & 6.01 & 1.08 & 38.48 & 0.00 & 3.21 & 0.00 \\
\hline MAR & 4.39 & 0.46 & 26.10 & 0.00 & 2.61 & 0.00 \\
\hline APR & 62.38 & 4.55 & 211.30 & 5.60 & 9.89 & 0.51 \\
\hline MAY & 277.27 & 10.70 & 548.70 & 125.11 & 17.70 & 6.58 \\
\hline JUN & 355.93 & 12.51 & 748.00 & 169.37 & 24.93 & 6.34 \\
\hline JUL & 312.96 & 11.53 & 762.00 & 73.90 & 24.58 & 3.21 \\
\hline AUG & 365.22 & 13.05 & 745.00 & 109.10 & 24.03 & 5.30 \\
\hline SEPT & 455.74 & 15.38 & 739.70 & 264.32 & 24.66 & 9.44 \\
\hline OCT & 515.38 & 17.43 & 915.30 & 257.40 & 29.53 & 8.88 \\
\hline NOV & 216.80 & 8.97 & 577.70 & 16.00 & 22.18 & 1.14 \\
\hline DEC & 23.70 & 3.34 & 101.31 & 0.64 & 11.17 & 0.00 \\
\hline
\end{tabular}

Table C.2. Summary of monthly and daily rainfall data in the Monteverde Zone for 2020 and 2021. Data collected from the MVI micro weather station.
\begin{tabular}{cccccccc} 
& \multicolumn{3}{c}{2021} & \multicolumn{3}{c}{2020} \\
\hline Month & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfal//Day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} \\
\hline JAN & 3.7 & 11 & 0.34 & 6 & 6 & 1.00 \\
\hline FEB & 2.9 & 2 & 1.45 & 0.1 & 1 & 0.10 \\
\hline MAR & 2.2 & 8 & 0.28 & 0.6 & 2 & 0.30 \\
\hline APR & 96.1 & 15 & 6.41 & 5.6 & 11 & 0.51 \\
\hline MAY & 172.6 & 23 & 7.50 & 377.4 & 24 & 15.73 \\
\hline JUN & 472 & 29 & 16.28 & 549.4 & 30 & 18.31 \\
\hline JUL & 564.2 & 30 & 18.81 & 506.2 & 31 & 16.33 \\
\hline AUG & 674.3 & 31 & 21.75 & 745 & 31 & 24.03 \\
\hline SEPT & 739.7 & 30 & 24.66 & 526.5 & 30 & 17.55 \\
\hline OCT & -- & -- & -- & 759.9 & 31 & 24.51 \\
\hline NOV & -- & -- & -- & 577.7 & 29 & 19.92 \\
\hline DEC & -- & -- & -- & 37.8 & 16 & 2.36 \\
\hline
\end{tabular}

Table C.3. Summary of monthly and daily rainfall data in the Monteverde Zone for 2018 and 2019. Data collected from the MVI micro weather station.
\begin{tabular}{ccccccc} 
& \multicolumn{3}{c}{2019} & \multicolumn{3}{c}{2018} \\
\hline Month & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} /\) day \()\)
\end{tabular} \\
\hline JAN & 0.2 & 0 & 0.00 & 2.6 & 3 & 0.87 \\
\hline FEB & 0 & 0 & 0.00 & 0.2 & 0 & 0.00 \\
\hline MAR & 0 & 0 & 0.00 & 0 & 0 & 0.00 \\
\hline APR & 9.4 & 4 & 2.35 & 14.39 & 11 & 1.31 \\
\hline MAY & 329.4 & 30 & 10.98 & 216.2 & 28 & 7.72 \\
\hline JUN & 190.1 & 30 & 6.34 & 260.14 & 29 & 8.97 \\
\hline JUL & 181.8 & 26 & 6.99 & 73.9 & 23 & 3.21 \\
\hline AUG & 260.9 & 30 & 8.70 & 111.4 & 21 & 5.30 \\
\hline SEPT & 535.2 & 29 & 18.46 & 398.56 & 30 & 13.29 \\
\hline OCT & 915.3 & 31 & 29.53 & 606.51 & 28 & 21.66 \\
\hline NOV & 79.1 & 26 & 3.04 & 76.2 & 16 & 4.76 \\
\hline DEC & 21.2 & 18 & 1.18 & 2 & 1 & 2.00 \\
\hline
\end{tabular}

Table C.4. Summary of monthly and daily rainfall data in the Monteverde Zone for 2016 and 2017. Data collected from the MVI micro weather station.
\begin{tabular}{|ccccccc} 
& \multicolumn{3}{c|}{2017} & \multicolumn{3}{c}{2016} \\
\hline Month & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} \\
\hline JAN & 1.01 & 0 & 0.00 & 0.04 & 1 & 0.04 \\
\hline FEB & 0 & 0 & 0.00 & 0 & 0 & 0.00 \\
\hline MAR & 0 & 0 & 0.00 & 0 & 0 & 0.00 \\
\hline APR & 45.9 & 14 & 3.28 & 83.06 & 16 & 5.19 \\
\hline MAY & 548.7 & 31 & 17.70 & 248.24 & 23 & 10.79 \\
\hline JUN & 341.5 & 29 & 11.78 & 391.41 & 29 & 13.50 \\
\hline JUL & 461.1 & 30 & 15.37 & 192.4 & 25 & 7.70 \\
\hline AUG & 302.2 & 28 & 10.79 & 337.99 & 26 & 13.00 \\
\hline SEPT & 540.6 & 30 & 18.02 & 494.3 & 29 & 17.04 \\
\hline OCT & 678.54 & 29 & 23.40 & 410.23 & 31 & 13.23 \\
\hline NOV & 165.4 & 21 & 7.88 & 576.65 & 26 & 22.18 \\
\hline DEC & 33.5 & 3 & 11.17 & 101.31 & 12 & 8.44 \\
\hline
\end{tabular}

Table C.5. Summary of monthly and daily rainfall data in the Monteverde Zone for 2014 and 2015. Data collected from the MVI micro weather station.
\begin{tabular}{ccccccc} 
& \multicolumn{3}{c}{2015} & \multicolumn{3}{c}{2014} \\
\hline Month & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} /\) day \()\)
\end{tabular} & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} /\) day \()\)
\end{tabular} \\
\hline JAN & 0.2 & 0 & 0.00 & 0.15 & 0 & 0.00 \\
\hline FEB & 1.6 & 1 & 1.60 & 0 & 0 & 0.00 \\
\hline MAR & 0.78 & 10 & 0.08 & 0.03 & 3 & 0.01 \\
\hline APR & 17.57 & 8 & 2.20 & 39.71 & 7 & 5.67 \\
\hline MAY & 125.11 & 19 & 6.58 & 240.9 & 24 & 10.04 \\
\hline JUN & 169.37 & 19 & 8.91 & 232.4 & 29 & 8.01 \\
\hline JUL & 202.56 & 17 & 11.92 & 89.26 & 13 & 6.87 \\
AUG & 109.1 & 12 & 9.09 & 283.21 & 24 & 11.80 \\
\hline SEPT & 343.83 & 29 & 11.86 & 434.27 & 30 & 14.48 \\
\hline OCT & 384.29 & 28 & 13.72 & 370.4 & 29 & 12.77 \\
\hline NOV & 361.02 & 25 & 14.44 & 55.51 & 19 & 2.92 \\
\hline DEC & 9.81 & 7 & 1.40 & 0.64 & 0 & 0.00 \\
\hline
\end{tabular}

Table C.6. Summary of monthly and daily rainfall data in the Monteverde Zone for 2012 and 2013. Data collected from the MVI micro weather station.
\begin{tabular}{cccccccc} 
& \multicolumn{3}{c}{2013} & \multicolumn{3}{c}{2012} \\
\hline Month & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} /\) day \()\)
\end{tabular} & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfal//Day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} \\
\hline JAN & 0.2 & 0 & 0.00 & 2.35 & 3 & 0.78 \\
\hline FEB & 1.1 & 1 & 1.10 & 8.1 & 3 & 2.70 \\
\hline MAR & 2.6 & 4 & 0.65 & 0.1 & 0 & 0.00 \\
\hline APR & 18.8 & 5 & 3.76 & 158.3 & 16 & 9.89 \\
\hline MAY & 205.5 & 23 & 8.93 & 229.94 & 27 & 8.52 \\
\hline JUN & 400.4 & 30 & 13.35 & 203.11 & 28 & 7.25 \\
\hline JUL & 219.9 & 27 & 8.14 & 120.52 & 23 & 5.24 \\
\hline AUG & 346.96 & 30 & 11.57 & 341.35 & 29 & 11.77 \\
\hline SEPT & 381.4 & 30 & 12.71 & 264.32 & 28 & 9.44 \\
\hline OCT & 442.8 & 28 & 15.81 & 292.2 & 28 & 10.44 \\
\hline NOV & 138 & 21 & 6.57 & 16 & 14 & 1.14 \\
\hline DEC & 14.4 & 3 & 4.80 & 22.3 & 9 & 2.48 \\
\hline
\end{tabular}

Table C.7. Summary of monthly and daily rainfall data in the Monteverde Zone for 2010 and 2011. Data collected from the MVI micro weather station.
\begin{tabular}{ccccccc} 
& \multicolumn{3}{c}{2011} & \multicolumn{3}{c}{\(\mathbf{2 0 1 0}\)} \\
\hline Month & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} / \mathbf{d a y})\)
\end{tabular} & \begin{tabular}{c} 
Rainfall \\
\((\mathbf{m m})\)
\end{tabular} & \begin{tabular}{c} 
Rain \\
Days
\end{tabular} & \begin{tabular}{c} 
Avg \\
Rainfall/Day \\
\((\mathbf{m m} /\) day \()\)
\end{tabular} \\
\hline JAN & 17.2 & 5 & 3.44 & 6.3 & 7 & 0.90 \\
\hline FEB & 19.6 & 7 & 2.80 & 38.48 & 12 & 3.21 \\
\hline MAR & 20.3 & 13 & 1.56 & 26.1 & 10 & 2.61 \\
\hline APR & 48.43 & 10 & 4.84 & 211.3 & 23 & 9.19 \\
\hline MAY & 285.84 & 26 & 10.99 & 347.4 & 27 & 12.87 \\
\hline JUN & 313.29 & 25 & 12.53 & 748 & 30 & 24.93 \\
\hline JUL & 381.7 & 29 & 13.16 & 762 & 31 & 24.58 \\
\hline AUG & 341.2 & 29 & 11.77 & 529 & 31 & 17.06 \\
\hline SEPT & 368.9 & 30 & 12.30 & 441.27 & 30 & 14.71 \\
\hline OCT & 551.6 & 31 & 17.79 & 257.4 & 29 & 8.88 \\
\hline NOV & 165.4 & 22 & 7.52 & 173.8 & 21 & 8.28 \\
\hline DEC & 16.4 & 10 & 1.64 & 1.3 & 1 & 1.30 \\
\hline
\end{tabular}
C. 2 Biogarden System Construction Plan Set

\section*{BIOGARDEN GREYWATER TREATMENT SYSTEM}

\section*{Centro de Educacion Creativa}

85CJ+3M8, Carretera Monterverde a Tilarán, Provincia de Puntarenas, Monteverde, Costa Rica






(1) PLAN VIEW

(2) \(\frac{A \cdot A^{\prime} \text { ' SIDE EIEVATION }}{\text { soan ine }}\)
notes

\section*{}









\section*{C. 3 Biogarden System Maintenance Guide}

\title{
Biogarden Maintenance Guide
}

\author{
Cloud Forest School
}


Prepared by the Monteverde Institute on April 20, 2022

\section*{I. INTRODUCTION}

In February of 2022, the Monteverde Institute (MVI) designed and installed a biogarden system on the campus of the Cloud Forest School Educacion Creativa (CEC) for the purpose of treating the greywater produced in the campus' kitchen. The biogarden system is composed of primary filtration, a grease trap, a checkpoint, two settling tanks, the biogarden, and a clarifier. This document outlines the required maintenance to ensure the biogarden at the CEC continues to function at its fullest potential year-round.

\section*{II. PERSONAL PROTECTION EQUIPMENT}

Direct interaction with certain parts of the CEC biogarden could result in illness, disease, or infection due to the fact that this system works with greywater which could possibly contain bacteria and viruses. For this reason, individuals directly handling the system for maintenance, cleaning, or testing should take precautions and wear the proper personal protection equipment (PPE). Below is a list of recommended PPE to serve as a barrier between the individual and smells, solids, and contaminated water.
- Gloves that cover the hands, wrist, and forearm (nitrile, latex, or rubber is recommended).
- Mask that covers the mouth and nose.
- Safety glasses in case of splashes.
- Long sleeve shirt and long pants.
- Close-toed shoes.

After working directly with the biogarden, it is recommended that the individual thoroughly washes his or her hands, along with any areas of exposed skin that came into direct contact with the greywater.

\section*{III. REQUIRED SYSTEM MAINTENANCE}

Each component of the CEC's biogarden system requires specific maintenance in order to ensure each part is working properly. Neglect of one part of the system will likely have a negative impact on the system as a whole. Below is a detailed description of the required maintenance for each system component. Maintenance ranges from annual to weekly maintenance depending on the component.

\section*{Kitchen Sink}

Best Sink Practices
\(\square\) Ensure sink strainers are always installed over sink drains.Food waste collected in the sink strainers should be composted.Only use biodegradable/eco-friendly dish soaps and sink cleaners.Do not put any toxic liquids or cleaners in the sink drains.

\section*{Food \& FOG Recommendations}

Do not put food waste or FOG (fats, oil, grease) directly down the sink drain.Food scraps should be properly composted.Grease should be collected in a separate container, allowed to cool, and then disposed of in the garbage.

\section*{Grease Trap}

Best Practices
\(\square\) Keep the lid on the grease trap at all times.After performing maintenance and checks, always remember to replace the lid on the grease trap.

\section*{Weekly Maintenance}
\(\square\) Ensure the grease trap inlet and outlet pipes are not clogged with food or grease. Note: water overflowing from the grease trap into the environment is a good indicator that the outlet pipe may be clogged.
\(\square\) Monitor the grease level on the surface of the water in the grease trap. Once the layer of grease is greater than \(1^{\prime \prime}(2.5 \mathrm{~cm})\) in depth, skim the grease off the water surface and dispose of in the trash.

\section*{Monthly Maintenance}Scrub the inlet and outlet pipes (both inside and outside) with a cleaning brush.Remove food waste and other sediments that may have settled on the bottom of the grease trap.

Annual Maintenance
\(\square\) Shut off the water in the kitchen and fully drain the grease trap. Clean the walls, floor, and lid of the grease trap with a hose and scrub brush.

\section*{Checkpoint}

Best PracticesKeep the lid on the checkpoint at all times.After performing maintenance and checks, always remember to replace the lid on the checkpoint.

Weekly Maintenance
\(\square\) Ensure the checkpoint inlet and outlet pipes are not clogged with food or grease. Note: water overflowing from the checkpoint into the environment is a good indicator that the outlet pipe may be clogged.

\section*{Monthly Maintenance}

Page 3Scrub the inlet and outlet pipes (both inside and outside) with a cleaning brush.Remove food waste and other sediments that may have settled on the bottom of the checkpoint.Skim off grease that may have accumulated on the surface of the water in the checkpoint.

\section*{Annual Maintenance}Shut off the water in the kitchen and drain the checkpoint. Clean the walls, floor, and lid of the checkpoint with a hose and scrub brush.

\section*{Settling Tanks}

\section*{Best Practices}Keep the lids on the settling tanks at all times.After performing maintenance and checks, always remember to replace the lids on the settling tanks.

\section*{Weekly Maintenance}Ensure the inlet pipe, the pipe connecting the settling tanks, and the outlet pipe are not clogged with food, grease, or other debris. Note: water overflowing from the first settling tank is a good indicator that the connecting pipe is clogged. Water overflowing from both settling tanks is a good indicator that the outlet pipe is clogged.
\(\square\) Monitor the sediment level on the bottom of the settling tanks. Once the sediment depth is greater than \(1^{\prime \prime}(2.5 \mathrm{~cm})\), remove the sediment from the bottom of the tanks and properly dispose of.

\section*{Monthly Maintenance}
\(\square\) Scrub the inlet, outlet, and connecting pipes (both inside and outside) with a cleaning brush.Scrub the inner walls of the tank with a cleaning brush.As needed: skim grease off the surface of the settling tanks (if grease makes it past the grease trap).

\section*{Annual Maintenance}
\(\square\) Shut off the water in the kitchen and fully drain the grease trap. Clean the walls, floor, and lid of the settling tank with a hose and scrub brush.

\section*{Biogarden}

Best PracticesRemove dead plants as needed.Add new plants as needed (preferably of the same species (i.e. heliconia, calathea, renealmia, etc.)).Cut back plants that are getting too large.Ensure the biogarden is exposed to sunlight for at least part of the day. Prune and cut back trees that are providing too much shade to the biogarden.Ensure rainfall runoff doesn't enter the biogarden by keeping the perimeter of the biogarden vegetated.

\section*{Clarifier}

Monthly MaintenanceMonitor the sediment level on the bottom of the clarifier. Once the sediment depth is greater than \(1^{\prime \prime}(2.5 \mathrm{~cm})\), remove the sediment from the bottom of the tank and properly dispose of.Scrub the inlet and outlet pipes (both inside and outside) with a cleaning brush.Scrub the inner walls of the tank with a cleaning brush.
Annual Maintenance
\(\square\) Shut off the water in the kitchen and fully drain the grease trap. Clean the walls, floor, and lid of the clarifier with a hose and scrub brush.

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