

# Photochemistry in Terrestrial Exoplanet Atmospheres I: Photochemistry Model and Benchmark Cases

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## ABSTRACT

We present a comprehensive photochemistry model for exploration of the chemical composition of terrestrial exoplanet atmospheres. The photochemistry model is designed from the ground up to have the capacity to treat all types of terrestrial planet atmospheres, ranging from oxidizing through reducing, which makes the code suitable for applications for the wide range of anticipated terrestrial exoplanet compositions. The one-dimensional chemical transport model treats up to 800 chemical reactions, photochemical processes, dry and wet deposition, surface emission and thermal escape of O, H, C, N and S bearing species, as well as formation and deposition of elemental sulfur and sulfuric acid aerosols. We validate the model by computing the atmospheric composition of current Earth and Mars and find agreement with observations of major trace gases in Earth's and Mars' atmospheres. We simulate several plausible atmospheric scenarios of terrestrial exoplanets, and choose three benchmark cases for atmospheres from reducing to oxidizing. The most interesting finding is that atomic hydrogen is always a more abundant reactive radical than the hydroxyl radical in anoxic atmospheres. Whether atomic hydrogen is the most important removal path for a molecule of interest also depends on the relevant reaction rates. We also find that volcanic carbon compounds (i.e., CH<sub>4</sub> and CO<sub>2</sub>) are chemically long-lived and tend to be well mixed in both reducing and oxidizing atmospheres, and their dry deposition velocities to the surface control the atmospheric oxidation states. Furthermore, we revisit whether photochemically produced oxygen can cause false positives for detecting oxygenic photosynthesis, and find that in 1-bar CO<sub>2</sub>-rich atmospheres oxygen and ozone may build up to levels that have been previously

arXiv:1210.6885v1 [astro-ph.EP] 25 Oct 2012

considered unique signatures of life, if there is no surface emission of reducing gases. The atmospheric scenarios present in this paper can serve as the benchmark atmospheres for quickly assessing the lifetime of trace gases in reducing, weakly oxidizing, and highly oxidizing atmospheres on terrestrial exoplanets for the exploration of possible biosignature gases.

*Subject headings:* radiative transfer — atmospheric effects — planetary systems — techniques: spectroscopic — astrobiology

## 1. Introduction

The search and characterization of super Earths is flourishing. A large number of super Earths are being detected (e.g., Rivera et al. 2005; Udry et al. 2007; Forveille et al. 2009; Léger et al. 2009; Charbonneau et al. 2009; Mayor et al. 2009; Vogt et al. 2010; Rivera et al. 2010; Dawson & Fabrycky 2010; Holman et al. 2010; Howard et al. 2011; Bonfils et al. 2011; Winn et al. 2011; Demory et al. 2011; Batalha et al. 2011; Lissauer et al., 2011; Borucki et al. 2011; Fressin et al 2012; Cochran et al. 2012). Attempts to observe super Earth atmospheres are growing (e.g., Batalha et al. 2011 for Kepler 10 b; Gillon et al. 2012 and Demory et al. 2012 for 55 Cnc e), and one super Earth/mini Neptune GJ 1214b is being observed in as much detail as possible (e.g., Bean et al. 2010; Croll et al. 2011; Désert et al. 2011; Berta et al. 2012). Although we distinguish between super Earths and mini Neptunes theoretically (super Earths are rocky planets with thin atmospheres whereas mini Neptunes are planets with massive gas envelopes), it is so far difficult to discriminate between the two categories observationally. Nonetheless, we focus on terrestrial planet atmospheres that include super Earths, since those planets hold the most interest on the path to finding and characterizing planets that might harbor life. In addition, the observational push to super Earth characterization has the potential to provide a handful of super Earth atmospheres to study in the coming years. In the more distant future, the community still holds hope that a direct-imaging space-based mission under the Terrestrial Planet Finder concept will enable planets to be observed in reflected light.

Super Earth atmospheres require understanding of photochemistry for their study. This is because the amounts of trace gases in the atmospheres depend critically on the component gas sources (surface emission) and sinks (chemical reactions initiated by UV photolysis, as well as surface deposition). This is in contrast to giant exoplanets, where there is no surface for emission, and where UV photolysis leads largely to perturbations on atmospheric composition, not to the definition of atmospheric composition. For super Earths and smaller terrestrial exoplanets, the key processes to consider in determining atmospheric composition

are photolysis, kinetics of the reactions between atmospheric components, vertical diffusion of molecules, atmospheric escape, dry and wet deposition, and condensation and sedimentation of condensable species. An atmospheric spectrum may have strong features from spectroscopically active trace gases whose lifetime depends on photochemistry; some of these trace gases may be hallmarks for specific atmospheric scenarios. Observational signatures of non-equilibrium chemistry have been observed for several transiting hot Jupiters and "hot Neptunes" (e.g., Swain et al. 2008; Stevenson et al. 2010; Madhusudhan & Seager 2011).

Theoretical studies of photochemistry on exoplanets have also been ongoing. One-dimensional photochemistry models have long been used to understand the atmospheres of planets and moons in the Solar System (see Yung & Demore 1999 and references therein), and such models and their networks of chemical reactions have been the foundation for exoplanet models. Photochemistry models have been very successful in understanding the atmosphere of Earth (e.g., Kasting et al. 1985; Zahnle 1986; Seinfeld & Pandis 2006 and references therein), Mars (e.g. Yung & Demore 1999; Zahnle et al. 2008), Venus (e.g. Krasnopolsky & Pollack 1994; Zhang et al. 2012), and Titan (e.g. Atreya et al. 2006). After the discoveries of transiting hot Jupiters, photochemistry models were adapted and applied to exoplanets. Liang et al. (2003) suggest that, driven by the photolysis of water, hot Jupiters have much higher H concentrations than Jupiter in their upper atmospheres. Zahnle et al. (2009a) and Line et al. (2010) investigated the hydrocarbon photochemistry in hot Jupiters' H<sub>2</sub>-dominated atmospheres with a complete chemical network (as compared to the work of Liang et al. (2003) that was based on a simplified hydrocarbon chemistry scheme). Zahnle et al. (2009b) studied sulfur photochemistry in hot Jupiters' atmospheres, and suggested that H<sub>2</sub>S photolysis becomes important at altitudes above the ~100 Pa pressure level. Moses et al. (2011) studied atmospheric chemistry of HD 209458b and HD 189733b, the most well-characterized hot Jupiters, with a complete chemical network involving C, H, O, N species and derived observational signatures of disequilibrium processes in their atmospheres. Kopparapu et al. (2012) presented a photochemistry model of a possibly carbon-rich hot Jupiter, WASP-12b, and suggested that C<sub>2</sub>H<sub>2</sub> and HCN, produced by photochemistry, may contribute significantly to the opacity of its atmosphere. More recently, Millier-Ricci Kempton et al. (2012) presented the first analysis of photochemistry in a H<sub>2</sub>-dominated atmosphere of mini Neptune GJ 1214b.

A key challenge in developing a photochemistry model for terrestrial exoplanet atmospheres is handling the very wide range of plausible atmospheric compositions. The broad possibilities for super Earth atmospheric composition arise from the ideas for atmospheric origin. Super Earth atmospheres may originate from the capture of nebular gases, degassing during accretion, and/or degassing from subsequent tectonic activity (Elkins-Tanton & Seager 2008; Schaefer & Fegley 2010). In principle, the atmospheres of super-Earths and ter-

restrial exoplanets may be reducing ( $\text{H}_2$ -rich), oxidized ( $\text{N}_2$ -rich, or  $\text{CO}_2$ -rich), or oxidizing ( $\text{O}_2$ -rich). It is also possible that some super-Earth atmospheres are water rich (Rogers & Seager 2010; Bean et al. 2010; Miller-Ricci Kempton et al. 2012). To date, photochemistry models are usually specific to certain types of atmospheres, because very different photochemical reactions dominate the chemistry of those atmospheres (for example in oxidized vs. reducing atmospheres). In particular, photochemistry of hydrogen-dominated atmospheres on terrestrial planets is yet to be explored; but hydrogen-dominated atmospheres may still create habitable surface temperature through collision-induced absorption (Pierrehumbert & Gaidos 2011; Wordsworth 2012).

A second significant challenge for a terrestrial exoplanet photochemistry model is the range of free parameters that describe key physical processes, namely vertical diffusion, fluxes of surface emission, and rates of dry and wet deposition. While the fundamental equations of continuity that govern the atmospheric composition are the same, these coefficients must be kept as free parameters in order to explore the range of atmospheric mixing and the range of plausible surface conditions, which yield the wide variety of possible exoplanets' atmospheres. The motivation of this work is to provide a photochemistry model that can be applied to study atmospheres of a wide range of redox states and that can handle the range of free parameters for physical processes in terrestrial exoplanet atmospheres.

In this paper, we present a photochemistry model developed from the ground up from basic chemical and physical principles and using both established and improved computer algorithms, which have the capacity of modeling very different terrestrial exoplanet atmospheres in a consistent way. The design of the photochemistry model aims at providing the maximum flexibility in treating atmospheres of very different compositions, especially oxidation states. Besides stellar parameters and planetary parameters (mass, radius, etc.), the photochemistry model accepts a series of input parameters including temperature structure of the atmosphere, dominant species and mean molecular mass of the atmosphere, coefficients of vertical diffusion, fluxes of surface emission and fluxes of dry and wet depositions. These input parameters are treated as free parameters so that the photochemistry model can simulate a wide range of atmospheric compositions.

In § 2 we describe our photochemistry model in detail. In § 3 we validate our photochemistry model by simulating the atmospheres of current Earth and Mars. In § 4 we present three benchmark cases for exoplanets, representing reducing, weakly oxidizing, and highly oxidizing atmospheres. We discuss key parameters that determine atmospheric compositions in § 4 and conclude in § 5.

## 2. A Photochemistry Model

The purpose of the photochemical model is to compute the steady-state chemical composition of an exoplanetary atmosphere. The system can be described by a set of time-dependent continuity equations, one equation for each species at each altitude. Each equation describes: chemical production; chemical loss; diffusion (contributing to production or loss); sedimentation (for aerosols only); and specified gains and losses on the lower and upper boundaries of the atmosphere. The lower boundary has assigned geological or biological source fluxes and assigned deposition rates of species and the upper boundary has diffusion-limited atmospheric escape, relevant for light species.

With the assumption of a one-dimensional plane-parallel atmosphere, the unknowns to be computed in the model are the number densities of each species at each altitude. Starting from an initial state, the system is evolved to the steady state in which production and loss are balanced for each species at each altitude. Because the removal timescales of different species are very different, the inverse Euler method is employed for the numerical time stepping. We allow the time step to be adjusted according to how fast the atmospheric components change (i.e., the variation timescale), and determine if the solution converges to the steady-state solution by evaluating the variation timescale for each species at each altitude, as well as the global production and loss balance for each species. Once the steady-state solution is found, we use a separate code to compute the exoplanet atmosphere spectrum for thermal emission, reflected stellar radiation, and transmission of stellar radiation.

We developed the photochemistry model from the ground up, and tested and validated the model by reproducing the atmospheric composition of Earth and Mars, in terms of globally-averaged 1D vertical mixing ratio profiles. For one of the tests, we started with a temperature-pressure profile of Earth’s atmosphere, and with a subset of Earth’s composition at present-day values, specifically  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CO}_2$  with assigned mixing ratios. We included surface emission of major trace gases, assumed to this exercise to be emitted according to typical globally averaged emission rates, for  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{OCS}$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{SO}_4$ . The code correctly predicts the amounts of these trace gases in Earth’s troposphere, and the amounts of ozone in the atmosphere as well as the location of the ozone layer. The code also produces vertical profiles of active hydrogen species ( $\text{OH}$  and  $\text{HO}_2$ ) and active nitrogen species ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{HNO}_3$ ) in the stratosphere that are consistent with observations. As another test, we reproduce the chemical composition of the current Mars atmosphere, in agreement with measured composition (e.g., Krasnopolsky 2006) and previous 1-D photochemistry model results (Nair et al. 1994; Yung & DeMore 1999; Zahnle et al. 2008). In particular, the code correctly illustrate the effect of  $\text{HO}_x$  catalytic chemistry that stabilizes Mars’  $\text{CO}_2$  atmosphere. The results of these tests are described in more detail

below (Section 3).

The photochemistry model is designed for exoplanet applications, and has features that are not needed for studies of individual Solar System objects but which are useful for study of potential exoplanet atmospheres. The most important feature that yields the capacity of treating reducing and oxidized atmospheres with the same code is the flexibility of choosing chemical species to be considered in photochemical equilibrium. The species that have lifetimes less than the numerical time step can be treated as being in photochemical equilibrium. Our photochemistry model features a “burn-in” period in which all species’ number densities are rigorously computed and then those species that satisfy the lifetime condition are treated in equilibrium so that the computation can be optimized for speed. We have coded the Jacobian matrix for the implicit Euler method analytically, which improves the numerical rigor of the code. In this way our photochemistry model can quickly find the steady-state solution of atmospheric composition starting from any sensible initial conditions for both reducing and oxidized atmospheres. We emphasize that the ability to compute atmospheric composition of different oxidation states and the elimination of the need of providing fine-tuned initial conditions are essential for exoplanet exploration, because the oxidation states are unknown for terrestrial exoplanets and there are no benchmark cases to provide common initial conditions.

Another important feature of our photochemistry model is that it treats a wide range of free parameters for terrestrial exoplanets. We do not hardwire any model parameters that meant to be free for exoplanet exploration, including those parameters for planets, such as stellar spectrum and surface gravity, those parameters for atmospheres, such as mean molecular mass, refractive indices, temperature profiles (which can also be self-consistently computed), and eddy diffusion coefficients, and those parameters that are specific to particular molecules, such as solubility, rainout rate, saturation vapor pressure, surface emission rate, and dry deposition velocity. The code thus has a clear structure that makes extensive parameter exploration possible.

The third important feature of our photochemistry model is that we offer the flexibility of choosing a subset of chemical species and chemical reactions for the computation. It is in particular important for exoplanet exploration to be able to isolate a chemical system from the complex network of atmospheric chemistry; and our photochemistry model responds to this need. We design our code to be able to include or exclude the effect of any species or reactions in the complex chemical network, in order to understand the fundamentals of atmospheric chemistry on terrestrial exoplanets. Also, we pay attention to the temperature range in which chemical kinetic rates and photochemical cross sections are valid. The temperature range of exoplanet atmospheres can be significantly larger than the Solar System

planet atmospheres. We label the chemical reactions whose rates are measured only at low temperatures ( $T < 400$  K) and the chemical reactions whose rates are measured only at high temperatures ( $T > 1000$  K), and use them only at appropriate temperature ranges. In addition, we consider the temperature dependence of photochemical cross sections in the model. Finally, we include a basic aerosol formation scheme in the model, the computation of which only relies on the saturation pressure of relevant substances and a timescale of condensation and sublimation. The aerosol scheme is simple, but could easily be expanded to treat non-conventional aerosols in the atmosphere.

We now present the detailed formulation of the photochemistry model.

## 2.1. Fundamental Equations

The coupled 1-dimensional continuity-transport equation that governs the chemical composition is

$$\frac{\partial n}{\partial t} = P - nL - \frac{\partial \Phi}{\partial z}, \quad (1)$$

where  $n$  is the number density of a certain species ( $\text{cm}^{-3}$ ),  $z$  is the altitude,  $P$  is the production rate of the species ( $\text{cm}^{-3} \text{s}^{-1}$ ),  $L$  is the loss rate of the species ( $\text{s}^{-1}$ ), and  $\Phi$  is the upward vertical transport flux of the species ( $\text{cm}^{-2} \text{s}^{-1}$ ). The flux can be approximated by the eddy diffusion together with the molecular diffusion, viz.,

$$\Phi = -KN \frac{\partial f}{\partial z} - DN \frac{\partial f}{\partial z} + Dn \left( \frac{1}{H_0} - \frac{1}{H} - \frac{\alpha_T}{T} \frac{dT}{dz} \right), \quad (2)$$

where  $K$  is the eddy diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ),  $D$  is the molecular diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ),  $N$  is the total number density of the atmosphere,  $f \equiv n/N$  is the mixing ratio of the species,  $H_0$  is the mean scale height,  $H$  is the molecular scale height,  $T$  is the temperature (K), and  $\alpha_T$  is the thermal diffusion factor (Banks & Kockarts 1973; Levine 1985; Krasnopolsky 1993; Yung & DeMore 1999; Bauer & Lammer 2004; Zahnle et al. 2006). The first term of equation (2) represents eddy diffusion, and the last two terms represent molecular diffusion. The vertical transport flux is written in terms of the derivatives of the mixing ratio rather than in terms of the number density because this form is simpler and more straightforward to be implemented in numerical schemes. We show that equation (2) is equivalent to the standard vertical diffusion equation in Appendix A.

The molecular diffusion coefficient  $D$  and the thermal diffusion factor  $\alpha_T$  can be determined from the gas kinetic theory, but the eddy diffusion coefficient is a more speculative parameter and must be estimated empirically. For molecular diffusion, we use the following

expressions in  $\text{cm}^2 \text{s}^{-1}$  for H and  $\text{H}_2$  in a  $\text{N}_2$ -based atmosphere

$$\begin{aligned} D(\text{H}, \text{N}_2) &= \frac{4.87 \times 10^{17} \times T^{0.698}}{N}, \\ D(\text{H}_2, \text{N}_2) &= \frac{2.80 \times 10^{17} \times T^{0.740}}{N}; \end{aligned} \quad (3)$$

and in a  $\text{CO}_2$ -based atmosphere

$$\begin{aligned} D(\text{H}, \text{CO}_2) &= \frac{3.87 \times 10^{17} \times T^{0.750}}{N}, \\ D(\text{H}_2, \text{CO}_2) &= \frac{2.15 \times 10^{17} \times T^{0.750}}{N}; \end{aligned} \quad (4)$$

and in a  $\text{H}_2$ -based atmosphere

$$D(\text{H}, \text{H}_2) = \frac{8.16 \times 10^{17} \times T^{0.728}}{N}. \quad (5)$$

In equations (3-5),  $T$  has a unit of K and  $N$  has a unit of  $\text{cm}^{-3}$ . The functional form of equations (3-5) is derived from the gas kinetic theory and the coefficients are obtained by fitting to experimental data (Marreo & Mason 1972; Banks & Kockarts 1973). The expressions for molecular diffusion coefficients are valid for a wide range of temperatures, up to 2000 K, except for  $D(\text{H}_2, \text{CO}_2)$  that is only valid at low temperatures, i.e.,  $T < 550$  K (Marreo & Mason 1972).  $D(\text{H}, \text{CO}_2)$  is assumed to be 1.8 times larger than  $D(\text{H}_2, \text{CO}_2)$  (Zahnle et al. 2008). The thermal diffusion factor  $\alpha_T$  is taken as a constant for H and  $\text{H}_2$  as  $\alpha_T = -0.38$  (Banks & Kockarts 1973). The negative sign of  $\alpha_T$  corresponds to the fact that the lightest molecules tend to diffuse to the warmest region.

The eddy diffusion coefficient is the major uncertainty in the 1-D photochemistry model. For Earth’s atmosphere, the eddy diffusion coefficient can be derived from the number density profile of trace gases (e.g. Massie & Hunten 1981). The eddy diffusion coefficient of Earth’s atmosphere is characterized by the convective troposphere and the non-convective stratosphere, which is not necessarily applicable for the exoplanets. The eddy diffusion coefficient may be typically parameterized as

$$\begin{aligned} K &= K_T \quad (z < z_T), \\ K &= \min\left(K_H, K_T \left(\frac{N(z_T)}{N}\right)^{1/2}\right) \quad (z > z_T), \end{aligned} \quad (6)$$

where  $K_T$ ,  $K_H$  and  $z_T$  are independent parameters satisfying  $K_H > K_T$ . This formula is adapted from Yung & DeMore (1999) with the requirement of continuity in  $K$ . Our code can either import eddy diffusion coefficient from a file or specify eddy diffusion coefficient according to equation (6).



The goal of the photochemistry model is to obtain a steady-state solution of each species, or a set of  $n(z)$ , which makes the left hand side of the equation (1) vanish and satisfies the boundary conditions. Assuming  $N_x$  species in the model and  $N_l$  equally stratified layers of the atmosphere, we transform the continuity equation (1) into a discrete form as

$$\frac{\partial n_i}{\partial t} = P_i - n_i L_i - \frac{\Phi_{i+1/2} - \Phi_{i-1/2}}{\Delta z}, \quad (7)$$

where the subscript  $i$  denotes physical quantities in the  $i$ th layer, and the subscripts  $i + 1/2$  and  $i - 1/2$  mean that the flux is defined at the upper and lower boundary of each layer. It is physically correct to define the flux term at the boundary of each layer, which is also crucial for numerically preserving hydrostatic equilibrium for an atmospheric transport scheme that uses number density as independent variables. According to equation (2),

$$\begin{aligned} \Phi_{i+1/2} = & -(K_{i+1/2} + D_{i+1/2})N_{i+1/2} \frac{f_{i+1} - f_i}{\Delta z} \\ & + D_{i+1/2} \frac{N_{i+1/2}}{2} \left[ \frac{(m_a - m)g}{k_B T_{i+1/2}} - \frac{\alpha_T}{T_{i+1/2}} \frac{T_{i+1} - T_i}{\Delta z} \right] (f_{i+1} + f_i), \end{aligned} \quad (8)$$

where  $m_a$  is the mean molecular mass of the atmosphere,  $m$  is the molecular mass of the species,  $g$  is the gravitational acceleration, and  $k_B$  is the Boltzmann constant. We have approximated  $f_{i+1/2}$  by  $(f_{i+1} + f_i)/2$  in equation (2).

The combination of equation (7) and (8) gives the following 2nd ordered centered discrete differential equation to be solved numerically,

$$\begin{aligned} \frac{\partial n_i}{\partial t} = & P_i - n_i L_i + \left( k_{i+1/2} \frac{N_{i+1/2}}{N_{i+1}} - d_{i+1/2} \frac{N_{i+1/2}}{N_{i+1}} \right) n_{i+1} \\ & - \left( k_{i+1/2} \frac{N_{i+1/2}}{N_i} + d_{i+1/2} \frac{N_{i+1/2}}{N_i} + k_{i-1/2} \frac{N_{i-1/2}}{N_i} - d_{i-1/2} \frac{N_{i-1/2}}{N_i} \right) n_i \\ & + \left( k_{i-1/2} \frac{N_{i-1/2}}{N_{i-1}} + d_{i-1/2} \frac{N_{i-1/2}}{N_{i-1}} \right) n_{i-1}, \end{aligned} \quad (9)$$

where

$$\begin{aligned} k_{i+1/2} &= \frac{K_{i+1/2} + D_{i+1/2}}{\Delta z^2}, \\ d_{i+1/2} &= \frac{D_{i+1/2}}{2\Delta z^2} \left[ \frac{(m_a - m)g\Delta z}{k_B T_{i+1/2}} - \frac{\alpha_T}{T_{i+1/2}} (T_{i+1} - T_i) \right]. \end{aligned}$$

In principle,  $\partial n/\partial t = 0$  is equivalent to a set of  $N_x N_l$  nonlinear algebraic equations. The set of nonlinear algebraic equations may be solved numerically by Newton-Raphson methods (Press et al. 1992). However, in practice, we find that Newton-Raphson methods require

an initial guess to be in the vicinity of the solution. Instead, we treat the problem as a time-stepping problem by evolving the system according to equation (9) to the steady state.

Implicit numerical methods are implemented to solve equation (9). Due to the orders-of-magnitude differences in chemical loss timescales, the system is numerically stiff. We use the inverse-Euler method for the time stepping, as in most previous photochemistry models (e.g., Kasting et al. 1985; Nair et al. 1994; Zahnle et al. 2008). For each time step, we need to invert a matrix of dimension  $N_x N_l$ . As seen in equation (9), the variation in any layer only depends on the number density in that layer and adjacent layers. As a result, the matrix is by nature block tridiagonal with a block dimension of  $N_x$ , which is solved efficiently by the Thomas algorithm (Conte & DeBoor 1972). The time step is self-adjusted in a way that the code updates the time step after each iteration according to the variation timescale of the whole chemical-transport system, i.e., the minimum variation timescale of each species at each altitude. As the system converges, larger and larger time steps are chosen.

The criteria of convergence to the steady-state solution is that the variation timescale of each species at each altitude is larger than the diffusion timescale of whole atmosphere, and the fluxes of gain and loss balance out for all species. The gain fluxes include surface emission, chemical production and condensation; whereas the loss fluxes include chemical loss, dry deposition, wet deposition, atmospheric escape, and condensation. We require that the ratio between the net global flux and the column-integrated number density for all long-lived species is small compared to the diffusion timescale. This condition is very important in the determination of convergence. If any possible long-term trends of major species can be detected, we run the code for an extended time period to test the convergence rigorously.

The current photochemistry model can compute concentrations of 111 molecules or aerosols made of C, H, O, N, S elements. These species are CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, O, O(<sup>1</sup>D), O<sub>3</sub>, H, OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, N, NH, NH<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>H<sub>2</sub>, N<sub>2</sub>H<sub>3</sub>, N<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>O, NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO, HNO<sub>2</sub>, HNO<sub>3</sub>, HNO<sub>4</sub>, C, CO, CH<sub>4</sub>, CH, CH<sub>2</sub>, CH<sub>2</sub><sup>1</sup>, CH<sub>3</sub>, CH<sub>2</sub>O, CHO, CH<sub>3</sub>O, CH<sub>3</sub>O<sub>2</sub>, CHO<sub>2</sub>, CH<sub>2</sub>O<sub>2</sub>, CH<sub>4</sub>O, CH<sub>4</sub>O<sub>2</sub>, C<sub>2</sub>, C<sub>2</sub>H, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>HO, C<sub>2</sub>H<sub>2</sub>O, C<sub>2</sub>H<sub>3</sub>O, C<sub>2</sub>H<sub>4</sub>O, C<sub>2</sub>H<sub>5</sub>O, HCN, CN, CNO, HCNO, S, S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, S<sub>8</sub>, SO, SO<sub>2</sub>, SO<sub>2</sub><sup>1</sup>, SO<sub>2</sub><sup>3</sup>, SO<sub>3</sub>, H<sub>2</sub>S, HS, HSO, HSO<sub>2</sub>, HSO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, OCS, CS, CH<sub>3</sub>S, CH<sub>4</sub>S, CH<sub>3</sub>NO<sub>2</sub>, CH<sub>3</sub>ONO<sub>2</sub>, CH<sub>5</sub>N, C<sub>2</sub>H<sub>2</sub>N, C<sub>2</sub>H<sub>5</sub>N, C<sub>3</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>3</sub>, CH<sub>3</sub>C<sub>2</sub>H, CH<sub>2</sub>CCH<sub>2</sub>, C<sub>3</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H, C<sub>4</sub>H<sub>2</sub>, C<sub>4</sub>H<sub>3</sub>, C<sub>4</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>5</sub>, 1-C<sub>4</sub>H<sub>6</sub>, 1,2-C<sub>4</sub>H<sub>6</sub>, 1,3-C<sub>4</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>9</sub>, C<sub>4</sub>H<sub>10</sub>, C<sub>6</sub>H, C<sub>6</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>8</sub>H<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> aerosols, S<sub>8</sub> aerosols and organic hazes.

An important feature of the photochemistry code is the flexibility to choose a subset of molecules and aerosols to study a particular problem. Since the computation time for each time step scales with  $N_x^3$ , decreasing the number of chemical species in the main loop greatly reduces the computation time. As is common practice in the effort to reduce the stiffness of

the system and improve the numerical stability, “fast” species with relatively short chemical loss timescales are computed directly from the diagnostic equation, namely

$$n = \frac{P}{L}, \quad (10)$$

which implies that photochemical equilibrium can be achieved within each time step. The choice of fast species varies with the atmospheric composition and should be considered on a case-by-case basis. The choices of “fast” species were usually hard-wired in previous photochemistry codes, which fundamentally limited their application to certain specific types of atmospheres (e.g., to Earth and to Mars). Our photochemistry code offers the flexibility to adjust the choice of species in photochemical equilibrium, which yields the capacity of treating atmospheres having very different oxidation states with the same code. We evaluate  $P$  and  $L$  in equation (10) at each time step using the number density of all species from previous time step and determine the number density of fast species according to equation (10) after the current time step linearly. We neglect nonlinearity due to multiple species in photochemical equilibrium; as a result, we do not allow strongly inter-dependent species to be concurrently considered as in photochemical equilibrium, for example for  $S_2$ ,  $S_3$ , and  $S_4$ . Our approach yields stable convergence to the steady-state solution from virtually any initial test solutions. We always verify the mass balance of the steady-state solution.

## 2.2. Chemical Kinetics

We compiled a comprehensive list of chemical and photochemical reactions from the literature. The production and loss rates in equation (7) are provided from all chemical and photochemical reactions that produce or consume the relevant molecule. In the generic model, we included 645 bimolecular reactions, 85 termolecular reactions, and 93 thermal dissociation reactions. We included the thermal dissociation reactions to make the photochemistry model potentially adaptable to simulate hot planets. We mainly used the updated reaction rates from the online NIST database (<http://kinetics.nist.gov>) and refer to the JPL publication (Sander et al. 2011) for the recommended rate when multiple measurements are presented in the NIST database. For termolecular reactions, we used the complete formula suggested by the JPL publication (Sander et al. 2011) when the low-pressure-limiting rate and the high-pressure-limiting rate are available. For all reaction rates we use the Arrhenius formula to account for the dependence on temperature when the activation energy data are available, otherwise we adopted the value of experimental measurements, which are usually under  $\sim 298$  K. We performed careful comparisons of our reaction lists and corresponding reaction rates with those used by Nair et al. (1994), Pavlov & Kasting (2002), and Zahnle et al. (2008). Most of our reaction rates are the same as those used by other codes. For a dozen

reactions, we find updated reaction rates listed in either the JPL publication or the NIST database updated after the publication of the cited photochemistry models. Also, for the general purpose of our photochemistry model, we include the reactions that are very slow at low temperatures (i.e., 200 - 400 K) but may become important at higher temperatures  $> 1000$  K. In addition, a number of reactions that lack laboratory-measured rates may be important for low-temperature (i.e., 200 - 400 K) applications. We have adopted the rates for unmeasured sulfur reactions from Turco et al. (1982), Kasting (1990), and Moses et al. (2002), and the rates for reactions of  $C>2$  hydrocarbons from Yung & DeMore (1999). All chemical reactions and their reaction rates are tabulated in Table 10.

Chemical reaction rates may sensitively depend on temperature. The reported reaction rates are usually valid in certain specific temperature ranges. For example, reaction rates recommended by the JPL publication (Sander et al. 2011) are the reactions relevant to Earth’s atmosphere, in general valid within the small range of 200 - 300 K. Hence it may be problematic to extend the rate expressions to high-temperature cases, such as hot planets. At the high-temperature end, the valid temperature range for some of the reaction rates measured in the combustion chemistry is a few thousand K. These reactions may be important for modeling hot Jupiters (e.g., Moses et al. 2011), but they should not be included in the computation of low-temperature cases, e.g., for Earth-like planets. We annotate the low-temperature reactions and the high-temperature reactions in Table 10. Moreover, most chemical reactions involving free radicals have very small activation energy, and thus weak temperature dependencies. Usually the reactions rate of free radicals are measured at room temperature and can be used in photochemistry models under different temperatures (Sander et al. 2011). Common atmospheric free radicals are:  $O(^1D)$ , OH, H, N,  $NH_2$ ,  $N_2H_3$ , C, CH,  $CH_2$ ,  $CH_2^1$ ,  $CH_3$ , CHO,  $CHO_2$ ,  $CH_3O$ ,  $CH_3O_2$ ,  $C_2$ ,  $C_2H$ ,  $C_2H_3$ ,  $C_2H_5$ ,  $C_2HO$ ,  $C_2H_3O$ ,  $C_2H_5O$ , CN, CNO, S,  $S_2$ ,  $SO_3$ , HS, HSO,  $HSO_2$ ,  $HSO_3$ ,  $CH_3S$  and CS. For reactions with these molecules, if no activation energy is reported in the literature, we assume that the activation energy is negligible and their kinetic rates do not depend on temperature.

### 2.3. Interaction with Radiation

Molecules in the atmosphere absorb ultraviolet (UV) and visible light from the host star. If the absorbed photon carries enough energy, the molecule may be photodissociated to form free radicals. The photodissociation rate is proportional to the number density of photons with UV and visible wavelengths at each altitude. For direct stellar radiation, the optical depth  $\tau$  includes the contribution from molecular absorption  $\tau_a$ , Rayleigh scattering  $\tau_r$ , and aerosol particle extinction  $\tau_m$ . For the multiple-scattered (diffusive) radiation, we

use the  $\delta$ -Eddington 2-stream method implemented based on the formulation of Toon et al. (1989). The actinic flux of the diffusive radiation is  $F_{\text{diff}} = 2(F^+ + F^-)$  where  $F^+$  and  $F^-$  are the diffusive flux in the upward and downward direction. The photolysis flux at a certain altitude includes both the direct radiation and the diffusive radiation, i.e.,

$$F(\lambda, z) = F_0(\lambda) \exp[-\tau(\lambda, z)/\mu_0] + F_{\text{diff}}, \quad (11)$$

where  $F_0$  is the radiation flux at the top of the atmosphere where  $\tau = 0$ , and  $\mu_0$  is the angle of the path of sunlight. By default we assume the zenith angle of the star to be  $57.3^\circ$  (see Appendix B for justification). The photodissociation rate is then

$$J(z) = \frac{1}{2} \int q(\lambda) \sigma_a(\lambda) L(\lambda, z) d\lambda, \quad (12)$$

where  $\sigma_a$  is the absorption cross section,  $q(\lambda)$  is the quantum yield that is defined as the ratio between the yield of certain photodissociation products and the number of photons absorbed, and  $L(\lambda, z)$  is the actinic flux with units of quanta  $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ . The 1/2 factor is included to account for diurnal variation (e.g. Zahnle et al. 2008), which is not used to model the dayside of a tidally lock planet. With the general-purpose model, we treat 70 photodissociation reactions. Different branches resulting from the photodissociation of one molecule are treated as different photodissociation reactions. The photodissociation reactions, the sources of data for cross sections and quantum yields, and the rates on the top of Earth’s atmosphere are tabulated in Table 7.

For the UV and visible cross sections and the quantum yields, we use the recommended values from the JPL publication (Sander et al. 2011) when available. We also use the cross sections from the MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules<sup>2</sup> when the JPL recommended values are not available or incomplete. There are a number of molecules of atmospheric importance that lack UV and visible cross sections and quantum yields, and we have estimated photolysis rates for them in the following way. The photodissociation timescale of  $\text{S}_2$  has been measured to be  $\sim 250$  s at 1 AU from the Sun (DeAlmeida & Singh 1986), from which we estimate the photolysis rate of  $\text{S}_2$ . For other molecules that have no UV or visible-wavelength cross sections available in the literature, we assume their

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<sup>1</sup>The actinic flux is the quantity of light available to molecules at a particular point in the atmosphere and which, on absorption, drives photochemical processes in the atmosphere. It is calculated by integrating the spectral radiance over all directions of incidence of the light. The actinic flux is distinguished from the spectral irradiance in the way that it does not refer to any specific orientation because molecules are oriented randomly in the atmosphere.

<sup>2</sup>[www.atmosphere.mpg.de/spectral-atlas-mainz](http://www.atmosphere.mpg.de/spectral-atlas-mainz)

photolysis rate to be the same as another molecule that has similar structure. For example, the photolysis rate of HNO is assumed to be the same as HNO<sub>2</sub> (Zahnle et al. 2008); the photolysis rate of HSO is assumed to be the same as HO<sub>2</sub> (Pavlov & Kasting 2002); and the photolysis rate of N<sub>2</sub>H<sub>2</sub> is assumed to be the same as N<sub>2</sub>H<sub>4</sub>.

Temperature dependencies of photolysis cross sections and quantum yields are considered. Notably, at 200 K, compared to room temperature, N<sub>2</sub>O, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, OCS, CO<sub>2</sub> have smaller UV cross sections, leading to photolysis rates more than 10% lower; whereas NO<sub>3</sub> has a larger UV cross section, leading to a photolysis rate more than 10% higher. SO<sub>2</sub> has complex band structures in its UV spectrum and the cross sections depend on temperature as well. We take into account any other temperature dependencies reported for a gas at temperatures outside 290 - 300K (see Table 7 for notes on temperature dependencies). In most cases, cross sections are also measured at lower temperature such as 200 K, primarily for Earth investigations (Sander et al. 2011). We use linear interpolation to simulate cross sections between 200 and 300 K, and do not extrapolate beyond this temperature range. It is worthwhile noting that UV cross sections of almost all gases at temperatures significantly higher than room temperature are unknown, and temperature dependencies of cross sections are not considered in previous high-temperature photochemistry models of hot exoplanets (e.g., Moses et al. 2011; Miller-Ricci Kempton et al. 2012). This may be a plausible simplification for gases without significant band structure in UV, but for gases such as H<sub>2</sub>, CO<sub>2</sub> and SO<sub>2</sub>, whose band structures are sensitive to temperature, extrapolation of cross sections to high temperature might induce significant errors. One needs to be cautious about the uncertainty of photolysis rate at temperatures much higher than room temperature.

Rayleigh scattering from atmosphere molecules introduces additional optical depth, particularly important for attenuation of UV radiation. The optical depth due to Rayleigh scattering is

$$\tau_r(\lambda, z) = \int_z^\infty N(z')\sigma_r(\lambda)dz', \quad (13)$$

in which the Rayleigh scattering cross section is (e.g., Liou 2002)

$$\sigma_r(\lambda) = C_r \frac{8\pi^3(m_r(\lambda)^2 - 1)^2}{3\lambda^4 N_s^2}, \quad (14)$$

where  $m_r$  is the real part of the refractive index of the molecule,  $C_r$  is a corrective factor to account for the anisotropy of the molecule, and  $N_s$  is the number density at the standard condition (1 atm, 273.15 K). The refractive index depends on the main constituent in the atmosphere. The refractive index of Earth’s atmosphere is from Seinfeld & Pandis (2006); the refractive index of H<sub>2</sub> is from Dalgarno & Williams (1962); the refractive index of N<sub>2</sub> is from Cox (2000); the refractive index of CO<sub>2</sub> is from Old et al. (1971); and refractive indices

of CO, and CH<sub>4</sub> are given in Sneep & Ubachs (2005). In principle the correction factor  $C_r$  depends on the molecule and the wavelength; but  $C_r$  is usually within a few percent with respect to the unity, except for  $C_r \sim 1.14$  for CO<sub>2</sub> (Sneep & Ubachs 2005). In the following we assume  $C_r = 1.061$ , the value for Earth’s atmosphere at  $\sim 200$  nm (Liou 2002).

For the spectrum of a solar-type star (G2V), we use the Air Mass Zero (AM0) reference spectrum produced by the American Society for Testing and Materials<sup>3</sup>. The AM0 spectrum covers a wavelength range from 119.5 nm to 10 microns. For the extreme-UV spectrum, we use the average quiet-Sun emission provided by Curdt et al. (2004).

## 2.4. Treatment of Aerosols

Microphysical processes involved in the formation of atmospheric aerosols are nucleation, condensational growth, and coagulation (Toon & Farlow 1981; Seinfeld & Pandis 2006). It is beyond the purpose of this work to simulate these microphysical processes in detail. For photochemically produced aerosols, the competition between coagulation and sedimentation mainly determines the particle size distribution. A complete treatment of the atmospheric aerosols involves solving the steady-state size distribution function (e.g. Seinfeld & Pandis 2006).

In our photochemical model, we simplify the problem by assuming the particle radius to be a free parameter. In Earth’s atmosphere, aerosols formed in the atmosphere often have a lognormal size distribution around 0.1 - 1  $\mu\text{m}$  (Seinfeld & Pandis 2006). We define a particle radius parameter,  $r_p$ , to be the surface area average radius. This parameterization allows us to separate the complexity of aerosol formation from the photochemistry model, as well as to explore how the particle size affects the overall chemical composition.

We compute the production and loss rate of a molecule in the condensed phase (i.e., aerosols) based on its condensation timescale. When the molecule becomes supersaturated at a certain altitude, condensation can happen and aerosols form. The condensation/evaporation timescale is given by Hamill et al. (1977) and Toon & Farlow (1981) as

$$\frac{1}{t_c} = \frac{m}{4\rho_p} \left( \frac{8k_B T}{\pi m} \right)^{1/2} \frac{n_g - n_v}{r_p}, \quad (15)$$

where  $t_c$  is the condensation/evaporation timescale,  $m$  is the mass of molecule,  $\rho_p$  is the particle density,  $k_B$  is the Boltzmann constant,  $T$  is the atmospheric temperature,  $n_g$  is the

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<sup>3</sup><http://rredc.nrel.gov/solar/spectra/am0/>

number density of the corresponding gas, and  $n_v$  is the saturated vapor number density at the corresponding pressure. The formula (15) is suitable for both condensation and evaporation processes. When  $n_g > n_v$ , the gas phase is saturated, so the condensation happens and  $t_c > 0$ . When  $n_g < n_v$ , the gas phase is unsaturated, so the evaporation is possible and  $t_c < 0$ . The production or loss rate of the molecule in the condensed phase is

$$P = \frac{n_g}{t_c}, \quad L = \frac{1}{t_c}. \quad (16)$$

We include gravitational settling in the mass flux term of the continuity-transport equation (equation 1) for aerosol particles in addition to eddy mixing. The additional gravitational downward flux of the aerosol particle is

$$\Phi_F = -v_F n_c, \quad (17)$$

where  $v_F$  is the settling velocity of the particle in the atmosphere. The settling velocity is reached when the gravitational force is balanced by the gas drag. For aerosols with diameter of order of  $1 \mu\text{m}$ , the settling velocity is reached within  $10^{-5}$  s in Earth’s atmosphere (Seinfeld & Pandis 2006). Therefore we assume the falling velocity to be the settling velocity. The settling velocity can be derived from the Stokes’ law (Seinfeld & Pandis, 2006) as

$$v_F = \frac{2 r_p^2 \rho_p g C_c}{9 \mu}, \quad (18)$$

where  $g$  is the gravitational acceleration,  $\mu$  is the viscosity of the atmosphere, and  $C_c$  is the slip correction factor related to the mean free path ( $\lambda$ ) of the atmosphere as

$$C_c = 1 + \frac{\lambda}{r_p} \left[ 1.257 + 0.4 \exp \left( - \frac{1.1 r_p}{\lambda} \right) \right]. \quad (19)$$

The treatment of photochemically produced aerosols described above is applicable to any molecules that could reach saturation as a result of photochemical production. In Earth’s atmosphere, the photochemical aerosols include sulfate aerosols ( $\text{H}_2\text{SO}_4$ ), sulfur aerosols ( $\text{S}_8$ ), organic hazes, nitric acid aerosols ( $\text{HNO}_3$ ), and hydrochloric acid aerosols ( $\text{HCl}$ ). For now we have implemented sulfate aerosols ( $\text{H}_2\text{SO}_4$ ) and sulfur aerosols ( $\text{S}_8$ ). These aerosols and water vapor are the common condensable materials at habitable temperatures that commonly exist in planetary atmospheres (e.g., Kasting et al. 1989; Pavlov et al. 2000; Seinfeld & Pandis 2006). The required data for including an aerosol species in the photochemistry model is the saturation vapor pressure. Saturation vapor pressure of  $\text{H}_2\text{SO}_4$  is taken as recommended by Seinfeld & Pandis (2006) for atmospheric modeling, with a validity range of 150 - 360 K. Saturation pressure of  $\text{S}_8$  is taken as the total sulfur saturation pressure



against liquid sulfur at  $T > 392$  K and solid (monoclinic) sulfur at  $T < 392$  K tabulated and expressed by Lyons (2008). In addition to aerosols, we use equation (15-16) to compute the process of condensation of water vapor in the atmosphere. We do not consider evaporation of condensed water in the atmosphere because water droplets may grow by aggregation and rapidly precipitate out (Seinfeld & Pandis 2006). Saturation pressure of water is taken as that against ice at temperature lower than 273.16 K (Murphy & Koop 2005), and that against liquid water at temperature higher than 273.16 K (Seinfeld & Pandis 2006).

We treat the optical effect of aerosols by considering both scattering and absorption. Assuming a homogeneous sphere, the Mie theory (see Van de Hulst, 1981 for a detail description) computes extinction cross section ( $\sigma_{\text{ext}}$ ), single scattering albedo ( $w_s$ ) and asymmetric factor ( $g_{\text{asym}}$ ), based on the following parameters: the refractive index of the material ( $m_r + m_i i$ ),  $r_p$ , and the wavelength. In this paper, we use the refractive index of  $S_8$  aerosols from Tian et al. (2010) for the UV and visible wavelengths and from Sasson et al. (1985) for infrared (IR) wavelengths. We use the refractive index of  $H_2SO_4$  aerosols (assumed to be the same as 75% sulfuric acid solution) from Palmer & William (1975) for UV to IR wavelengths, and Jones (1976) for far IR wavelengths.

## 2.5. Boundary Conditions

The atmospheric chemical composition of a terrestrial exoplanet is ultimately determined by boundary conditions. The upper boundary conditions describe the atmospheric escape. The lower boundary conditions describe the surface emission, the deposition of molecules and aerosols to the surface, or the presence of a large surface reservoir of certain molecule (e.g.  $H_2O$ ). The boundary conditions need to be properly provided to capture the physics of an exoplanet atmosphere.

The upper boundary conditions describe the atmospheric escape of an terrestrial exoplanet. The escape rates of exoplanet atmospheres are fairly uncertain depending on stellar soft X-ray and UV luminosity, exosphere chemistry, existence of magnetic fields, etc (e.g., Yelle et al. 2008; Tian 2009). We thus provide the following options of specifying escape rates in the photochemistry code:

Type 1:  $\Phi_{N_i+1/2} = 0$ , or no escape;

Type 2:  $\Phi_{N_i+1/2} = n_{N_i} V_{\text{lim}}$ , where  $V_{\text{lim}}$  is the diffusion-limited escape velocity;

Type 3:  $\Phi_{N_i+1/2}$  is a assigned nonzero value.

Here we use the same notation for flux as in equation (7-8), such that the upper boundary condition replaces the flux at the upper boundary of the layer  $N_l$  in equation (8). For the type 2 upper boundary condition (atmospheric escape), the diffusion-limited velocity ( $V_{\text{lim}}$ ) is

$$V_{\text{lim}} = D_{N_l+1/2} \left( \frac{1}{H_0} - \frac{1}{H} \right), \quad (20)$$

where  $D_{N_l+1/2}$  is the molecular diffusion coefficient evaluated at the top of the atmosphere. The diffusion-limited flux is the highest escape flux of an atmosphere in hydrostatic equilibrium (Hunten 1974). For Mars, the Jeans escape of  $\text{H}_2$  reaches the diffusion-limited flux when the exobase temperature is above 400 K (Zahnle et al. 2008). We use the Type 2 upper boundary condition for the escape of H and  $\text{H}_2$  in our model, and generally we assume no escape for all other species, i.e., the Type 1 upper boundary condition. The Type 3 upper boundary condition may be used when processes above the neutral atmosphere are important. For example, an influx of atomic N can represent the photodissociation of  $\text{N}_2$  in the upper atmosphere. The Type 3 boundary condition may also be used when hydrodynamic escape has to be considered.

The lower boundary conditions describe the interaction between the atmosphere and the surface, which includes surface emission and surface deposition. The three types of lower boundary conditions are:

Type 1:  $n_1$  is assigned;

Type 2:  $\Phi_{1/2} = -n_1 V_{\text{DEP}}$  where  $V_{\text{DEP}}$  is molecule-specific dry deposition velocity;

Type 3:  $\Phi_{1/2}$  is assigned.

Again we use the same notation for flux as in equation (7-8), and  $\Phi_{1/2}$  replaces the flux at the lower boundary of the layer 1 in equation (8).

The Type 1 lower boundary condition presents a large reservoir at the surface and for this paper we use this condition for water vapor to simulate the effect of a surface with oceans. This approach is equivalent to setting the relative humidity at the surface to be a constant. Note that specifying the Type 1 lower boundary condition means decreasing the number of free variables;  $n_1$  is fixed as the lower boundary condition and is no longer considered as a variable in the main computation loop.

The Type 2 lower boundary condition specifies the dry deposition velocity, which is a key parameter that determines the chemical composition of the atmosphere and is a major unknown. The deposition velocity depends on both the dynamical properties of the lower

atmosphere and the chemistry of the planet’s surface. With the number density at the bottom layer ( $n_1$ ) computed from the photochemistry model, the interaction between the bottom layer of atmosphere and the surface consists of two steps: first, the molecular transport across a thin stagnant layer of air adjacent to the surface, called the *quasi-laminar sublayer*; second, the uptake at the surface (Seinfeld & Pandis 2006). A parameterization of dry deposition velocity involving these two steps is described in Appendix C.

Physically the dry deposition requires a sink at the surface; for a gas without effective surface sink the dry deposition velocity should be zero. In particular, the surface deposition of a number of gases, including CO, H<sub>2</sub>, CH<sub>4</sub>, and NH<sub>3</sub>, is primarily removed by microorganisms on Earth (e.g., Kharecha et al. 2005; Seinfeld & Pandis 2006; Kasting, 2012, private communication), and the canonical values for their dry deposition velocities are not applicable for presumably abiotic planets. Take carbon monoxide for an example. If a planet has no ocean, there is no known reaction that can consume CO at the surface, and therefore the dry deposition velocity of CO for an abiotic desiccated planet should be zero (like Mars). If the surface has an ocean, the dissolved CO may be naturally and slowly converted into acetates by OH in sea water, or biologically converted into acetates at a much faster rate. The CO deposition velocity has been estimated to be  $1.2 \times 10^4$  cm s<sup>-1</sup> for the most efficient biological removal and  $10^{-8} \sim 10^{-9}$  cm s<sup>-1</sup> on an abiotic ocean planet (Kasting 1990; Kharecha et al. 2005). For another example, it is common to use a fairly large dry deposition velocity for SO<sub>2</sub> ( $\sim 1$  cm s<sup>-1</sup>) to study the sulfur cycle in Earth’s marine atmosphere (e.g., Toon et al. 1987). In contrast, the dry deposition velocity is assumed to be zero, or reduced by an arbitrary factor of up to 1000, to mimic a putative Mars ocean that is believed to be saturated with dissolved SO<sub>2</sub> and other sulfur species (e.g., Halevy et al. 2007; Tian et al. 2010). In general, the dry deposition velocity depends on a broad context of planetary geochemistry, notably on the surface mineralogy, the acidity of ocean, and the surface pressure and temperature. Therefore it is critical for exoplanet exploration to understand the interaction between atmospheric chemistry composition of terrestrial exoplanets and the surface deposition.

In addition to the dry deposition at the surface, we also include the wet deposition throughout the atmosphere as a removal process for soluble species. We use the parameterization of Giorgi & Chameides (1985) as

$$k_R(z) = f_R \times \frac{n_{\text{H}_2\text{O}}(z)k_{\text{H}_2\text{O}}(z)}{55A_V[L \times 10^{-9} + (H'RT(z))^{-1}]}, \quad (21)$$

where  $f_R$  is a reduction factor adjustable in the model,  $k_{\text{H}_2\text{O}}$  is the precipitation rate taken to be  $2 \times 10^{-6}$  s<sup>-1</sup>,  $A_V$  is the Avogadro’s number,  $L$  is the liquid water content taken to be 1 g m<sup>-3</sup> in the convective layer near the surface, and  $H'$  is the effective Henry’s Law

constant measuring the solubility of the molecule in the unit of  $\text{mol dm}^{-3} \text{ atm}^{-1}$ . The effective Henry’s law constant may differ from the standard Henry’s law constant when taking into account dissociation in the aqueous phase (Giorgi & Chameides 1985; Seinfeld & Pandis 2006). In the model we use the effective Henry’s Law constant published in Giorgi & Chameides (1985) as well as the standard Henry’s Law constants from the NIST Chemistry Webbook (<http://webbook.nist.gov/chemistry/>). Since the parameterization of equation (21) is primarily for modeling Earth’s atmosphere, the specific reduction factor  $f_R$  should be applied when it is reasonable to believe the hydrological cycle is reduced on an exoplanet (e.g., Tian et al. 2010).

The Type 3 lower boundary condition has assigned flux that represents the surface emission. Note that the dry deposition (Type 2) and assigned flux (Type 3) lower boundary conditions can be used at the same time, but assigned number density (Type 1) boundary condition over-rules other lower boundary conditions. For example,  $\text{SO}_2$  may be deposited to the surface at a rate proportional to the number density of the bottom layer, and also be emitted from the surface to the atmosphere at an assigned flux.

We finish this section with a definition of the so-called “redox balance”, the requirement of which arises when the fixed mixing ratio lower boundary condition (Type-1) is used in the photochemistry model. Following Kasting & Brown (1998), Zahnle et al. (2006), and Segura et al. (2007), we define  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$  as redox neutral, and assign the redox number ( $\mathcal{R}$ ) of any H-O-C-N-S molecule as the number of hydrogen in excess, i.e.,

$$\mathcal{R}(\text{H}_{a_1} \text{O}_{a_2} \text{N}_{a_3} \text{C}_{a_4} \text{S}_{a_5}) = a_1 - 2a_2 + 4a_4 + 4a_5. \quad (22)$$

Note that our definition of the redox number differs from Zahnle et al. (2006) and Segura et al. (2007) in the way that we count the number of H and they count the number of  $\text{H}_2$ . With our definition, for example, the redox number of  $\text{H}_2\text{S}$  is 6, and the redox number of  $\text{H}_2\text{SO}_4$  is -2. The redox balance says that the total redox influx to the atmosphere (i.e., surface emission) should be balanced by the total redox outflux from the atmosphere (i.e., atmospheric escape, dry deposition, and wet deposition), otherwise the atmosphere is being oxidized or reduced. The redox balance is equivalent to the conservation of total budget of hydrogen in the atmosphere, and is equivalent to the conservation of the total number of electrons in the atmosphere. One might consider the redox balance to be redundant. The redox balance is redundant if the lower and upper boundary conditions for all species are specified in fluxes (and not in mixing ratios). In many applications, however, it is useful to use the Type-1 lower boundary condition, which specifies mixing ratio. In that case, the mass conservation would not necessarily guarantee the redox balance. After all, an imbalance in the redox budget for a steady-state solution indicates either bugs in chemistry kinetics or unphysical boundary conditions. We explicitly check the redox balance for all our model

outputs.

### 3. Model Validation

We validate the photochemistry model by computing atmospheric compositions of current Earth and Mars. Due to the one-dimensional nature of the photochemistry model, we intend to compare with global averages of observations, if available. In most cases, however, the global average is only an order-of-magnitude representation of chemical composition of Earth’s and Mars’ atmospheres, because of strong diurnal and spatial variations. We should therefore expect our one-dimensional chemical-transport model to match quantitatively with the global average values to within a factor of two or three. For Mars, vertical profiles of most trace gas content have not yet been measured. We therefore compare our results with other photochemistry model outputs from the literature.

#### 3.1. Transport-Only Model for an Earth-like Atmosphere

As a test of transport-related schemes of the photochemical model, we first consider a transport-only case. In theory, for species whose removal timescales are significantly larger than their transport timescales, such as  $\text{CO}_2$  in Earth’s atmosphere, their mixing ratios do not change with altitude, i.e., they are well-mixed.

We turn off the chemical network deliberately and compute a model using Earth’s temperature profile to test the eddy diffusion transport, molecular diffusion transport, condensation, and rainout schemes of our chemical-transport model. A valid transport model should preserve hydrostatic equilibrium, predict well mixed mixing ratios for long-lived species, and predict a mixing ratio gradient for species that is rapidly removed in the atmosphere. We have verified that the transport scheme, although written in terms of number density rather than mixing ratio, preserves hydrostatic equilibrium. The fact that the code maintains hydrostatic equilibrium indicates that the transport scheme is numerically correct. We verify that long-lived species are well mixed, such as  $\text{CO}_2$  throughout the atmosphere, as shown in Figure 1. We assign a mixing ratio for  $\text{CO}_2$  at the surface and the code is able to predict a well-mixed vertical profile. We also verify that for  $\text{H}_2$  molecular diffusion tends to increase the mixing ratio when the molecular diffusion coefficient is comparable with the eddy diffusion coefficient (i.e., the homopause; see Figure 1). With a diffusion-limited escape, the effect of molecular diffusion and the effect of escape on the  $\text{H}_2$  vertical profile near the homopause largely cancel out (Figure 1), consistent with the definition of diffusion-limited escape. We

also show the behaviour of  $\text{H}_2\text{S}$ , a poorly mixed species, to compare with well-mixed  $\text{CO}_2$ . In this simplified model the only way to remove  $\text{H}_2\text{S}$  is photolysis, which requires photons with wavelengths shorter than 260 nm. Most of the photons in this wavelength range are effectively shielded by the major species  $\text{O}_2$ , so that removal rate of  $\text{H}_2\text{S}$  by photolysis near the surface is smaller than that in the stratosphere (see Figure 1).

Water vapor content in a rocky exoplanet’s atmosphere is controlled by the water reservoir at the planetary surface, vertical transport, and condensation. In our model, the mixing ratio of water vapor at the surface is assigned according to appropriate temperature-dependent relative humidity. Water vapor can be transported up into the atmosphere by eddy diffusion, and as the temperature decreases the atmosphere may become supersaturated in water as the altitude increases. For an Earth-like planet atmosphere, it is appropriate to assume a water vapor mixing ratio of 0.01 at the surface (which corresponds to a relative humidity of about 60%). The condensation scheme becomes effective when water vapor is supersaturated, which keeps the water vapor profile along the saturation profile. Such an approach to computing the atmosphere water vapor content is commonly adopted by other previously described photochemistry models of terrestrial planets (e.g., Nair et al. 1994; Yung & Demore 1999; Zahnle et al. 2008).

The one-dimensional transport model tends to saturate the tropopause and over-predict the amount of water vapor in the stratosphere. In fact, when using the US Standard Atmosphere 1976 as the temperature profile, the tropopause temperature is 217 K, much warmer than the required “cold trap” temperature ( $\sim 200$  K) in order to maintain a dry stratosphere (water vapor mixing ratio in a few ppm). Common 1-D transport-condensation schemes may over-predict the amount of water vapor above the cold trap by a few orders of magnitude, and therefore over-predict the strength of  $\text{HO}_x$  cycle in the stratosphere. This is a well known problem in modeling Earth’s atmosphere, mainly due to spatial and temporal variability of tropopause temperatures (K. Emmanuel, 2012, private communication). Tropospheric convection is most effective in transporting water vapor in tropics, where the tropopause temperature is the lowest and the number density of water vapor at the tropopause is the lowest compared with other latitudes. It is therefore likely that the tropopause is highly unsaturated as a global average. We use the temperature profile of the equatorial region in January (see Figure 1), and limit the water vapor saturation ratio to within 20%. In this way we reproduce the water vapor profile of the US Standard Atmosphere 1976, which has a dry stratosphere (Figure 1). The classic Manabe-Wetherald relative humidity profile for 1-D photochemistry models of Earth’s atmosphere also has 20% relative humidity at the tropopause (Manabe & Wetherald 1967).

As a result of water vapor condensation and rain, soluble gases are removed from the

atmosphere by wet deposition (rainout). We expect to see a decreasing slope in mixing ratio of the species being rained out, which depends on the rainout rate, itself dependent on the solubility of the species. For example,  $\text{SO}_2$  is much more soluble than  $\text{H}_2\text{S}$ , so that  $\text{SO}_2$  is more effectively rained out in the troposphere and cannot accumulate in the troposphere (see Figure 1).

### 3.2. Present-Day Earth

We compute a photochemical model to simulate the present-day Earth, and compare our results with globally averaged measurements. The most important photochemical process in Earth’s atmosphere is formation of the ozone layer, which leads to the temperature inversion in the stratosphere (e.g., Seinfeld & Pandis 2006). On the other hand, the tropospheric chemistry is mostly controlled by the hydrological cycle and surface emission of  $\text{CH}_4$ ,  $\text{NO}_x$  (i.e.,  $\text{NO}$  and  $\text{NO}_2$ ) and  $\text{SO}_2$ , and involves coupled processes of photochemistry and deposition. The reproduction of current Earth atmospheric composition is therefore a comprehensive validation of various aspects of the photochemistry model.

We start with a nominal 80%  $\text{N}_2$  and 20%  $\text{O}_2$  composition, having well-mixed  $\text{CO}_2$  of 350 ppm. We assume the water vapor mixing ratio at the surface is 0.01 (i.e., type-1 lower boundary condition), and let the water vapor be transported in the atmosphere and condense near the tropopause. The temperature profiles are assumed to be the 1976 US Standard Atmosphere (subsequently referred to as “Model A”) or a reference tropical atmosphere in January of 1986 from COSPAR<sup>4</sup> International Reference Atmosphere (CIRA, subsequently referred to as “Model B”; ), and the eddy diffusion coefficient is adopted from Massie & Hunten (1981), who have derived it from vertical profiles of trace gases. We model the atmosphere from 0 to 86 km altitude as 43 equally spaced layers. The incoming solar radiation is cut off for wavelengths shorter than 100 nm to account for the thermosphere absorption. The photolysis rates at the top layer of the atmosphere are tabulated in Table 7. Key trace species are assigned emission rates from the surface according to typical global values (Seinfeld & Pandis 2006). Emission rates and dry deposition velocities of these species are tabulated in Table 1.

Our models correctly simulate the photochemistry in Earth’s stratosphere. First, the formation of the ozone layer is correctly predicted. The modeled vertical profiles and amounts of ozone are consistent with the globally averaged measurements, as shown in Figure 2. Second, the nitrogen oxide cycle and the  $\text{HO}_x$  cycle are properly simulated. In Earth’s

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<sup>4</sup>Committee on Space Research

Table 1: Photochemistry model validation. For the surface emission and dry deposition velocities, measured surface mixing ratios are compared to our models using the 1976 US Standard Atmosphere (Model A) and using the reference tropical temperature profile (Model B).

Species	Surface Emission <sup>a</sup> (molecule cm <sup>-2</sup> s <sup>-1</sup> )	V <sub>DEP</sub> (cm s <sup>-1</sup> )	Surface Mixing Ratio		
			Measured <sup>e</sup>	Model A	Model B
CO	$3.7 \times 10^{11}$	0.03 <sup>b</sup>	40-200 ppb	113 ppb	101 ppb
CH <sub>4</sub>	$1.4 \times 10^{11}$	0.03 <sup>b</sup>	700-1745 ppb <sup>f</sup>	1939 ppb	1235 ppb
NH <sub>3</sub>	$7.7 \times 10^9$	1 <sup>d</sup>	0.1-10 ppb	0.24 ppb	0.24 ppb
N <sub>2</sub> O	$1.0 \times 10^9$	0 <sup>b</sup>	276-315 ppb <sup>f</sup>	302 ppb	290 ppb
NO	$7.0 \times 10^9$	0.016 <sup>b</sup>	0.02-10 ppb <sup>g</sup>	0.024 ppb	0.025 ppb
SO <sub>2</sub>	$9.0 \times 10^9$	1 <sup>c</sup>	30-260 ppt	237 ppt	239 ppt
OCS	$5.0 \times 10^7$	0.01 <sup>d</sup>	510 ppt	188 ppt	185 ppt
H <sub>2</sub> S	$2.0 \times 10^8$	0.015 <sup>c</sup>	1-13 ppt	3.92 ppt	3.62 ppt
H <sub>2</sub> SO <sub>4</sub>	$7.0 \times 10^8$	1 <sup>d</sup>	5-70 ppt <sup>h</sup>	127 ppt <sup>h</sup>	126.7 ppt <sup>h</sup>

<sup>a</sup>Typical globally averaged emission rates are taken from Seinfeld & Pandis (2006).

<sup>b</sup>Typical dry deposition velocities are taken from the compilation of Hauglustaine et al. (1994).

<sup>c</sup>Typical dry deposition velocities are taken from the compilation of Sehmel (1980).

<sup>d</sup>Dry deposition velocities are assumed by considering the solubility and reactivity of gases (see Appendix C).

<sup>e</sup>Mixing ratios at the surface are taken from Seinfeld & Pandis (2006).

<sup>f</sup>Ranges are from the preindustrial mixing ratio to the present-day value.

<sup>g</sup>Ranges are mixing ratio of NO<sub>x</sub> at the planetary boundary layer.

<sup>h</sup>Mixing ratio of SO<sub>4</sub><sup>2-</sup> in both gaseous and aqueous phases.

stratosphere, chemical species are rapidly converted to each other within the NO<sub>x</sub> group and the HO<sub>x</sub> group, and both cycles lead to catalytic destruction of ozone (e.g., Seinfeld & Pandis 2006). We reproduce the vertical profiles of NO<sub>x</sub> and HO<sub>x</sub> in the stratosphere (see Figure 2), qualitatively consistent with mid-latitude measurements. It appears that the models tend to over-predict the amounts of NO in the lower stratosphere. Third, for relatively long lived species in the stratospheres like N<sub>2</sub>O and CH<sub>4</sub>, our models produce correct altitude gradient of mixing ratios.

The key element of the tropospheric chemistry is the production of the hydroxyl radical OH, because OH is the major removal pathway for most species emitted from the surface. It has been established that OH in Earth’s troposphere is produced by reactions between



$O(^1D)$  and  $H_2O$ , and  $O(^1D)$  is produced by photolysis of  $O_3$  (Seinfeld & Pandis, 2006). In turn, the main source of tropospheric ozone is the  $NO_x$  cycle, with non-negligible effects of  $HO_x$  cycle and hydrocarbon chemistry as well. We find the surface ozone mixing ratio is 19 ppb and 22 ppb for Model 1976 and Model 1986 respectively, and the surface OH number density is  $2.0 \times 10^6 \text{ cm}^{-3}$  for Model 1976 and  $2.2 \times 10^6 \text{ cm}^{-3}$  for Model 1986, very close to the commonly adopted OH number density of  $1.0 \times 10^6 \text{ cm}^{-3}$ . We also confirm that the steady-state mixing ratios of major trace gases near the surface are consistent with ground measurements (see Table 1). The main removal mechanism of CO,  $CH_4$ , and  $NH_3$  is through reactions of OH, and  $N_2O$  is long-lived in the troposphere and is transported up to the stratosphere. Considering the significant spatial and temporal variability of the amount of OH, we conclude that our photochemistry model correctly computes the chemistry in Earth’s troposphere.

Our photochemistry model correctly treats the sulfur chemistry in Earth’s atmosphere (see Table 1). All sulfur-bearing emission, if not deposited, is oxidized in multiple steps in the troposphere and eventually converted into sulfate. Sulfite ( $S^{4+}$ ) and sulfate ( $S^{6+}$ ) are soluble in water and effectively removed from the atmosphere by rainout. Our photochemistry models simulate these processes, and find steady-state mixing ratios of sulfur-bearing species (e.g.,  $H_2S$  and  $SO_2$ ) consistently with the ground measurements. The models also predict the saturation of sulfate and the formation of sulfate aerosols as expected. The modeled mixing ratio of sulfate is slightly larger than observations, which might be related to the fact that we do not consider the hydration of  $H_2SO_4$ , nor the sulfate-facilitated cloud formation in our models.

In summary, we validate our photochemistry model by reproducing the chemical composition of current Earth’s atmosphere (see Table 1 and Figure 2). The photochemistry model is successful in predicting the formation of the ozone layer, treating key chemical cycles in both the stratosphere and the troposphere, computing oxidation of hydrocarbon, ammonia and sulfur-bearing species in the troposphere, and transporting long-lived species from the troposphere to the stratosphere. These aspects involve all chemical kinetics, photolysis, and transport processes, which not only verify that our photochemistry model is suitable for applications in oxidizing atmospheres, but also allows our model to be applied to other atmospheric scenarios.

### 3.3. Present-Day Mars

We validate our photochemistry model by simulating the atmosphere of present-day Mars. The current atmosphere of Mars is a thin  $CO_2$ -based atmosphere and its bulk chemical

composition is known from extensive ground-based observations (see Krasnopolsky 2006 and references therein). We validate our photochemistry code by reproducing the observed mixing ratios of CO and O<sub>3</sub>, and comparing with previous results regarding Martian atmosphere photochemistry. Key parameters and results of the present-Mars atmosphere model are shown in Table 2 and Figure 3. We emphasize that it is important to use temperature-dependent UV cross sections for modeling the photolysis and UV penetration in the Martian environment (see Anbar et al. 1993 for an error analysis of temperature-dependence of CO<sub>2</sub> in the Martian atmosphere).

The most important aspect of Martian atmospheric photochemistry is the stabilization of the CO<sub>2</sub> atmosphere by H, OH, and HO<sub>2</sub> (commonly referred to as odd hydrogens; Nair et al. 1994; Krasnopolsky 2006; Zahnle et al. 2008). Odd hydrogens, as catalysts, facilitate the recombination of photochemically produced CO and O<sub>2</sub> and maintain the CO<sub>2</sub> dominance of the Mars’ atmosphere (e.g. Nair et al. 1994; Krasnopolsky 2006; Zahnle et al. 2008). A pure CO<sub>2</sub> atmosphere is unstable against photolysis, because CO<sub>2</sub> can only be restored with a slow three-body reaction  $\text{CO} + \text{O} + \text{M} \longrightarrow \text{CO}_2 + \text{M}$  (e.g., Yung & DeMore 1999). Odd hydrogen species, including H, OH and HO<sub>2</sub>, are produced by photolysis of water vapor; and trace amounts of odd hydrogens can effectively stabilize the CO<sub>2</sub> dominant atmosphere (e.g. Nair et al. 1994; Krasnopolsky 2006; Zahnle et al. 2008). Nonetheless, one-dimensional photochemistry models tend to over-address the problem, predicting amounts of CO, O<sub>2</sub> and O<sub>3</sub> several times smaller than the observed values (e.g. Nair et al. 1994; Krasnopolsky 2006). By considering a slow dry deposition of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> to the surface, Zahnle et al. (2008) are able to predict the amount of CO, O<sub>2</sub> and H<sub>2</sub> that match observations. We follow the assumptions of Zahnle et al. (2008), and confirm the finding of appropriate amounts of O<sub>2</sub>, CO and H<sub>2</sub> (see Table 2 and Figure 3). We therefore reproduce the photochemical stability of the current Martian atmosphere.

The timescale of CH<sub>4</sub> removal can also be used for model validation. Rapid variation (over several years) of the amount of CH<sub>4</sub> in Mars’ atmosphere has been reported (e.g., Mumma et al. 2009), but the modeling of coupled general circulation and gas-phase chemistry find no known gas-phase chemistry path that allow such a rapid removal (e.g., Lefèvre & Forget 2009). Based on our fiducial model of Mars’ atmosphere, the loss timescale for CH<sub>4</sub> is computed to be about 240 years, within the same order of the magnitude of Lefèvre & Forget (2009).

In summary, we validate our photochemistry model by reproducing the atmospheric compositions of current Earth and Mars. We find that the model gives consistent results compared to observations and previous photochemistry models. All physical and chemical processes including photolysis, chemical reactions, transports, condensation, and deposition

Table 2: Photochemistry model validation. For the upper boundary flux and dry deposition velocities, measured mixing ratios of major trace gases on Mars are compared to our model.

Species	Upper Boundary Flux <sup>a</sup> (molecule cm <sup>-2</sup> s <sup>-1</sup> )	$V_{\text{DEP}}^{\text{b}}$ (cm s <sup>-1</sup> )	Column Averaged Mixing Ratio	
			Measured <sup>e</sup>	Modeled
O <sub>2</sub>	0	0	1200-2000 ppm	1545 ppb
CO	$-2.0 \times 10^7$	0	800 ppm	572 ppb
H <sub>2</sub>	$3.6 \times 10^8$	0	17 ppm	23 ppb
H <sub>2</sub> O <sub>2</sub>	0	0.02	0 ~ 40 ppb <sup>f</sup>	18 ppb
O <sub>3</sub>	0	0.02	0 ~ 120 ppb <sup>f</sup>	18 ppb

<sup>a</sup>H<sub>2</sub> upper boundary flux is computed from diffusion-limited escape velocity after finding the steady state. Besides tabulated values, influx of N of  $2.0 \times 10^6$  molecule cm<sup>-2</sup> s<sup>-1</sup>, NO of  $2.0 \times 10^7$  molecule cm<sup>-2</sup> s<sup>-1</sup>, and outflux of O of  $2.0 \times 10^7$  molecule cm<sup>-2</sup> s<sup>-1</sup>, are considered as input to the model.

<sup>b</sup>Dry deposition velocity is assumed to be 0.02 for reactive species, including H, O, O(<sup>1</sup>D), O<sub>3</sub>, OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, CHO<sub>2</sub>, CH<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>, CH<sub>4</sub>O<sub>2</sub>, NH<sub>3</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, and HNO<sub>4</sub> (e.g., Zahele et al. 2008). Dry deposition velocity is assumed to be zero for all other species.

<sup>e</sup>Mars data are from the compilation of Krasnopolsky (2006).

<sup>f</sup>Mixing ratios of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> have significant diurnal, seasonal and latitudinal variations.

are rigorously tested in these examples.

#### 4. Exoplanet Benchmark Cases

We now present three benchmark atmospheric scenarios of rocky exoplanets and summarize the effects of key photochemistry processes. The goal is to provide baseline models to assess the stability of molecules in different kinds of atmospheres in order to: identify the dominant stable molecules; calculate the lifetime of spectrally significant gases; and identify the amounts of the main reactive species that control molecule lifetimes. The benchmark cases are also intended to serve as the test cases for independent photochemistry models for rocky exoplanet atmospheres.

The key to assess molecular stability is the oxidation state of the atmosphere, because the main reactive species are linked to the oxidation state of the atmosphere. In an oxidizing atmosphere, OH and O are created by photochemistry and are the main reactive radicals. In a reducing atmosphere, H, also created by photochemistry, is the main reactive species. Although we expect the atmospheric composition will be highly varied, based on the nearly

continuous range of masses and orbits of exoplanets, we believe that the primary dimension of chemical characterization for terrestrial exoplanet atmospheres is their oxidation states. For the benchmark cases, therefore, we have chosen three endmembers in terms of atmospheric oxidizing power. The scenarios are a reducing (90% $\text{H}_2$ -10% $\text{N}_2$ ) atmosphere, a weakly oxidizing  $\text{N}_2$  atmosphere ( $> 99\%\text{N}_2$ ), and a highly oxidizing (90% $\text{CO}_2$ -10% $\text{N}_2$ ) atmosphere. We consider Earth-like volcanic gas composition that consists of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{SO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{S}$ , with emission rates comparable to current Earth. We assume that the planet surface has a substantial fraction of its surface covered by a liquid water ocean so that water is transported from the surface and buffered by the balance of evaporation/condensation. Key assumptions of the parameters of the three atmospheric scenarios are summarized in Table 3 and rationals of important model parameters are given in § 4.3.

We now describe the key results of the three atmosphere scenarios, for the 1-bar atmosphere on an Earth-size and Earth-mass habitable rocky exoplanet around a Sun-like star. We also describe qualitatively the behaviors of the atmospheres in the habitable zone of a quiet M dwarf, based on our numerical explorations. Mixing ratios of emitted gases, photochemical products, and reactive species in the three scenarios are tabulated in Table 4 and shown in Figure 4. Schematic illustrations of key non-equilibrium processes in the three scenarios are shown in Figure 5. We start with a qualitative overview of the key results, and then present the chemical properties of the three benchmark scenarios.

#### 4.1. General Results

We here list our main findings on general chemistry properties of atmospheres on habitable terrestrial exoplanets.

Atomic hydrogen (H) is a more abundant reactive radical than hydroxyl radical (OH) in anoxic atmospheres. Atomic hydrogen is mainly produced by water vapor photodissociation; and in anoxic atmospheres the main ways to remove atomic hydrogen is its recombination and reaction with CO. This is in contrast to oxygen-rich atmospheres (e.g., current Earth’s atmosphere) in which H is quickly consumed by  $\text{O}_2$ . As a result, removal of a gas by H is likely to be an important removal path for trace gases in an anoxic atmosphere. Atomic oxygen is the most abundant reactive radical in  $\text{CO}_2$  dominated atmospheres. Due to the photochemical origin of the reactive species including H, OH, and O, their abundances in the atmosphere around a quiet M dwarf are 2 orders of magnitude lower than their abundances around a Sun-like star.

Dry deposition velocities of long-lived compounds, notably major volcanic carbon com-

Table 3: Basic parameters for the terrestrial exoplanet benchmark scenarios. The benchmark scenarios are H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> atmospheres on habitable terrestrial exoplanets with Earth-like volcanic emissions. Note that we do not consider any known biosignature gas emission or biotic contribution to the dry deposition velocities.

Parameters	Reducing	Weakly Oxidizing	Highly Oxidizing
Main component	90%H <sub>2</sub> , 10%N <sub>2</sub>	> 99%N <sub>2</sub>	90%CO <sub>2</sub> , 10%N <sub>2</sub>
Mean molecular mass	4.6	28	42.4
<i>Planetary parameters</i>			
Stellar type	G2V	G2V	G2V
Semi-major axis	1.6 AU	1.0 AU	1.3 AU
Mass	$M_{\oplus}$	$M_{\oplus}$	$M_{\oplus}$
Radius	$R_{\oplus}$	$R_{\oplus}$	$R_{\oplus}$
<i>Temperature profile</i>			
Surface temperature	288 K	288 K	288 K
Surface pressure	10 <sup>5</sup> Pa	10 <sup>5</sup> Pa	10 <sup>5</sup> Pa
Tropopause altitude	120 km	13.4 km	8.7 km
Temperature above tropopause	160 K	200 K	175 K
Maximum altitude	440 km	86 km	51 km
<i>Eddy diffusion coefficient</i>			
In the convective layer	$6.3 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$	$1.0 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$	$6.8 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$
Minimum	$2.5 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$	$3.9 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$	$2.7 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$
Altitude for the minimum	107 km	17.0 km	11.6 km
Near the top of atmosphere	$7.1 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$	$1.1 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$	$7.6 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$
<i>Water and rainout</i>			
Liquid water ocean	Yes	Yes	Yes
Water vapor boundary condition	$f(\text{H}_2\text{O}) = 0.01$	$f(\text{H}_2\text{O}) = 0.01$	$f(\text{H}_2\text{O}) = 0.01$
Rainout rate <sup>a</sup>	Earth-like	Earth-like	Earth-like
<i>Gas emission<sup>b</sup></i>			
CO <sub>2</sub>	$3 \times 10^{11} \text{ cm}^{-2}$	$3 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$	N/A
H <sub>2</sub>	N/A	$3 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$	$3 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$
SO <sub>2</sub>	$3 \times 10^9 \text{ cm}^{-2}$	$3 \times 10^9 \text{ cm}^{-2}$	$3 \times 10^9 \text{ cm}^{-2}$
CH <sub>4</sub>	$3 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$	$3 \times 10^8 \text{ cm}^{-2}$	$3 \times 10^8 \text{ cm}^{-2}$
H <sub>2</sub> S	$3 \times 10^8 \text{ cm}^{-2}$	$3 \times 10^8 \text{ cm}^{-2}$	$3 \times 10^8 \text{ cm}^{-2}$
<i>Dry deposition velocity<sup>c</sup></i>			
H <sub>2</sub>	0		
CH <sub>4</sub>	0		
C <sub>2</sub> H <sub>6</sub>	$1.0 \times 10^{-5}$ (Assumed)		
CO	$1.0 \times 10^{-8} \text{ cm s}^{-1}$ (Kharecha et al. 2005)		
CH <sub>2</sub> O	$0.1 \text{ cm s}^{-1}$ (Wagner et al. 2002)		
CO <sub>2</sub>	$1.0 \times 10^{-4} \text{ cm s}^{-1}$ (Archer 2010)		
O <sub>2</sub>	0		
O <sub>3</sub>	$0.4 \text{ cm s}^{-1}$ (Hauglustaine et al. 1994)		
H <sub>2</sub> O <sub>2</sub>	$0.5 \text{ cm s}^{-1}$ (Hauglustaine et al. 1994)		
H <sub>2</sub> S	$0.015 \text{ cm s}^{-1}$ (Sehmel 1980)		
SO <sub>2</sub>	$1.0 \text{ cm s}^{-1}$ (Sehmel 1980)		
S <sub>8</sub> (A)	$0.2 \text{ cm s}^{-1}$ (Sehmel 1980)		
H <sub>2</sub> SO <sub>4</sub> (A)	$0.2 \text{ cm s}^{-1}$ (Sehmel 1980)		

<sup>a</sup>Rainout rates for H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and O<sub>2</sub> are generally assumed to be zero to simulate an ocean surface saturated with these gases on an abiotic exoplanet.

<sup>b</sup>The volcanic gas emission rates from the planetary surface are assigned for each model scenario. H<sub>2</sub>O emission is not explicitly considered because the surface has a large water reservoir, i.e., an ocean.

<sup>c</sup>We here list the dry deposition velocities (with references) for emitted gases and their major photochemical byproducts, and dry deposition velocities that are important for the mass and redox balance of the atmosphere. Dry deposition velocities are assumed to be identical for the three scenarios. C<sub>2</sub>H<sub>6</sub> dry deposition velocity is assumed to take into account the loss of carbon due to organic haze formation and deposition. CO<sub>2</sub> dry deposition velocity is estimated from a 10,000-year lifetime that matches with the lifetime of silicate weathering on Earth (Archer 2010; S. Solomon, private communication).

pounds including methane, carbon monoxide, and carbon dioxide, have significant effects on the atmospheric oxidation states. The specific choice of dry deposition velocities for emitted gases and their major photochemical byproducts in the atmosphere is critical to determine the atmospheric composition on terrestrial exoplanets.

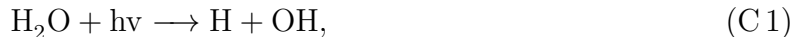
Volcanic carbon compounds (i.e., CH<sub>4</sub> and CO<sub>2</sub>) are chemically long-lived and tend to be well mixed in terrestrial exoplanet atmospheres, whereas volcanic sulfur compounds (i.e., H<sub>2</sub>S and SO<sub>2</sub>) are short-lived. CH<sub>4</sub> and CO<sub>2</sub> have chemical lifetime longer than 10,000 years in all three benchmark atmospheres ranging from reducing to oxidizing, implying that a relatively small volcanic input can result in a high steady-state mixing ratio. The chemical lifetime CO, another possible volcanic carbon compound, ranges from 0.1 to 700 years depending on the OH abundance in the atmosphere.

We find abiotic O<sub>2</sub> and O<sub>3</sub>, photochemically produced from CO<sub>2</sub> photolysis, build up in the 1-bar CO<sub>2</sub> dominated atmosphere if volcanic emission rates of reducing gases (i.e., H<sub>2</sub> and CH<sub>4</sub>) is more than one order of magnitude lower than current Earth’s volcanic rates. Abiotic O<sub>2</sub> can be a false positive for detecting oxygenic photosynthesis, but the combination of O<sub>2</sub>/O<sub>3</sub> and reducing gases remains rigorous biosignature.

## 4.2. Chemistry of H<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> Dominated Atmospheres

### 4.2.1. H<sub>2</sub> Dominated Atmospheres

The main reactive agent in the H<sub>2</sub> dominated atmosphere is atomic hydrogen (H). The abundance of atomic hydrogen is five orders of magnitudes higher than that of hydroxyl radical (Figure 4). The source of both H and OH is water vapor photodissociation. In the H<sub>2</sub> dominated atmosphere, most of the OH molecules produced from water vapor photodissociation react with H<sub>2</sub> to reform H<sub>2</sub>O and produce H through the reactions:



Therefore the abundance of atomic hydrogen is much higher than that of OH. We note that H production via water photodissociation is much more efficient than the direct photodissociation of H<sub>2</sub>, which requires radiation in wavelengths less than 85 nm. As water vapor is the primary source of H and OH in anoxic atmospheres, the amounts of H and OH depends on the mixing ratio of water vapor above the cold trap, which is in turn sensitively controlled by the cold trap temperature. Water vapor mixing ratio spans 3 orders of magnitudes for the cold trap temperature ranging in 160 - 200 K; consequently, the number densities of H

Table 4: Atmospheric compositions of terrestrial exoplanet benchmark scenarios. For the surface emission in 1-bar H<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> dominated atmospheres, mixing ratios of emitted gases, photochemical products and reactive agents are computed by the photochemistry model.

Scenario	Column Averaged Mixing Ratio		
	Emitted Gases	Photochemical Products <sup>a</sup>	Reactive Agents <sup>b</sup>
Reducing 90%H <sub>2</sub> , 10%N <sub>2</sub>	CO <sub>2</sub> : $8.9 \times 10^{-5}$	CO: $8.0 \times 10^{-6}$	H: $2.1 \times 10^{-9}$
	SO <sub>2</sub> : $9.9 \times 10^{-12}$	C <sub>2</sub> H <sub>6</sub> : $4.7 \times 10^{-10}$	OH: $2.0 \times 10^{-14}$
	CH <sub>4</sub> : $5.9 \times 10^{-6}$	S <sub>8</sub> : $3.5 \times 10^{-10}$	O: $1.2 \times 10^{-11}$
	H <sub>2</sub> S: $9.1 \times 10^{-10}$	CH <sub>2</sub> O: $2.9 \times 10^{-10}$	O( <sup>1</sup> D): $2.2 \times 10^{-21}$
		CH <sub>4</sub> O: $5.6 \times 10^{-11}$	
Weakly oxidizing N <sub>2</sub>	CO <sub>2</sub> : $1.3 \times 10^{-4}$	CO: $1.7 \times 10^{-7}$	H: $1.2 \times 10^{-9}$
	H <sub>2</sub> : $4.5 \times 10^{-4}$	C <sub>2</sub> H <sub>6</sub> : $9.0 \times 10^{-9}$	OH: $9.3 \times 10^{-14}$
	SO <sub>2</sub> : $8.9 \times 10^{-12}$	CH <sub>4</sub> O: $1.4 \times 10^{-9}$	O: $6.5 \times 10^{-10}$
	CH <sub>4</sub> : $3.1 \times 10^{-5}$	O <sub>2</sub> : $3.4 \times 10^{-10}$	O( <sup>1</sup> D): $1.8 \times 10^{-20}$
	H <sub>2</sub> S: $1.1 \times 10^{-14}$	S <sub>8</sub> : $3.0 \times 10^{-10}$	
		CH <sub>2</sub> O: $4.0 \times 10^{-11}$	
	C <sub>2</sub> H <sub>2</sub> : $1.5 \times 10^{-11}$		
Highly oxidizing 90%CO <sub>2</sub> , 10%N <sub>2</sub>	H <sub>2</sub> : $1.0 \times 10^{-3}$	CO: $7.7 \times 10^{-3}$	H: $6.0 \times 10^{-11}$
	SO <sub>2</sub> : $1.6 \times 10^{-10}$	O <sub>2</sub> : $6.4 \times 10^{-7}$	OH: $7.8 \times 10^{-15}$
	CH <sub>4</sub> : $3.7 \times 10^{-5}$	C <sub>2</sub> H <sub>6</sub> : $6.1 \times 10^{-10}$	O: $2.0 \times 10^{-8}$
	H <sub>2</sub> S: $1.4 \times 10^{-10}$	H <sub>2</sub> O <sub>2</sub> : $3.7 \times 10^{-10}$	O( <sup>1</sup> D): $3.0 \times 10^{-18}$
		H <sub>2</sub> SO <sub>4</sub> : $5.0 \times 10^{-11}$	
		CH <sub>2</sub> O: $2.5 \times 10^{-12}$	

<sup>a</sup>Species produced in the atmosphere from the emitted volcanic gases via photochemistry and subsequent series of chemical reactions, listed in the order of decreasing abundance. S<sub>8</sub> and H<sub>2</sub>SO<sub>4</sub> mixing ratios include both the gas phase and the condensed phase; whereas the condensed phase is found to contain more than 85% of mass.

<sup>b</sup>Common reactive agents in the atmosphere are H, OH, O, O(<sup>1</sup>D). We list the abundance of these gases in all three scenarios for as useful reference for the future assessment of chemical lifetime of trace gases.

and OH in the atmosphere can easily vary by one order of magnitude, depending on the cold trap temperature. The removal of atomic hydrogen is mainly by recombination to H<sub>2</sub>, which can be more efficient with the presence of CO, via



As a result of low OH abundance in the H<sub>2</sub> dominated atmosphere, both CH<sub>4</sub> and CO are long-lived and therefore well mixed. CH<sub>4</sub> emitted from the surface is slowly oxidized in the atmosphere into methanol, which gives methane a chemical lifetime of  $8 \times 10^4$  years. CO is produced by CO<sub>2</sub> photodissociation in our benchmark model; it is emitted by volcanoes on Earth at a much lower rate than CO<sub>2</sub>, but it can presumably be the main carbon-bearing gas produced by volcanoes if the upper mantle is more reduced than the current Earth’s (e.g., Holland 1984). We find that CO is long-lived in the H<sub>2</sub> atmosphere as well.

The lack of efficient atmospheric sink of CH<sub>4</sub> and CO in the H<sub>2</sub> atmosphere implies that surface sink, if any, is the major sink for these two carbon compounds. CH<sub>4</sub> and CO have zero or very small dry deposition velocities on an abiotic planet, so they can build up to significant amounts in the H<sub>2</sub> atmosphere (Figure 4). If a nonzero deposition velocity is adopted for CH<sub>4</sub> and CO, their steady-state mixing ratios will be much lower than the benchmark model. For example, using a deposition velocity for CH<sub>4</sub> standard on Earth ( $\sim 0.01 \text{ cm s}^{-1}$ ) results in a mixing ratio of less than 1 ppb for CH<sub>4</sub>, compared to a mixing ratio of 6 ppm in the benchmark model. The dry deposition velocity is indeed the controlling factor for the steady-state abundance of the long-lived carbon compounds. In comparison, the emitted sulfur compounds (H<sub>2</sub>S and SO<sub>2</sub>) are short-lived. In the H<sub>2</sub> atmosphere, sulfur emission from the surface is readily converted to elemental sulfur aerosols (S<sub>8</sub>) in the atmosphere.

Interestingly, CO<sub>2</sub> is fairly long-lived and well mixed in the H<sub>2</sub> atmosphere, meaning that the reduction of CO<sub>2</sub> in the H<sub>2</sub> dominated atmosphere is not efficient (Figure 4). Only 1/3 of emitted CO<sub>2</sub> is reduced in the atmosphere, and the rest is deposited to the surface by dry and wet deposition. It is the balance between surface emission and surface deposition that sets the steady-state mixing ratio of CO<sub>2</sub>.

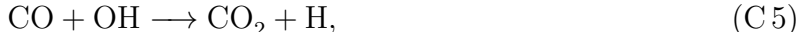
#### 4.2.2. N<sub>2</sub> Dominated Atmospheres

Both reducing radicals (i.e., H) and oxidizing radicals (i.e., O and OH) are relatively abundant in the N<sub>2</sub> atmosphere compared with the H<sub>2</sub> atmosphere (Figure 4). Like in H<sub>2</sub> dominated atmospheres, H abundance is orders of magnitude larger than OH abundance,



because most of OH molecules from water photolysis react with H<sub>2</sub> to reform H<sub>2</sub>O and produce H. The molecular hydrogen that consumes OH and boosts H is emitted volcanically, so a general N<sub>2</sub> atmosphere can be more oxidizing (i.e., having lower H and higher OH) if there is a lower volcanic H<sub>2</sub> emission and mixing ratio than the benchmark model.

An important feature of the N<sub>2</sub> dominated atmosphere is that both H and OH are relatively abundant near the surface. Comparing the N<sub>2</sub> dominated atmosphere with the H<sub>2</sub> dominated atmosphere (Figure 4), we find that both the OH and the H number densities are higher near the surface due to the lower H<sub>2</sub> number density. The relatively high OH number density leads to relatively fast removal of CO by



as shown in Figure 4. With a low CO abundance the recombination of H via reactions (C 3-C 4) is inefficient. Counter-intuitively, a high OH number density helps preserve H in this specific case. This example shows the complexity and the nonlinearity of an atmospheric chemical network. The feature of simultaneous high OH and H abundances near the surface is sensitive to the specification of surface hydrogen emission and eddy diffusion coefficients (see section 4.3 for relevant rationale).

The chemical lifetimes of CH<sub>4</sub> and CO mainly depend on the amount of OH. In the N<sub>2</sub> atmosphere, CH<sub>4</sub> is well mixed because its chemical lifetime is long. CH<sub>4</sub> is photodissociated and oxidized slowly in the atmosphere into methanol (CH<sub>4</sub>O) with a chemical lifetime of  $\sim 6 \times 10^4$  years. The photolysis of methane is a secondary source of atomic hydrogen, which concentrates at the pressure level of 10 Pa. Interestingly, methane photolysis causes the apparent trough of O<sub>2</sub> mixing ratio profile at  $\sim 10$  Pa. It is the shielding of the UV radiation that dissociates methane by methane itself that determines this pressure level (see Appendix D for an analytical formula for assessing the pressure level at which the photolysis of a certain gas is important).

CO<sub>2</sub> is actively photodissociated into CO and O in the upper atmosphere, but most of the CO produced is efficiently converted back to CO<sub>2</sub> by reacting with OH (reaction C 5). In equilibrium the net chemical removal of CO<sub>2</sub> is minimal, so the CO<sub>2</sub> mixing ratio is set by the balance between emission and deposition. The steady-state amount of CO<sub>2</sub> can be directly estimated by the mass balance between emission and deposition, viz.,

$$F = f_1 = \frac{n_1}{N_1} = \frac{\Phi_{1/2}}{V_{\text{DEP}} N_1}, \quad (23)$$

where the overall mixing ratio ( $F$ ) is the same as the near-surface mixing ratio ( $f_1$ ), and  $\Phi_{1/2}$  is the surface emission rate. For CO<sub>2</sub> in the N<sub>2</sub> dominated atmosphere, using equation (23), with  $V_{\text{DEP}}(\text{CO}_2) = 1 \times 10^{-4} \text{ cm s}^{-1}$ , we find the steady-state mixing ratio is  $1.3 \times 10^{-4}$ ,

consistent with the full photochemical model (see Table 4 and Figure 4). The steady-state mixing ratio of a long-lived volcanic gas that is primarily removed by surface deposition is inversely proportional to its dry deposition velocity.

Sulfur-bearing gases emitted from the surface are effectively converted into elemental sulfur and sulfuric acids. Elemental sulfur, mainly in the condensed phase (i.e., aerosols), is the major sulfur-bearing species in the steady state because of relatively high  $\text{H}_2$  mixing ratio in the benchmark model. In separate numerical simulations we find that sulfuric acid aerosols may outnumber elemental sulfur aerosols when the  $\text{H}_2$  emission is reduced by more than 1 order of magnitude and the atmosphere is more oxidizing than the benchmark model.

#### 4.2.3. $\text{CO}_2$ Dominated Atmospheres

$\text{CO}_2$  photodissociation produces CO, O, and  $\text{O}_2$ . Atomic oxygen is the most abundant reactive radicals in the  $\text{CO}_2$  dominated atmosphere (Figure 4), because H is readily removed by  $\text{O}_2$  and OH is readily removed by CO. As a result of low H and OH, CO is long-lived in the atmosphere and can build up to very high mixing ratios in the atmosphere depending on its dry deposition velocity; and  $\text{CH}_4$  emitted from the surface is also long-lived in the atmosphere with a chemical lifetime of  $\sim 6 \times 10^4$  years. The steady-state abundance of CO and  $\text{CH}_4$  is therefore controlled by their dry deposition velocities. Most of the emitted  $\text{SO}_2$  is deposited to the surface, because there are very few OH or O radicals near the surface. A small fraction of the  $\text{SO}_2$  is transported upwards and converted into sulfuric acid aerosols in the radiative layer.

Based on our benchmark model of  $\text{CO}_2$  dominated atmospheres, we now revisit whether photochemically produced  $\text{O}_2$  can cause false positive for detecting oxygenic photosynthesis. Oxygen and ozone are the most studied biosignature gases for terrestrial exoplanet characterization (e.g., Owen 1980; Angel 1986; Léger et al. 1993, 1996; Beichman et al. 1999). One of the main concerns of using  $\text{O}_2/\text{O}_3$  as biosignature gases is that  $\text{O}_2$  may be produced abiotically from photodissociation of  $\text{CO}_2$ . A number of authors have studied the abiotic production of oxygen in terrestrial atmospheres, either for understanding prebiotic Earth’s atmosphere (e.g., Walker 1977; Kasting et al. 1979; Kasting & Catling 2003), or for assessing whether abiotic oxygen can be a false positive for detecting photosynthesis on habitable exoplanets (Selsis et al. 2002; Segura et al. 2007). It has been proposed that abiotic oxygen from  $\text{CO}_2$  photodissociation is not likely to build up in the atmosphere on a planet having active hydrological cycle (Segura et al. 2007).

We find that the steady-state number density of  $\text{O}_2$  and  $\text{O}_3$  in the  $\text{CO}_2$  dominated

atmosphere is mainly controlled by the surface emission of reducing gases such as  $\text{H}_2$  and  $\text{CH}_4$ , and without surface emission of reducing gas photochemically produced  $\text{O}_2$  can build up in a 1-bar  $\text{CO}_2$  dominated atmosphere. In addition to the benchmark model, we have simulated  $\text{CO}_2$  dominated atmospheres with relatively low and zero emission rates of  $\text{H}_2$  and  $\text{CH}_4$  (Table 5 and Figure 6). We see that the  $\text{O}_2$  mixing ratio near the surface increases dramatically in 1-bar  $\text{CO}_2$  atmospheres when the emission of reducing gases decreases.  $\text{O}_2$  is virtually nonexistent at the surface for the Earth-like emission rates of  $\text{H}_2$  and  $\text{CH}_4$ ; but  $\text{O}_2$  mixing ratio can be as high as  $10^{-3}$  if no  $\text{H}_2$  or  $\text{CH}_4$  is emitted (Figure 6). In particular, if no  $\text{H}_2$  or  $\text{CH}_4$  is emitted, the  $\text{O}_3$  column integrated number density can reach one third of the present-day Earth’s atmospheric levels (Table 5), which constitutes a potential false positive.

In the 1-bar  $\text{CO}_2$  dominated atmosphere  $\text{O}_3$  can potentially build up to a false-positive level even on a planet with active hydrological cycle. Segura et al. (2007) have based their conclusion on simulations of 20%  $\text{CO}_2$  1-bar atmospheres with and without emission of  $\text{H}_2$  and  $\text{CH}_4$  and simulations of 2-bar  $\text{CO}_2$  atmospheres with emission of  $\text{H}_2$  and  $\text{CH}_4$ . We have been able to reproduce all results of Segura et al. (2007) quantitatively to within a factor of two. Where we differ from Segura et al. (2007) is that we successfully simulated high  $\text{CO}_2$  1-bar atmospheres with minimal volcanic reducing gas emission (Figure 6). This is a parameter space that Segura et al. (2007) did not cover, but we find that this is the parameter space for high abiotic  $\text{O}_2$ .

### 4.3. Rationale of Model Parameters

We here provide rationale for our specification of the atmospheric temperature profile, the eddy diffusion coefficients, and the dry deposition velocities.

First, the surface temperatures for the three scenarios are assumed to be 288 K, and the semi-major axis of the planet is adjusted according to appropriate amounts of greenhouse effect. The semi-major axis around a Sun-like star for  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  dominated atmospheres is found to be 1.6 AU, 1.0 AU, and 1.3 AU. We have compared the planetary thermal emission flux and the incidence stellar flux to determine the semi-major axis, a similar procedure as Kasting et al. (1993) taking into account  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_4$  absorption,  $\text{H}_2$  collision-induced absorption, and 50% cloud coverage and a Bond albedo of 30%. The temperature profiles are assumed to follow appropriate dry adiabatic lapse rate (i.e., the convective layer) until 160 K ( $\text{H}_2$  atmosphere), 200 K ( $\text{N}_2$  atmosphere), and 175 K ( $\text{CO}_2$  atmosphere) and to be constant above (i.e., the radiative layer). We simulate the atmosphere up to the altitude of about 10 scale heights, or the pressure level of 0.1 Pa. The adopted

Table 5: Mixing ratios of O<sub>2</sub> and O<sub>3</sub> and redox budget for CO<sub>2</sub>-dominated atmospheres on rocky exoplanets having different surface emission of reducing gases. The redox number for each species is defined according to equation (22). In the redox balance, all values have unit of molecule cm<sup>-2</sup> s<sup>-1</sup>, and defined as positive for hydrogen flux into the atmosphere. The redox budget for our atmosphere models is balanced, meaning that the atmosphere is not becoming more oxidized or reduced.

Chemical species	CO <sub>2</sub> -dominated atmospheres		
	$\Phi_{1/2}(\text{H}_2) = 3 \times 10^{10} \text{ cm s}^{-1}$	$\Phi_{1/2}(\text{H}_2) = 3 \times 10^9 \text{ cm s}^{-1}$	No H <sub>2</sub> Emission
<i>Column-averaged mixing ratio</i>			
O <sub>2</sub>	6.4E-7	3.8E-6	1.3E-3
O <sub>3</sub>	7.0E-11	3.7E-10	1.3E-7
<i>Redox balance</i>			
Atmospheric escape			
H	-7.0E+8	-2.4E+8	-1.2E+6
H <sub>2</sub>	-5.9E+10	-5.8E+9	-2.0E+6
Surface emission			
H <sub>2</sub>	6.0E+10	6.0E+9	0
CH <sub>4</sub>	2.4E+9	2.4E+9	0
H <sub>2</sub> S	1.8E+9	1.8E+9	1.8E+9
Dry and wet deposition			
O <sub>3</sub>	0	6.3E+4	1.1E+10
HO <sub>2</sub>	3.1E+4	7.8E+7	1.2E+8
H <sub>2</sub> O <sub>2</sub>	1.7E+5	1.5E+9	2.7E+9
CO	-3.7E+9	-5.6E+9	-1.5E+10
CH <sub>2</sub> O	-1.3E+6	-7.2E+4	0
OrganicHaze	-2.0E+6	-8.1E+1	0
H <sub>2</sub> S	-4.9E+8	-2.5E+8	-3.2E+8
H <sub>2</sub> SO <sub>4</sub>	1.2E+8	6.3E+7	2.9E+7
Balance	4.9E+3	-9.5E+2	-1.3E+3

temperature profiles are consistent with significant greenhouse effects in the convective layer and no additional heating above the convective layer for habitable exoplanets. The results discussed above do not change significantly if these temperature profiles are changed by several tens of K.

Second, we have used eddy diffusion coefficients empirically determined on Earth and scaled the values to account for different mean molecular masses. The eddy diffusion coefficient at a certain pressure level is assumed to be that of current Earth’s atmosphere at the same pressure level (see Figure 1), scaled by 6.3, 1.0, and 0.68 for the H<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> dominated atmospheres, respectively to account for different dominant molecules. We have roughly scaled the eddy diffusion coefficient assuming  $K \propto H_0$  where  $H_0$  is the atmospheric scale height. The reasoning of the scaling is as follows. According to the mixing length theory,  $K \propto lw$ , where  $l$  is the typical mixing length and  $w$  is the mean vertical velocity. The mixing length is a fraction of the pressure scale height (e.g., Smith 1998). The mean vertical velocity is related to the vertical convective energy flux, as  $F \propto pw$ , where  $p$  is the pressure (e.g., Lindzen 1990). For a certain planet  $F$  should have the same order of magnitude for different atmosphere compositions. As we apply the scaling from pressure surface to pressure surface, we have roughly  $K \propto H_0$ . The scaling is an approximation and we only intend to provide a consistent description of eddy diffusion for atmospheres with very different mean molecular mass. The eddy diffusion coefficients for the three scenarios are also consistent with their temperature profiles, featuring minima near the tropopause. The general results discussed above are not sensitive to the variation of eddy diffusion coefficients by an order of magnitude.

Third, the typical deposition velocity on Earth is sometimes not directly applicable for terrestrial exoplanets, because the major surface sink of a number of gases (notably, H<sub>2</sub>, CH<sub>4</sub>, CO) on Earth is actually microorganisms. In this paper we focus on the scenarios assuming no biotic contribution in neither surface emission nor surface deposition. For H<sub>2</sub> and CH<sub>4</sub>, a sensible dry deposition velocity without biotic surface sink is zero (J. Kasting, 2012, private communication). For CO<sub>2</sub>, the dry deposition velocity should match with the timescale of weathering and carbonate formation, which is 10,000 years (Archer et al. 2010). For CO, the rate limiting step for converting CO into bicarbonate has been proposed to the hydration of CO in the ocean, which corresponds to a deposition velocity of  $1.0 \times 10^{-9} \sim 10^{-8}$  cm s<sup>-1</sup> (Kharecha et al. 2005). The adopted or assumed values of dry deposition velocities are tabulated in Table 3.

For completeness, we now comment on our assumptions for nitrogen chemistry and organic haze. We do not track the bulk nitrogen cycle, instead assuming 10% N<sub>2</sub> for H<sub>2</sub> and CO<sub>2</sub> dominated atmospheres. Our model does not treat abiotic nitrogen fixation by lightning

(see Kasting & Walker 1981; Zahnle 1986; Tian et al. 2011 for specific analysis), so  $\text{N}_2$  is considered as inert in our models. We include the formation of elemental sulfur aerosols and sulfuric acid aerosols in our models; but we do not include the less-understood hydrocarbon chemical network for hydrocarbon molecules that have more than 2 carbon atoms or the formation of hydrocarbon haze. Organic haze may be formed in anoxic atmospheres based on methane photolysis and hydrocarbon polymerization. The number density of hydrocarbons that have more than 4 carbon atoms (usually considered to be condensable) is  $\sim 4$  orders of magnitude smaller than the number density of  $\text{C}_2\text{H}_6$  at the steady state (e.g. Allen et al. 1980; Yung et al. 1984; Pavlov et al. 2001). To account for the loss of carbon due to possible organic haze formation and deposition, we apply an *ad hoc* dry deposition velocity of  $1.0 \times 10^{-5} \text{ cm s}^{-1}$  for  $\text{C}_2\text{H}_6$ . This small velocity results from a scaling based on typical sub-micron particle deposition velocity ( $\sim 0.2 \text{ cm s}^{-1}$ , Sehmel 1980) and the number density ratio of  $\text{C}_4$  hydrocarbons and  $\text{C}_2\text{H}_6$  (e.g., Yung et al. 1984). An accurate treatment for organic haze is not the purpose of this paper, because the efficiency of haze formation depends on oxidation states of atmospheres, stellar UV radiation, and a number of less-understood reaction rates. Nonetheless, for all simulated scenarios, the carbon loss due to haze formation is less than 1% of the methane emission flux; therefore we do not expect our simplification of organic haze formation would impact our results. We will fully explore the formation of organic haze and its implication on atmospheric chemistry in a separate paper (Hu et al., in prep.).

## 5. Summary

We have developed a comprehensive photochemistry model for the study of terrestrial exoplanet atmospheres. The photochemistry model solves the one-dimensional chemical-transport equation for 111 O, H, C, N, S species including  $\text{S}_8$  and  $\text{H}_2\text{SO}_4$  aerosols. The output is the steady state of molecular mixing ratios in which concentrations of all species at all altitudes do not vary. In order to find the steady-state solution from arbitrary initial conditions for a wide variety of atmospheric compositions, required for the study of exoplanets, we have designed a numerical scheme that allows the selection of chemical species to be treated in fast or slow reactions automatically. The steady-state solution depends on a pool of input parameters, among which the major chemical species, surface emission, deposition velocities of long-lived species, and ultraviolet radiation are found to be critical. We validate the photochemistry model by simulating the atmospheric composition of current Earth and Mars.

Based on the photochemistry model, we have investigated the main chemistry processes

and lifetimes of key spectrally active species for rocky exoplanet atmospheres by simulating benchmark cases of atmospheres having redox states ranging from reducing to oxidizing. We find that atomic hydrogen is a more abundant reactive radical than hydroxyl radical in anoxic atmospheres, and therefore reactions with atomic hydrogen are likely to be an important removal pathway for spectrally important trace gases. The source of H and OH is water vapor photolysis in anoxic atmospheres, and the abundance of H in the atmosphere is always larger than the amount of OH because OH can react with  $\text{H}_2$  or CO to produce H. In addition to atomic hydrogen, in weakly oxidizing  $\text{N}_2$  atmospheres, OH, despite its lower abundance than H, is important in removing  $\text{CH}_4$  and CO. In highly oxidizing  $\text{CO}_2$  atmospheres, atomic oxygen is the most abundant reactive species.

As a general observation we find that volcanic carbon compounds are long-lived and volcanic sulfur compounds are short-lived. In particular, due to the scarcity of OH in anoxic atmospheres, methane is always long-lived having chemical lifetime longer than 10,000 years. We also find that the reduction of  $\text{CO}_2$  to CO and formaldehyde is minimal in  $\text{N}_2$  atmospheres and limited in  $\text{H}_2$  dominated atmospheres. In contrast to carbon species, volcanic sulfur compounds (i.e.,  $\text{H}_2\text{S}$  and  $\text{SO}_2$ ) are readily converted into either elemental sulfur or sulfuric acid aerosols in atmospheres from reducing to oxidizing. We will discuss in detail the sulfur chemistry in an accompanying paper (Hu et al. 2012).

The photochemistry is critical for prospecting the possible atmospheric composition that will eventually be characterized by a TPF-like mission. We have shown that volcanic carbon compounds including  $\text{CH}_4$  and  $\text{CO}_2$  are likely to be abundant in terrestrial exoplanet atmospheres; and in the accompany paper we will show that an enhanced volcanic activity leads to formation of optically thick sulfur or sulfate aerosols. As for biosignatures, we here have shown that photochemically produced  $\text{O}_2$  and  $\text{O}_3$  can be a potential false positive biosignature in thick  $\text{CO}_2$  atmospheres. We also find that oxygen and ozone can only build up without  $\text{H}_2$  and  $\text{CH}_4$  emission; so we confirm that simultaneous detection of ozone and methane remains a rigorous biosignature. More generally, the three benchmark models presented in this paper can serve as the standard atmospheres for reducing, weakly oxidizing, and highly oxidizing atmospheres on habitable exoplanets for assessing chemical lifetime of potential biosignature gases.

We thank James Kasting for helpful suggestions about the photochemical model. We thank Kerry Emanuel for enlightening discussion about modeling the Earth’s hydrological cycle. We thank Linda Elkins-Tanton for helpful suggestions on the mantle degassing. We thank Susan Solomon for discussions about  $\text{CO}_2$  cycle on terrestrial exoplanets. We thank the anonymous referee for the improvement of the manuscript. RH is supported by the NASA Earth and Space Science Fellowship (NESSF/NNX11AP47H).

### A. Formulation of Vertical Diffusion Flux

The vertical diffusion flux can be derived rigorously from the general diffusion equation for a minor constituent in a heterogenous atmosphere that

$$\Phi = -K \left[ \frac{\partial n}{\partial z} + n \left( \frac{1}{H_0} + \frac{1}{T} \frac{dT}{dz} \right) \right] - D \left[ \frac{\partial n}{\partial z} + n \left( \frac{1}{H} + \frac{1 + \alpha_T}{T} \frac{dT}{dz} \right) \right], \quad (\text{A1})$$

in which the first term is the eddy diffusion flux ( $\Phi_K$ ) and the second term is the molecular diffusion flux ( $\Phi_D$ ). Note that  $n = Nf$ , and then the eddy diffusion flux can be simplified as

$$\begin{aligned} \Phi_K &= -K \left[ \frac{\partial n}{\partial z} + n \left( \frac{1}{H_0} + \frac{1}{T} \frac{dT}{dz} \right) \right], \\ &= -K \left[ N \frac{\partial f}{\partial z} + fN \left( \frac{1}{N} \frac{\partial N}{\partial z} + \frac{1}{H_0} + \frac{1}{T} \frac{dT}{dz} \right) \right], \\ &= -K \left[ N \frac{\partial f}{\partial z} + fN \left( \frac{1}{N} \frac{\partial N}{\partial z} - \frac{1}{P} \frac{\partial P}{\partial z} + \frac{1}{T} \frac{dT}{dz} \right) \right], \\ &= -KN \frac{\partial f}{\partial z}, \end{aligned} \quad (\text{A2})$$

in which we have used the definition of atmospheric scale height and the ideal gas law.

The fundamental difference between the molecular diffusion and the eddy diffusion is in the scale height term. The molecular diffusion depends on the specific scale height for the molecule, whereas the total atmospheric pressure falls according to the mean scale height. The molecular diffusion term can be similarly simplified as

$$\begin{aligned} \Phi_D &= -D \left[ \frac{\partial n}{\partial z} + n \left( \frac{1}{H} + \frac{1 + \alpha_T}{T} \frac{dT}{dz} \right) \right], \\ &= -D \left[ \frac{\partial n}{\partial z} + n \left( \frac{1}{H_0} + \frac{1}{T} \frac{dT}{dz} \right) - n \left( \frac{1}{H_0} - \frac{1}{H} - \frac{\alpha_T}{T} \frac{dT}{dz} \right) \right], \\ &= -DN \frac{\partial f}{\partial z} + Dn \left( \frac{1}{H_0} - \frac{1}{H} - \frac{\alpha_T}{T} \frac{dT}{dz} \right), \end{aligned} \quad (\text{A3})$$

which yields equation (2).

### B. Mean Stellar Zenith Angle for 1-Dimensional Photochemistry Model

All 1-dimensional photochemistry models need to assume a zenith angle ( $\theta_0$ ) for the incoming stellar radiation as a global average. Various values have been adopted in previous photochemistry models, for example  $\theta_0 = 50^\circ$  (Zahnle et al. 2006),  $\theta_0 = 57.3^\circ$  (Zahnle et al.



2008), and  $\theta_0 = 48^\circ$  (Moses et al. 2011). We find that all these assumptions are plausible and provide justification as follows.

At different location of star-facing hemisphere of the planet, the local stellar zenith angle is  $\mu \equiv \cos \theta = \cos \psi \cos \phi$  where  $\psi$  and  $\phi$  are the local latitude and longitude, respectively. A dayside disk average should be weighted by the radiation intensity at certain optical depth  $\tau$ , viz.

$$\exp(-\tau/\mu_0) = \frac{1}{\pi} \int_{-\pi/2}^{\pi/2} \int_{-\pi/2}^{\pi/2} \exp(-\tau/\cos \psi \cos \phi) \cos^2 \psi \cos \phi d\psi d\phi. \quad (\text{B1})$$

Equation (B1) is well-defined for any particular level of optical depth, and can be solved numerically. The relationship between the average zenith angle and the optical depth of concern is illustrated in Figure 7.

We see in Figure 7 that the appropriate mean zenith angle depends on the optical depth of concern. We find that optical depth between 0.1 and 1.0 corresponds to a mean zenith angle between  $57^\circ$  and  $48^\circ$ . In the extreme of zero optical depth, the appropriate mean zenith angle is  $60^\circ$ . In general, it is appropriate to assume the mean zenith angle to be  $48^\circ \sim 60^\circ$  for the application of 1-dimensional photochemistry model.

### C. Deposition Velocities

In the photochemical model we calculate the number density in the bottom layer of the atmosphere. The interaction between the bottom layer and the surface consists of two steps: first, the molecular transport across a thin stagnant layer of air adjacent to the surface, called the *quasi-laminar sublayer*; second, the uptake at the surface. Each step provides a resistance to the overall dry deposition, viz.

$$V_{\text{DEP}}^{-1} = r_b + r_c, \quad (\text{C1})$$

in which  $r_b$  is the quasi-laminar resistance and  $r_c$  is the surface resistance. The quasi-laminar resistance is

$$r_b = \frac{5 \text{ Sc}^{2/3}}{u_*}, \quad (\text{C2})$$

in which Sc is the dimensionless Schmidt number defined as the ratio between the kinetic viscosity of air and the molecular diffusivity of the molecule considered, and  $u_*$  is the friction velocity (Seinfeld & Pandis 2006). The friction velocity depends on the wind speed adjacent to the surface and the roughness of the surface. In the current model, the friction velocity  $u_*$  should be treated as a free parameter varying from 0.1 to 1 m s<sup>-1</sup>.

The surface resistance is more complicated and largely depends on the property of the surface and the solubility of the molecule. For example, we consider two general types of surfaces, ocean and land. For the land we envisage desert-like surface and do not consider the complications of foliage.

For the deposition to the ocean, the surface resistance is

$$r_c = \frac{1}{k_G} + \frac{1}{k_L H}, \quad (\text{C3})$$

in which  $k_G$  is the gas phase mass transfer coefficient,  $k_L$  is the liquid phase mass transfer coefficient and  $H$  is the dimensionless Henry’s law constant (Seinfeld & Pandis 2006). These parameters depend on the wind speed (or the friction velocity), and the Schmidt number of the molecule in sea water.

The surface resistance to the land is even more complicated and depends on the properties of land, for example, surface morphology, roughness, vegetation, canopy, etc. There have been tremendous efforts to measure and parameterize the surface resistance of different molecules on different types of land on Earth. For example, the surface resistance to a featureless desert can be expressed as

$$r_c = \left( \frac{10^{-5} H}{r_S} + \frac{f_0}{r_O} \right)^{-1}, \quad (\text{C4})$$

in which  $H$  is in the unit of  $\text{M atm}^{-1}$ ,  $f_0$  is a normalized (0 to 1) reactivity factor,  $r_S = 1000 \text{ s m}^{-1}$  and  $r_O = 400 \text{ s m}^{-1}$  (Seinfeld & Pandis, 2006).

We present the deposition velocities of slightly soluble gases (such as  $\text{H}_2\text{S}$ ), highly soluble gases (such as  $\text{SO}_2$ ), not soluble but reactive gases (such as  $\text{O}_3$ ) to the ocean and the land in Figure 8. The deposition velocity to the ocean critically depends on the solubility of the gas. For poorly soluble gas, the deposition velocity to the ocean is negligible. For the highly soluble gas, the deposition velocity is limited by the friction velocity, or the wind speed. For the reactive gas, the deposition velocity can be also very high. In particular, the deposition velocity of  $\text{H}_2\text{S}$  to the land is negligible, and in most cases, the deposition velocity of  $\text{H}_2\text{S}$  to the ocean is smaller than  $0.1 \text{ cm s}^{-1}$ . The estimate of dry deposition velocity here only considers the surface uptake, but not the eventual loss of a gas at or beneath the surface. The effective dry deposition velocity might be smaller than what we estimate if no effective loss mechanism is available at the surface and the surface is saturated (e.g., Kharecha et al. 2005).

### D. Photochemical Stability of Atmospheric Trace Gases

We here present an analytical treatment of the photochemical stability of radiative trace gases. The goal of the analytical treatment is to obtain a useful formula that computes the critical pressure level of any radiative trace gas above which the photodissociation of the gas is important. The key idea is that the photolysis rate at any certain altitude (denoted as  $z^*$ ) is proportional to the radiation flux in the dissociating wavelengths at this altitude, which is attenuated by absorptions above  $z^*$ . The problem can be significantly simplified, if the absorption is mainly due to the gas itself. This is an analog to the concept of the Chapman layer in the ionosphere (e.g., Banks & Kockarts 1973).

In the following we first derive the analytical formula for the case of self-shielding and then extend the formula to the generic situation.

We intend to relate the ultraviolet optical depth to the pressure level. The ultraviolet optical depth in the dissociating wavelength range of a specified gas is

$$\tau_{\text{UV}} = \frac{\sigma_{\text{UV}}}{\mu_0} \int_{z^*}^{\infty} n(z) dz, \quad (\text{D1})$$

where  $\sigma_{\text{UV}}$  is the characteristic cross section in the wavelengths that lead to photolysis. Under hydrostatic conditions,

$$P_{\text{atm}} = M_{\text{atm}} g \int_{z^*}^{\infty} N(z) dz, \quad (\text{D2})$$

where  $P_{\text{atm}}$  is the atmospheric pressure at the altitude of  $z^*$  and  $M_{\text{atm}}$  is the mean molecular mass. We can define the column averaged mixing ratio as

$$F = \frac{\int_{z^*}^{\infty} n(z) dz}{\int_{z^*}^{\infty} N(z) dz}, \quad (\text{D3})$$

and then the UV optical depth at  $z^*$  can be related to the atmospheric pressure as

$$\tau_{\text{UV}} = \frac{\sigma_{\text{UV}} F P_{\text{atm}}}{\mu_0 g M_{\text{atm}}}. \quad (\text{D4})$$

The molecule is subject to rapid photodissociation if the UV optical depth is smaller than unity, or  $\tau_{\text{UV}} < 1$ , so that the critical pressure level above which photolysis is important is

$$P^* = \frac{\mu_0 g M_{\text{atm}}}{\sigma_{\text{UV}} F}. \quad (\text{D5})$$

The equation (D5) can be readily extended to include other gases in the atmosphere may provide additional shielding, viz.,

$$P^* = \frac{\mu_0 g M_{\text{atm}}}{\sigma_{\text{UV}} F + \sigma'_{\text{UV}} F'}, \quad (\text{D6})$$

where  $\sigma'_{UV}$  and  $F'$  is the cross section and the mixing ratio of the interfering species.

Equations (D5, D6) define a critical pressure level (or altitude) for each radiative trace gas subject to photolysis. Above the critical altitude, the gas is readily photodissociated and its mixing ratio decreases with altitude rapidly if no efficient reformation pathway exists; below the critical altitude, photolysis is not important and the gas is likely to be well-mixed. The critical pressure (altitude) is also defined for a certain mixing ratio. If the mixing ratio is larger, the critical pressure is smaller, and the gas is photochemically stable up to a higher altitude. Mean cross sections in dissociating wavelengths and the critical pressure level corresponding to 1 ppm mixing ratio of common spectrally active gases are tabulated in Table 6.

Table 6: Mean cross sections in dissociating wavelengths of common atmospheric trace gases and the critical pressures of photolysis. The mean cross sections are weighted by the Solar spectrum and quantum yields in the dissociation wavelengths. The critical pressure is evaluated according to equation (D5) with the conditions of  $\mu_0 = 0.5$ ,  $g = 9.8 \text{ m s}^{-1}$ ,  $M_{\text{atm}} = 4.65 \times 10^{-26} \text{ kg}$  ( $\text{N}_2$ -dominated atmosphere), and  $F = 10^{-6}$  (1 ppm). The additional shielding from other gases and reforming reactions are omitted in the estimate of critical pressures.

Name	Dissociation Wavelength (nm)	Mean Cross Section ( $\text{cm}^2$ )	1-ppm Critical Pressure (Pa)
$\text{H}_2$	18 – 85	1.10E-17	2.07E+02
$\text{O}_2$	4 – 245	7.18E-21	3.17E+05
$\text{H}_2\text{O}$	6 – 198	1.72E-18	1.33E+03
$\text{NH}_3$	8 – 230	1.31E-18	1.73E+03
$\text{N}_2\text{O}$	130 – 240	1.38E-20	1.65E+05
$\text{CH}_4$	52 – 152	1.81E-17	1.26E+02
$\text{CO}_2$	35 – 205	7.44E-22	3.06E+06
$\text{H}_2\text{S}$	5 – 259	1.11E-18	2.05E+03
$\text{OCS}$	186 – 296	2.74E-20	8.33E+04
$\text{SO}_2$	5 – 395	3.74E-18	6.09E+02

Despite simplicity, equations (D5, D6) predict the behavior of trace gases in the upper part of terrestrial exoplanet atmospheres, in agreement with results from the full photochemistry code. For example, 10-ppm methane in the  $\text{N}_2$  atmosphere is photodissociated above an altitude of  $\sim 10 \text{ Pa}$  pressure level, in agreement with Table 6. Using equation (D6) we estimate the 10-ppm critical pressure for methane in the  $\text{CO}_2$  atmosphere to be about 0.1

Pa, consistent with results from the full photochemistry code as shown in Figure 4. For another example, for  $\text{H}_2\text{S}$  in the  $\text{H}_2$  atmosphere, the near-surface mixing ratio is about  $10^{-9}$ , and according to Table 6, we find the critical pressure is in the order of  $10^5$  Pa, i.e.,  $\text{H}_2\text{S}$  is photodissociated at all altitudes of the  $\text{H}_2$  atmosphere. This is again consistent with the full photochemistry model (see the upper panel of Figure 4).

Equations (D5, D6) provide an order-of-magnitude assessment on whether or not a vertically well mixed distribution of gas is a good assumption when investigating spectra of super Earths. When the critical pressure defined by equations (D5, D6) is smaller than the pressure level that generates the spectral feature, it is plausible to assume the gas is vertically well-mixed. However, if the critical pressure is larger than the pressure level that generates the spectral feature, cautions should be taken because the gas could be photochemically depleted. If data suggests an abundance of a certain gas above its critical altitude, an additional mechanism, such as ultraviolet shielding by other gases, or efficient reformation, must be at play. In summary, equations (D5, D6) provide a simplified approach to take into account the effects of photochemistry for the interpretation of spectral features and for observation planning.

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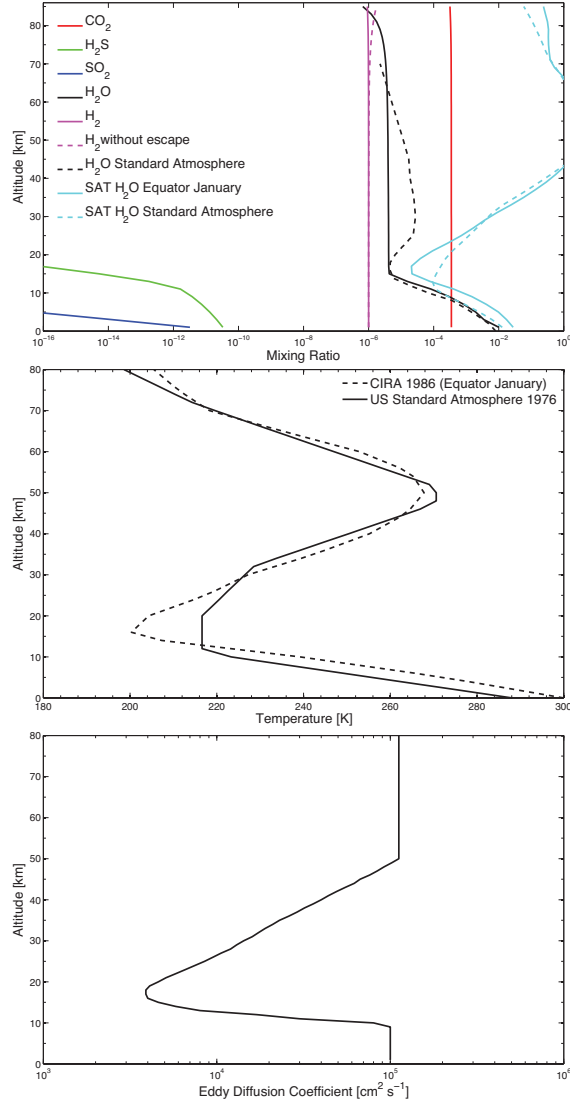


Fig. 1.— Validation of the transport and condensation schemes of our photochemistry code. Only vertical transport via eddy diffusion, molecular diffusion (for  $\text{H}_2$  only), dry deposition, wet deposition, condensation of water vapor, diffusion-limited escape of  $\text{H}_2$ , and photolysis of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{SO}_2$  and  $\text{H}_2\text{S}$  are considered for an Earth-like atmosphere. We omit all chemical kinetics to exclusively test the transport-related schemes.  $\text{H}_2\text{S}$  and  $\text{SO}_2$  are the only sulfur compounds in this test and they are considered as removed once photo-dissociated or deposited. The atmosphere has the temperature-pressure profile of COSPAR International Reference Atmosphere (CIRA) 1986 at the equator in January, as shown by the dashed line on the middle panel, and major constituents of 20%  $\text{O}_2$  and 80%  $\text{N}_2$ . Also on the middle panel we plot the temperature profile of US Standard Atmosphere 1976 for comparison. We adopt the eddy diffusion coefficient empirically derived from vertical profiles of trace gases (Massie & Hunten, 1981), shown in the lower panel. The boundary conditions are set as follows:  $\text{CO}_2$  mixing ratio at the surface 350 ppm;  $\text{H}_2\text{O}$  mixing ratio at the surface 0.01;  $\text{H}_2$  mixing ratio at the surface 1 ppm;  $\text{SO}_2$  surface emission flux  $9.0 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ ;  $\text{H}_2\text{S}$  surface emission flux  $2.0 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ . Water vapor in the atmosphere is limited by condensation. Steady-state mixing ratios are shown on the left panel, and the solid and dashed lines for  $\text{H}_2$

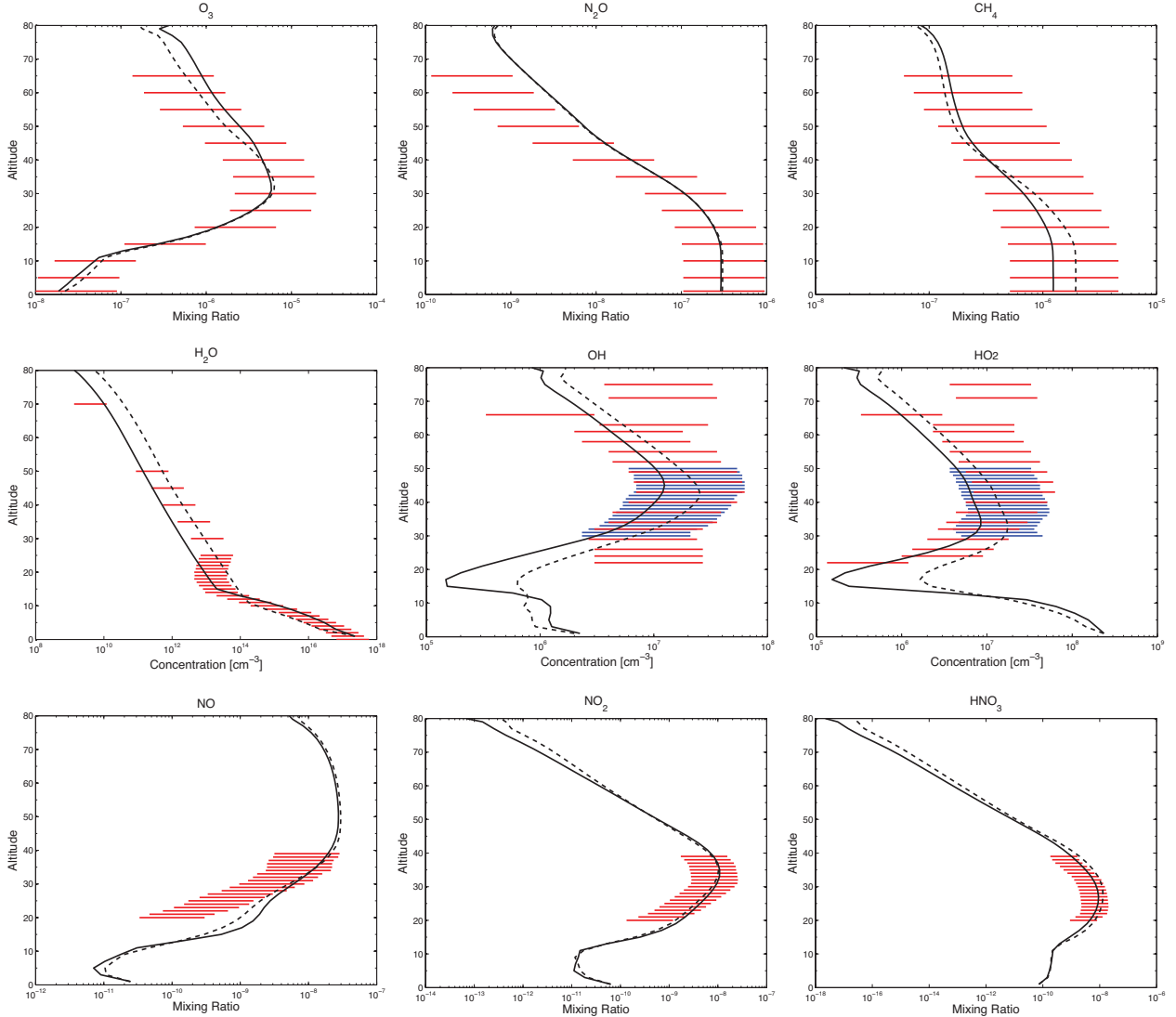


Fig. 2.— Profiles of key molecules in Earth’s atmosphere predicted by our photochemistry models using the US Standard Atmosphere 1976 for mid-latitudes (Model A; dashed lines) and the reference tropical temperature profile (Model B; solid lines), compared with selected observations (horizontal lines). We adopt the eddy diffusion coefficient empirically derived from vertical profiles of trace gases (Massie & Hunten, 1981), as shown in Figure 1. The error bars of observations are uniformly set to 1 order of magnitude to account for diurnal and spatial variations. The terrestrial data are: (1) globally averaged mixing ratios of O<sub>3</sub>, N<sub>2</sub>O and CH<sub>4</sub> compiled by Massie & Hunten (1981); (2) number density of H<sub>2</sub>O from the US Standard Atmosphere 1976 for mid-latitudes; (3) number densities of OH and HO<sub>2</sub> from balloon observations in Fairbanks, AK in 1997 (blue lines; Jucks et al. 1998); (4) number densities of OH and HO<sub>2</sub> from AURA satellite observations using the Microwave Limb Sounder that are zonally averaged over a latitude interval of 20° for a period of 15 days (Pickett et al. 2006); (5) mixing ratios of NO, NO<sub>2</sub> and HNO<sub>3</sub> from balloon observations at Lat~35°N in 1993 (Sen et al. 1998).



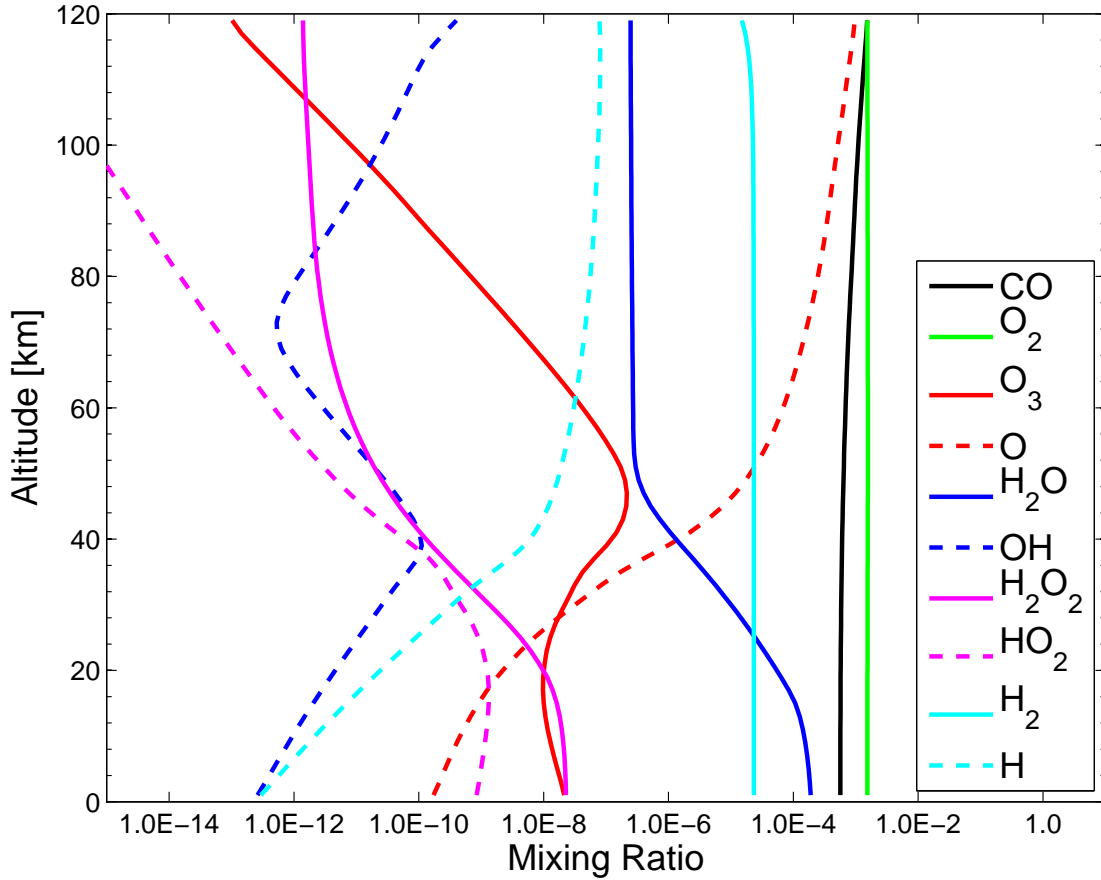


Fig. 3.— Profiles of key molecules in Mars’ atmosphere predicted by our photochemistry model. The chemical-transport model is computed with a 2-km grid from 0 to 120 km. For the UV flux computation, unattenuated solar flux at 1.524 AU and surface albedo of 0.1 are used. UV cross sections are computed at 200 K when their temperature dependencies are available from laboratory measurements. All C, H, O, N species and relevant reactions are computed. Ter-molecular reaction rates are multiplied by 2.5 to account for CO<sub>2</sub> being the third body (e.g., Zahnle et al. 2008). The eddy diffusion coefficient is assumed to have a profile as equation (6) with  $K_T = 10^6 \text{ cm}^2 \text{ s}^{-1}$ ,  $K_H = 10^8 \text{ cm}^2 \text{ s}^{-1}$  and  $z_T = 20 \text{ km}$ . The atmospheric temperature profile is assumed as Zahnle et al. (2008): surface temperature 210 K, lapse rate of  $1.4 \text{ K km}^{-1}$  until 50 km and then isothermal of 140 km up to 120 km. The relative humidity at the surface is fixed at 0.19, and the water vapor is transported up into atmosphere by eddy mixing, limited by condensation. The maximum saturation of water vapor of 60% is imposed, which gives a column number density of 9.8 precipitable microns. Wet deposition is reduced compared to Earth, with the rainout factor assumed to be 0.01 in the model.

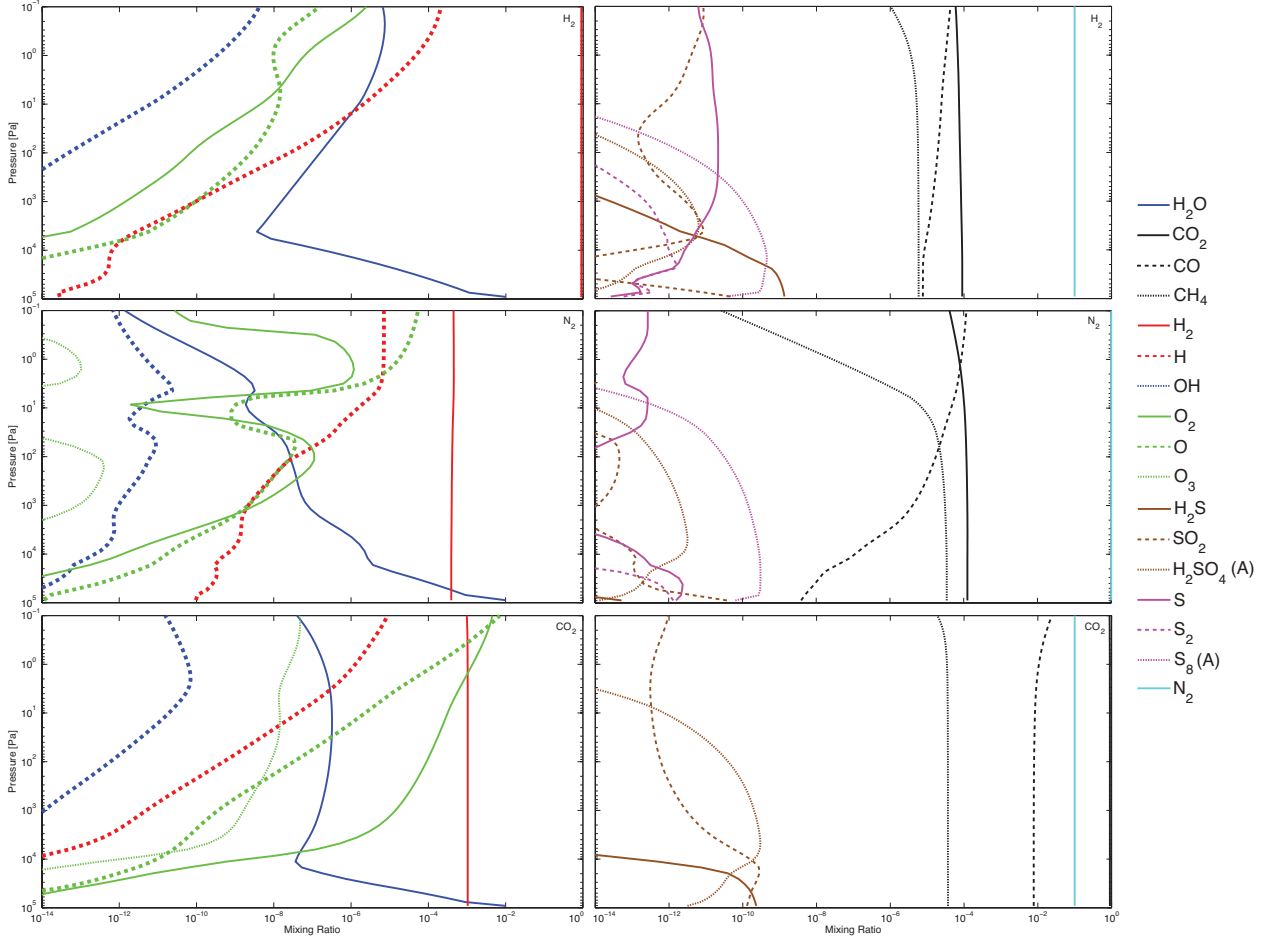


Fig. 4.— Compositions of the three scenarios of rocky exoplanet atmospheres tabulated in Table 4. The left column shows mixing ratios of H and O species, and the right column shows mixing ratios of N, C, and S species. From top to bottom, the three panels correspond to the reducing (H<sub>2</sub>-dominated), oxidized (N<sub>2</sub>-dominated), and highly oxidized (CO<sub>2</sub>-dominated) atmospheres. The vertical scales are expressed in pressure, which allows comparison between different scenarios that have very different mean molecular masses, and hence the altitude difference for a given pressure change. We highlight the profiles of three reactive species, H, OH, and O by thick lines.

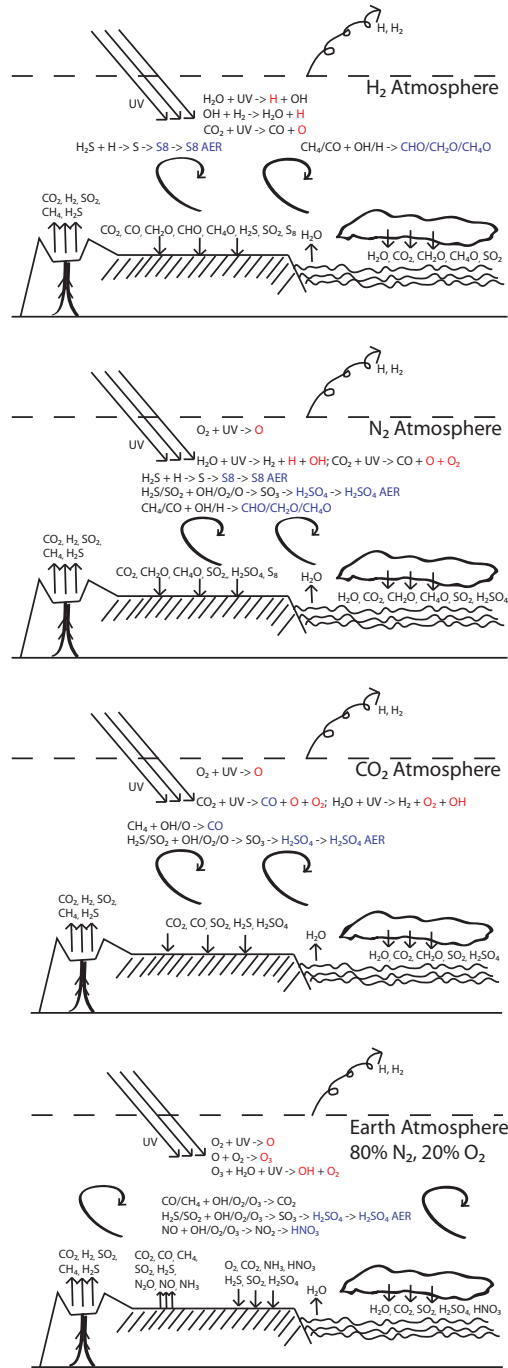


Fig. 5.— Schematic illustrations of key non-equilibrium processes in the 3 scenarios of rocky exoplanet atmospheres considered in this paper (Table 4), in comparison with the current Earth. From top to bottom, the four panels correspond to the H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> atmospheres, and the atmosphere of Earth. The red color highlights the reactive radicals in each atmospheric scenario, and the blue color highlights the major photochemical products in the atmosphere.

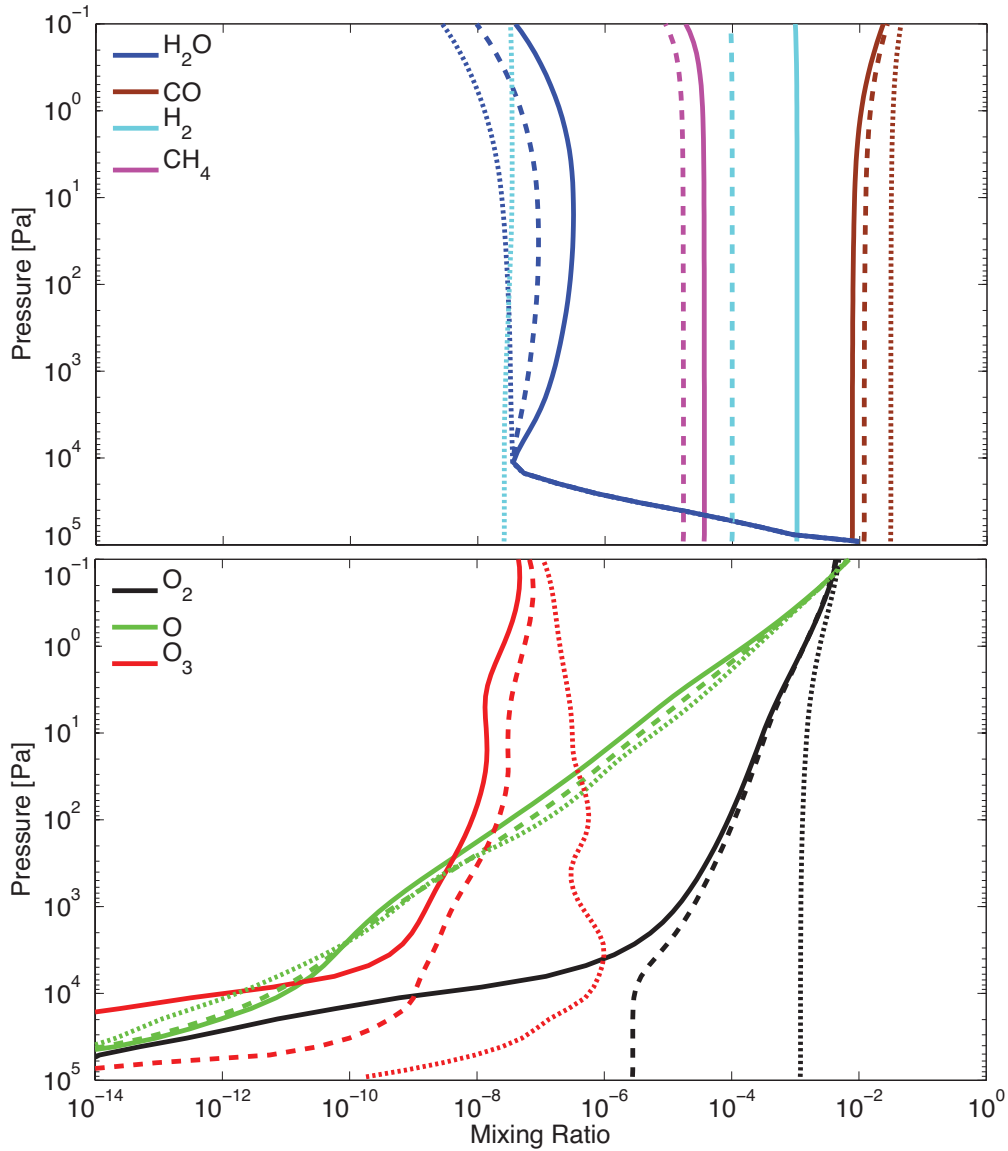


Fig. 6.— Effects of the surface volcanic emission for  $CO_2$ -dominated atmospheres on rocky exoplanets. The upper panel shows mixing ratios of  $H_2O$ ,  $CO$ ,  $H_2$ , and  $CH_4$ , and the lower panel shows mixing ratios of  $O_2$ ,  $O$ , and  $O_3$ . The solid lines show the chemical composition of the benchmark scenario whose parameters are tabulated in Table 3. In particular the emission rate of  $H_2$  is  $3 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ . The dashed lines show the chemical composition of the same scenario, but with an  $H_2$  emission rate of  $3 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ ; and the dotted lines show the chemical composition for zero emission of  $H_2$  and  $CH_4$ . We see a dramatic increase of  $O_2$  and  $O_3$  mixing ratios as a result of a decrease of the surface emission of reduced gases.

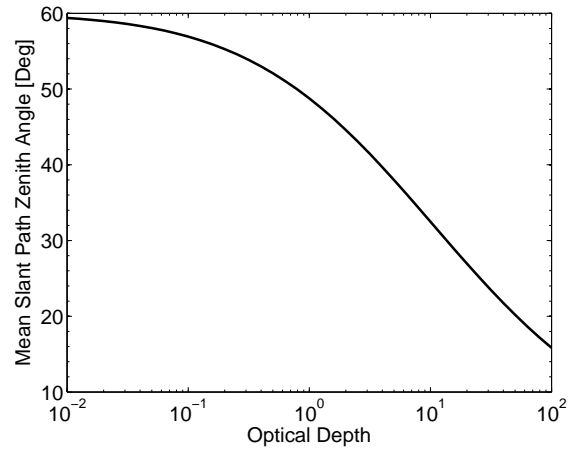


Fig. 7.— Mean zenith angle of stellar radiation for photochemistry models as a function of optical depth.

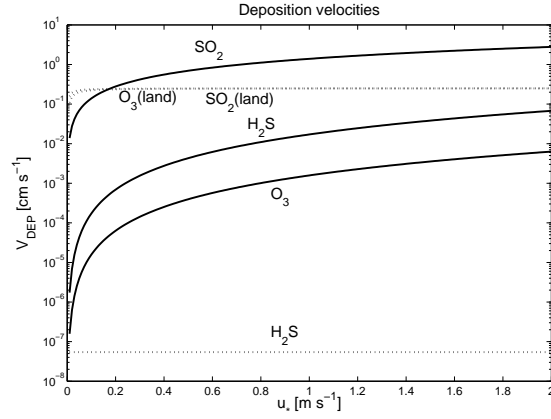


Fig. 8.— Deposition velocities to the ocean (solid lines) and the land (dotted lines) as a function of the friction velocity  $u_*$ . The calculation is for the terrestrial atmosphere at  $T = 273.15 \text{ K}$ ,  $P = 1 \text{ atm}$ . The ocean is assumed to have a pH of about 6.5. The land is assumed to be featureless desert.

Table 7: Photolysis reactions in our photochemistry model. The rates ( $s^{-1}$ ) are computed with the unattenuated Solar spectrum at 1 AU with cross sections and quantum yields at 295 K and 200 K, and divided by 2 for diurnal average.

No.	Reactants	Products	Rate 295 K	Rate 200 K	Cross Sections	T <sup>a</sup>	Quantum Yields	T <sup>a</sup>	Note
1	O2	O + O	3.52E-7	3.52E-7	4-108nm: Brion et al. (1979) 108-129nm: Ogawa & Ogawa (1975)	N N	<139nm: 0.5 139-175nm: 0 175-242nm: 1.0	N N N	
2	O2	O + O(1D)	1.40E-6	1.40E-6	129-173nm: Yoshino et al. (2005) 176-203nm: Kockarts (1976) 205-245nm: JPL Rec (2011)	N N	<139nm: 0.5 139-175nm: 1.0 175-242nm: 0	N N N	
3	O3	O2 + O	6.33E-4	6.28E-4	110-172nm: Mason et al. (1996) 186-230nm: JPL Rec (2011) 230-1070nm: Bogumil et al. (2003)	N N Y	<186nm: 0.71 186-220nm: JPL Rec (2011) 220-340nm: Matsumi et al. (2002) 340-411nm: 0.92 >411nm: 1.0	N N Y Y N	
4	O3	O2 + O(1D)	3.66E-3	3.63E-3			<186nm: 0.29 186-220nm: JPL Rec (2011) 220-340nm: Matsumi et al. (2002) 340-411nm: 0.08 >411nm: 0	N Y N N	
5	HO2	O + OH	2.87E-4	2.87E-4	190-260nm: JPL Rec (2011)	N	190-260nm: 1.0	N	
6	H2O	H + OH	5.78E-6	5.78E-6	6-120nm: Chan et al. (1993) 121-198nm: JPL Rec (2011)	N N	6-198nm: 1.0	N	
7	H2O2	OH + OH	4.77E-5	4.57E-5	190-350nm: JPL Rec (2011)	Y	190-350nm: 1.0	N	
8	NO2	NO + O	4.49E-3	4.13E-3	16-200nm: Au & Brion (1997) 205-235nm: Atkinson et al. (2004) 238-667nm: Vandaele et al. (1998) 667-910nm: Bogumil et al. (2003)	N Y Y Y	<398nm: 1.0 398-428nm: JPL Rec (2011) >428nm: 0	N Y N	
9	NO3	NO + O2	1.05E-2	1.43E-2	403-691nm: JPL Rec (2011)	Y	403-691nm: JPL Rec (2011)	Y	
10	NO3	NO2 + O	8.32E-2	1.02E-1			403-691nm: JPL Rec (2011)	Y	
11	N2O	N2 + O(1D)	6.94E-7	5.53E-7	130-160nm: Nicolet & Peetermans (1972) 160-240nm: JPL Rec (2011)	N Y	130-140nm: 0 140-230nm: 1.0 230-240nm: 0	N N N	
12	N2O5	NO3 + NO2	8.55E-5	4.82E-5	200-410nm: JPL Rec (2011)	Y	<248nm: 1.0 248-300nm: Linear interpolation >300nm: 0	N N N	
13	N2O5	NO3 + NO + O	1.51E-4	1.45E-4			<248nm: 0 248-300nm: Linear interpolation >300nm: 0.7	N N N	
14	HNO2	NO + OH	8.40E-4	8.40E-4	184-396nm: JPL Rec (2011)	N	184-396: 1.0	N	
15	HNO3	NO2 + OH	6.16E-5	5.43E-5	105-191nm: Suto & Lee (1984) 192-350nm: JPL Rec (2011)	N Y	<193nm: 0.33 193-200nm: Linear interpolation 200-350nm: 1.0	N N N	
16	HNO3	HNO2 + O	1.94E-5	1.92E-5			<193nm: 0.39 193-200nm: Linear interpolation 200-350nm: 0.0	N N N	
17	HNO3	HNO2 + O(1D)	1.40E-5	1.38E-5			<193nm: 0.28 193-200nm: Linear interpolation 200-350nm: 0.0	N N N	
18	HNO4	NO2 + HO2	1.83E-4	1.83E-4	190-350nm: JPL Rec (2011)	N	190-350nm: JPL Rec (2011)	N	
19	HNO4	NO3 + OH	4.89E-5	4.89E-5			190-350nm: JPL Rec (2011)	N	
20	CH2O	CHO + H	4.16E-5	4.16E-5	226-375nm: JPL Rec (2011)	Y	226-250nm: 0.31 250-375nm: JPL Rec (2011)	N N	
21	CH2O	H2 + CO	3.55E-5	3.31E-5			226-250nm: 0.49 250-375nm: JPL Rec (2011)	N Y	P dependence omitted
22	C2H4O	CH3 + CHO	2.59E-5	2.59E-5	202-360nm: JPL Rec (2011)	N	<256nm: 0.29 256-332nm: JPL Rec (2011) >332nm: 0	N N N	
23	C2H4O	CH4 + CO	3.14E-6	3.14E-6			<256nm: 0.48 256-332nm: JPL Rec (2011) >332nm: 0	N N N	

Table 8: Table 7 continued ...

24	CH4O2	CH3O + OH	2.53E-5	2.53E-5	210-405nm: JPL Rec (2011)	N	210-405nm: 1.0	N	
25	CH3NO2	CH3O + NO	1.58E-3	1.58E-3	190-440nm: JPL Rec (2011)	N	190-440nm: 1.0	N	
26	CH3NO3	CH3O + NO2	1.40E-4	1.36E-4	190-344nm: JPL Rec (2011)	Y	190-344nm: 1.0	N	
27	CH2O2	CHO + OH	6.20E-6	6.20E-6	195-250nm: JPL Rec (2011)	N	195-250nm: 0.7	N	
28	CH2O2	CHO2 + H	1.33E-6	1.33E-6		N	195-250nm: 0.15	N	
29	CH2O2	H2O + CO	1.33E-6	1.33E-6		N	195-250nm: 0.15	N	
30	SO3	SO2 + O	2.33E-5	2.33E-5	140-180nm: Hintze et al. (2003) 180-330nm: JPL Rec (2011)	N N	140-330nm: 1.0	N	
31	OC5	CO + S	1.99E-5	1.69E-5	186-296nm: JPL Rec (2001)	Y	186-296nm: 1.0	N	
32	CH4	CH3 + H	1.95E-6	1.95E-6	52-125nm: Kameta (2002) 125-142nm: Chen & Wu (2004) 142-152nm: Lee et al. (2001)	N	0.41 (Smith & Raulin 1999)	N	
33	CH4	<sup>1</sup> CH2 + H2	2.52E-6	2.52E-6		N	0.53 (Smith & Raulin 1999)	N	
34	CH4	CH + H2 + H	2.85E-7	2.85E-7		N	0.06 (Smith & Raulin 1999)	N	
35	CO	C + O	3.94E-7	3.94E-7	6-177nm: Chan et al. (1993)	N	<111nm: 1.0 >111nm: 0	N N	
36	CO2	CO + O	5.65E-9	3.71E-9	35-197nm: Huestis & Berkowitz (2011) 197-270nm: Ityakov et al. (2008)	Y N	<167nm: 0 167-205nm: 1.0 >205nm: 0	N N N	
37	CO2	CO + O(1D)	5.57E-7	5.48E-7	Note: 108-118nm: Stark et al. (2007, 195K) 118-163nm: Yoshino et al. (1996, 195K) 163-193nm: Parkinson et al. (2003, 195K)		<167nm: 1.0 167-205nm: 0 >205nm: 0	N N N	
38	H2	H + H	1.68E-8	1.68E-8	18-70nm: Lee et al. (1976) 70-87nm: Cook & Metzger (1964) 87-124nm: Backx et al. (1976)	N N N	<80nm: 0.1 (Mentall & Gentieu 1970) 80-85nm: 1.0 >85nm: 0	N N N	
39	N2	N + N	5.61E-7	5.61E-7	6-108nm: Chan et al. (1993)	N	6-108nm: 1.0	N	
40	CH4O	CH3O + H	5.97E-6	5.97E-6	16-106nm: Burton et al. (1992) 106-165nm: Nee et al. (1985) 165-220nm: Cheng et al. (2002)	N N N	16-220nm: 1.0	N	
41	HCN	H + CN	3.16E-7	3.16E-7	133-145nm: Macpherson & Simons (1978)	N	133-145nm: 1.0		Incomplete wavelength coverage
42	NH3	NH2 + H	6.89E-5	6.89E-5	8-106nm: Samson et al. (1987) 106-140nm: Wu et al. (2007) 140-230nm: Cheng et al. (2006)	N	<106nm: 0.3 (Lilly et al. 1973)	N	
43	NH3	NH + H2	1.55E-6	1.55E-6		N	106-165nm: Linear interpolation >165nm: 1.0	N N	
44	NO	N + O	4.69E-6	4.69E-6	7-177nm: Lida et al. (1986) 186-227nm: Thompson et al. (1968)	N	<191nm: 1.0 >191nm: 0	N	
45	H2S	HS + H	1.48E-4	1.52E-4	5-160nm: Feng et al. (1999) 160-260nm: Wu & Chen (1998)	Y Y	5-260nm: 1.0	N	
46	SO2	SO + O	1.06E-4	8.61E-5	5-106nm: Feng et al. (1999) 106-171nm: Manett & Lane (1993) 171-239nm: Wu et al. (2000) 239-395nm: Bogumil et al. (2003)	N	<220nm: 1.0	N	
47	SO2	SO2 <sup>1</sup>	8.26E-4	8.17E-4		Y	220-340nm: 0 >340nm: 0	N N	
48	SO2	SO2 <sup>3</sup>	7.51E-7	1.66E-6		Y	<220nm: 0 220-340nm: 1.0 >340nm: 0	N N N	
49	HSO	HS + O	2.87E-4	2.87E-4	190-260nm: JPL Rec (2011)	N	<340nm: 0 >340nm: 1.0	N N	
50	H2SO4	SO3 + H2O	1.41E-5	1.41E-5	118-180nm: Mills et al. (2005) 510-735nm: Lane & Kjaergaard (2008)	N N	190-260nm: 1.0	N	Assumed as HO2
							118-180nm: 1.0 510-735nm: 1.0	N N	



Table 9: Table 7 continued ...

51	SO	S + O	3.70E-4	3.70E-4	100-190nm: Linear interpolation 190-235nm: Phillips (1981)	N N	100-235nm: 1.0	N	
52	S2	S + S	4.00E-3	4.00E-3	Photolysis around 280nm, value estimated by De Almeida & Singh (1986).				
53	S3	S2 + S	5.76E-1	5.76E-1	350-475nm: Billmers & Smith (1991)	N	350-475nm: 1.0	N	
54	S4	S2 + S2	1.10E-1	1.10E-1	425-575nm: Billmers & Smith (1991)	N	425-575nm: 1.0	N	
55	C2H2	C2H + H	5.86E-6	5.42E-6	6-137nm: Cooper et al. (1995) 137-185nm: Smith et al. (1991) 185-236nm: Benilan et al. (2000)	N Y Y	6-217nm: 1.0 (Lauter et al. 2002) >217nm: 0	N	
56	C2H3	C2H2 + H	6.25E-3	6.25E-3	225-238nm: Fahr et al. (1999) 400-446nm: Hunziker et al. (1983)	N N	225-446nm: 1.0	N	Incomplete Wavelength Coverage
57	C2H4	C2H2 + H2	6.52E-6	6.52E-6	50-105nm: Holland et al. (1997) 105-175nm: Lu et al. (2004) 175-209nm: Orkin et al. (1997)	N	50-209nm: 0.4	N	
58	C2H4	C2H2 + 2H	8.15E-6	8.15E-6		N	50-209nm: 0.5	N	
59	C2H4	C2H3 + H	1.63E-6	1.63E-6		N	50-209nm: 0.1	N	
60	C2H5	CH3 + CH2 <sup>1</sup>	4.24E-4	4.24E-4		200-260nm: Fagerstrom et al. (1993)	N	200-260nm: 1.0	N
61	C2H6	C2H4 + H2	8.84E-7	8.84E-7	13-120nm: Kameta et al. (1996) 120-150nm: Chen & Wu (2004) 150-160nm: Lee et al. (2001)	N	13-160nm: 0.14 (Akimoto et al. 1965)	N	
62	C2H6	C2H4 + 2H	1.96E-6	1.96E-6		N	13-160nm: 0.31	N	
63	C2H6	C2H2 + 2H2	1.71E-6	1.71E-6		N	13-160nm: 0.27	N	
64	C2H6	CH4 + CH2 <sup>1</sup>	1.39E-6	1.39E-6		N	13-160nm: 0.22	N	
65	C2H6	CH3 + CH3	3.79E-7	3.79E-7		N	13-160nm: 0.06	N	
66	N2H2	N2 + H2	1.13E-4	1.13E-4	191-291nm: Vaghjiani (1993)	N	191-291nm: 1.0	N	Assumed as N2H4
67	N2H4	N2H3 + H	1.13E-4	1.13E-4	191-291nm: Vaghjiani (1993)	N	191-291nm: 1.0	N	
68	CH5N	HCN + 2H2	1.21E-5	1.21E-5	5-83nm: Burton et al. (1994) 83-247nm: Hubin-Franskin et al. (2002)	N N	5-247nm: 0.08	N	
69	C2H5N	HCN + CH3+ H	2.67E-5	2.67E-5	111-213nm: Basch et al. (1969)	N	111-213nm: 0.1	N	
70	HNO	NO + H	8.40E-4	8.40E-4	184-396nm: JPL Rec (2011)	N	184-396: 1.0	N	Assumed as HNO2

<sup>a</sup>Temperature dependence of cross sections and quantum yields: Y indicates temperature dependence is taken into account for the respective wavelength range.

Table 10:: Reaction rates of bi-molecular reactions (R), ter-molecular reactions (M) and thermo-dissociation reactions (T) in the photochemistry model. In the column “Temperature” we note the temperature range for which each reaction rate is valid. We annotate “Low Temperature” and “High Temperature” to the reaction rates only valid at temperatures lower than 300 K and higher than 1000 K, respectively. For low-temperature applications, including explorations of Solar-System terrestrial planets and habitable exoplanets, we exclude those reactions marked as “High Temperature”.

No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R1	C + CH <sub>2</sub>	→ CH + CH	$2.69 \times 10^{-12} \exp(-23573.0/T)$	NIST	1000-4000	
R2	C + CN	→ C <sub>2</sub> + N	$4.98 \times 10^{-10} \exp(-18041.0/T)$	NIST	5000-8000	
R3	C + H <sub>2</sub>	→ CH + H	$6.64 \times 10^{-10} \exp(-11700.0/T)$	NIST	1520-2540	
R4	C + H <sub>2</sub> S	→ CH + HS	$2.1 \times 10^{-10}$	NIST	298	
R5	C + N <sub>2</sub>	→ CN + N	$8.7 \times 10^{-11} \exp(-22611.0/T)$	NIST	2000-5000	
R6	C + O <sub>2</sub>	→ CO + O	$5.1 \times 10^{-11} (T/298.0)^{-0.3}$	NIST	15-295	Low Temperature
R7	C + OCS	→ CO + CS	$1.01 \times 10^{-10}$	NIST	298	
R8	C + SO <sub>2</sub>	→ CO + SO	$6.91 \times 10^{-11}$	NIST	298	
R9	C <sub>2</sub> H + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	$1.6 \times 10^{-12}$	NIST	300-2500	
R10	H <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>5</sub> + H	$1.69 \times 10^{-11} \exp(-34277.6/T)$	NIST	300-2500	
R11	C <sub>2</sub> H + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>2</sub>	$3.0 \times 10^{-12}$	NIST	300-2500	
R12	C <sub>2</sub> H + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	$6.0 \times 10^{-12}$	NIST	300-2500	
R13	C <sub>2</sub> H + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + C <sub>2</sub> HO	$4.0 \times 10^{-11}$	NIST	300-2500	
R14	C <sub>2</sub> H + CH <sub>4</sub> O	→ C <sub>2</sub> H <sub>2</sub> + CH <sub>3</sub> O	$2.0 \times 10^{-12}$	NIST	300-2500	
R15	C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H	$4.5 \times 10^{-13} \exp(-11800.0/T)$	NIST	300-2500	
R16	C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>3</sub>	$1.6 \times 10^{-12} \exp(-2300.0/T)$	NIST	290-310	Low Temperature
R17	C <sub>2</sub> H <sub>2</sub> + CN	→ HCN + C <sub>2</sub> H	$2.2 \times 10^{-10}$	NIST	294	
R18	C <sub>2</sub> H <sub>3</sub> + C <sub>2</sub> H <sub>4</sub> O	→ C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>3</sub> O	$1.35 \times 10^{-13} \exp(-1850.0/T)$	NIST	480-520	Low Temperature
R19	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>3</sub> + C <sub>2</sub> H <sub>6</sub>	$5.83 \times 10^{-14} (T/298.0)^{3.13} \exp(-9060.0/T)$	NIST	300-2500	
R20	C <sub>2</sub> H <sub>4</sub> + CN	→ HCN + C <sub>2</sub> H <sub>3</sub>	$2.1 \times 10^{-10}$	NIST	294	
R21	C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>4</sub>	$4.4 \times 10^{-11}$	NIST	298	
R22	C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>2</sub>	$2.4 \times 10^{-11}$	NIST	298	
R23	C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>4</sub> O	→ C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>3</sub> O	$2.1 \times 10^{-12} \exp(-4280.0/T)$	NIST	357-676	Low Temperature
R24	C <sub>2</sub> H <sub>5</sub> + CNO	→ HCN + C <sub>2</sub> H <sub>4</sub> O	$8.7 \times 10^{-13}$	NIST	293	
R25	C <sub>2</sub> H <sub>5</sub> + CNO	→ HCNO + C <sub>2</sub> H <sub>4</sub>	$1.1 \times 10^{-10}$	NIST	293	
R26	C <sub>2</sub> H <sub>5</sub> O + O <sub>2</sub>	→ C <sub>2</sub> H <sub>4</sub> O + HO <sub>2</sub>	$6.3 \times 10^{-14} \exp(-550.0/T)$	JPL	200-300	Low Temperature
R27	C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>4</sub>	$1.46 \times 10^{-13} (T/298.0)^{3.3} \exp(-5280.0/T)$	NIST	300-2500	
R28	C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>4</sub> O + C <sub>2</sub> H <sub>5</sub>	$1.91 \times 10^{-13} (T/298.0)^{2.75} \exp(-8820.0/T)$	NIST	300-2500	
R29	C <sub>2</sub> H <sub>6</sub> + CN	→ HCN + C <sub>2</sub> H <sub>5</sub>	$1.36 \times 10^{-11} (T/298.0)^{1.26} \exp(208.0/T)$	NIST	300-2500	
R30	CH + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>4</sub> + CH <sub>3</sub>	$1.3 \times 10^{-10}$	NIST	298	
R31	CH + CH	→ C <sub>2</sub> H <sub>2</sub>	$2.0 \times 10^{-10}$	NIST	298	
R32	CH + CH <sub>2</sub> O	→ C <sub>2</sub> H <sub>3</sub> O	$1.57 \times 10^{-10} \exp(260.0/T)$	NIST	297-670	Low Temperature
R33	CH + CH <sub>4</sub>	→ C <sub>2</sub> H <sub>4</sub> + H	$1.7 \times 10^{-11}$	NIST	298	
R34	CH <sub>2</sub> + C <sub>2</sub> H	→ C <sub>2</sub> H <sub>2</sub> + CH	$3.0 \times 10^{-11}$	NIST	300-2500	

Continued on next page ...

No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R35	CH <sub>2</sub> + C <sub>2</sub> H <sub>2</sub> O	→ C <sub>2</sub> H <sub>4</sub> + CO	2.1 × 10 <sup>-10</sup>	NIST	298	
R36	CH <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + CH <sub>3</sub>	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R37	CH <sub>2</sub> + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>2</sub> O + CH <sub>3</sub>	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R38	CH <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>4</sub> + CH <sub>3</sub>	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R39	CH <sub>2</sub> + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + CH <sub>3</sub>	1.07 × 10 <sup>-11</sup> exp(-3980.0/T)	NIST	296-707	Low Temperature
R40	NH <sub>2</sub> + OH	→ NH <sub>2</sub> + O	2.94 × 10 <sup>-12</sup> (T/298.0) <sup>0.1</sup> exp(5800.0/T)	NIST	298-3000	
R41	H <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>3</sub> + H	4.0 × 10 <sup>-12</sup> exp(-32714.0/T)	NIST	300-2500	
R42	CH <sub>2</sub> + CH <sub>2</sub>	→ C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub>	2.62 × 10 <sup>-9</sup> exp(-6010.0/T)	NIST	1100-2700	High Temperature
R43	CH <sub>2</sub> + CH <sub>2</sub>	→ C <sub>2</sub> H <sub>2</sub> + H + H	3.32 × 10 <sup>-10</sup> exp(-5530.0/T)	NIST	1100-2700	High Temperature
R44	CH <sub>2</sub> + CH <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + H	7.0 × 10 <sup>-11</sup>	NIST	300-2500	
R45	CH <sub>2</sub> + CH <sub>3</sub> O	→ C <sub>2</sub> H <sub>4</sub> + OH	4.0 × 10 <sup>-11</sup>	NIST	300-2500	
R46	CH <sub>2</sub> + CH <sub>3</sub> O	→ CH <sub>2</sub> O + CH <sub>3</sub>	2.0 × 10 <sup>-12</sup>	NIST	300-2500	
R47	CH <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>2</sub> O + CH <sub>3</sub> O	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R48	CH <sub>2</sub> + CH <sub>4</sub>	→ CH <sub>3</sub> + CH <sub>3</sub>	7.12 × 10 <sup>-12</sup> exp(-5050.0/T)	NIST	296-707	Low Temperature
R49	CH <sub>2</sub> + CH <sub>4</sub> O	→ CH <sub>3</sub> + CH <sub>3</sub> O	1.12 × 10 <sup>-15</sup> (T/298.0) <sup>3.1</sup> exp(-3490.0/T)	NIST	300-2500	
R50	CH <sub>2</sub> + CHO	→ CO + CH <sub>3</sub>	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R51	CH <sub>2</sub> O + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + CHO	8.07 × 10 <sup>-14</sup> (T/298.0) <sup>2.81</sup> exp(-2950.0/T)	NIST	300-2500	
R52	CH <sub>2</sub> O + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>4</sub> O + CHO	3.0 × 10 <sup>-13</sup> exp(-6500.0/T)	NIST	300-2500	
R53	CH <sub>2</sub> O + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + CHO	8.19 × 10 <sup>-14</sup> (T/298.0) <sup>2.81</sup> exp(-2950.0/T)	NIST	300-2500	
R54	CH <sub>2</sub> O + CH <sub>3</sub> O <sub>2</sub>	→ CHO + CH <sub>4</sub> O <sub>2</sub>	3.3 × 10 <sup>-12</sup> exp(-5870.0/T)	NIST	300-2500	
R55	CH <sub>2</sub> O + CN	→ HCN + CHO	7.0 × 10 <sup>-11</sup>	NIST	500-2500	
R56	CH <sub>2</sub> O + CNO	→ HCNO + CHO	1.0 × 10 <sup>-11</sup>	NIST	500-2500	
R57	CH <sub>3</sub> + C <sub>2</sub> H <sub>2</sub>	→ CH <sub>4</sub> + C <sub>2</sub> H	3.0 × 10 <sup>-13</sup> exp(-8700.0/T)	NIST	300-2500	
R58	CH <sub>3</sub> + C <sub>2</sub> H <sub>2</sub> O	→ CO + C <sub>2</sub> H <sub>5</sub>	8.3 × 10 <sup>-12</sup>	NIST	1640-1950	High Temperature
R59	CH <sub>3</sub> + C <sub>2</sub> H <sub>3</sub>	→ CH <sub>4</sub> + C <sub>2</sub> H <sub>2</sub>	1.5 × 10 <sup>-11</sup> exp(385.0/T)	NIST	300-900	
R60	CH <sub>3</sub> + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>6</sub> + CO	5.4 × 10 <sup>-11</sup>	NIST	298	
R61	CH <sub>3</sub> + C <sub>2</sub> H <sub>3</sub> O	→ CH <sub>4</sub> + C <sub>2</sub> H <sub>2</sub> O	3.52 × 10 <sup>-12</sup> (T/298.0) <sup>-0.8</sup>	NIST	300-2500	
R62	CH <sub>3</sub> + C <sub>2</sub> H <sub>4</sub>	→ CH <sub>4</sub> + C <sub>2</sub> H <sub>3</sub>	1.57 × 10 <sup>-14</sup> (T/298.0) <sup>3.7</sup> exp(-4780.0/T)	NIST	300-2500	
R63	CH <sub>3</sub> + C <sub>2</sub> H <sub>4</sub> O	→ CH <sub>4</sub> + C <sub>2</sub> H <sub>3</sub> O	2.97 × 10 <sup>-16</sup> (T/298.0) <sup>5.64</sup> exp(-1240.0/T)	NIST	300-1250	
R64	CH <sub>3</sub> + C <sub>2</sub> H <sub>5</sub>	→ CH <sub>4</sub> + C <sub>2</sub> H <sub>4</sub>	1.88 × 10 <sup>-12</sup> (T/298.0) <sup>-0.5</sup>	NIST	300-2500	
R65	CH <sub>3</sub> + C <sub>2</sub> H <sub>6</sub>	→ CH <sub>4</sub> + C <sub>2</sub> H <sub>5</sub>	1.74 × 10 <sup>-16</sup> (T/298.0) <sup>6</sup> exp(-3040.0/T)	NIST	300-1500	
R66	CH <sub>3</sub> + CH <sub>2</sub> O	→ CH <sub>4</sub> + CHO	1.6 × 10 <sup>-16</sup> (T/298.0) <sup>6.1</sup> exp(-990.0/T)	NIST	300-2000	
R67	CH <sub>3</sub> + CH <sub>3</sub> O	→ CH <sub>2</sub> O + CH <sub>4</sub>	4.0 × 10 <sup>-11</sup>	NIST	300-2500	
R68	CH <sub>3</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + CH <sub>3</sub> O	4.0 × 10 <sup>-11</sup>	NIST	300-2500	
R69	CH <sub>3</sub> + CH <sub>4</sub> O	→ CH <sub>4</sub> + CH <sub>3</sub> O	1.12 × 10 <sup>-15</sup> (T/298.0) <sup>3.1</sup> exp(-3490.0/T)	NIST	300-2500	
R70	CH <sub>3</sub> + CHO	→ C <sub>2</sub> H <sub>4</sub> O	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R71	CH <sub>3</sub> + CHO	→ CH <sub>4</sub> + CO	2.0 × 10 <sup>-10</sup>	NIST	300-2500	
R72	CH <sub>3</sub> + CNO	→ CH <sub>2</sub> O + HCN	4.2 × 10 <sup>-13</sup>	NIST	293	
R73	CH <sub>3</sub> O + C <sub>2</sub> H	→ CH <sub>2</sub> O + C <sub>2</sub> H <sub>2</sub>	6.0 × 10 <sup>-11</sup>	NIST	300-2500	
R74	CH <sub>3</sub> O + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>3</sub> + CH <sub>2</sub> O	1.2 × 10 <sup>-12</sup> exp(-4529.0/T)	NIST	300-2500	
R75	CH <sub>3</sub> O + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + CH <sub>2</sub> O	4.0 × 10 <sup>-11</sup>	NIST	300-2500	
R76	CH <sub>3</sub> O + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>4</sub> + CH <sub>4</sub> O	4.0 × 10 <sup>-12</sup>	NIST	300-2500	
R77	CH <sub>3</sub> O + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + CH <sub>2</sub> O	4.0 × 10 <sup>-11</sup>	NIST	300-2500	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R78	CH <sub>3</sub> O + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + CH <sub>4</sub> O	$4.0 \times 10^{-13} \exp(-3570.0/T)$	NIST	300-2500	
R79	CH <sub>3</sub> O + CH <sub>2</sub> O	→ CH <sub>4</sub> O + CHO	$1.7 \times 10^{-13} \exp(-1500.0/T)$	NIST	300-2500	
R80	CH <sub>3</sub> O + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>2</sub> O + CH <sub>4</sub> O <sub>2</sub>	$5.0 \times 10^{-13}$	NIST	300-2500	
R81	CH <sub>3</sub> O + O <sub>2</sub>	→ CH <sub>2</sub> O + HO <sub>2</sub>	$9.1 \times 10^{-12}$	JPL	200-300	Low Temperature
R82	CH <sub>3</sub> O <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	→ CH <sub>3</sub> O + C <sub>2</sub> H <sub>3</sub> O	$4.0 \times 10^{-11}$	NIST	300-2500	
R83	CH <sub>3</sub> O <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>5</sub> O + CH <sub>3</sub> O	$4.0 \times 10^{-11}$	NIST	300-2500	
R84	CH <sub>3</sub> O <sub>2</sub> + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + CH <sub>4</sub> O <sub>2</sub>	$4.9 \times 10^{-13}$	NIST	300-2500	
R85	CH <sub>3</sub> O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + CH <sub>3</sub> O + O <sub>2</sub>	$5.9 \times 10^{-14} \exp(390.0/T)$	JPL	200-300	Low Temperature
R86	CH <sub>3</sub> O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>4</sub> O + CH <sub>2</sub> O + O <sub>2</sub>	$3.6 \times 10^{-14} \exp(390.0/T)$	JPL	200-300	Low Temperature
R87	CH <sub>3</sub> O <sub>2</sub> + CH <sub>4</sub> O	→ CH <sub>4</sub> O <sub>2</sub> + CH <sub>3</sub> O	$3.0 \times 10^{-12} \exp(-6900.0/T)$	NIST	300-2500	
R88	CH <sub>3</sub> S + CO	→ OCS + CH <sub>3</sub>	$8.43 \times 10^{-13} (T/298.0)^{1.57} \exp(-3359.0/T)$	NIST	200-3000	
R89	CH <sub>3</sub> S + O <sub>2</sub>	→ CH <sub>3</sub> + SO <sub>2</sub>	$6.23 \times 10^{-8} (T/298.0)^{-3.8} \exp(-6189.2/T)$	NIST	200-2000	
R90	CH <sub>3</sub> S + O <sub>2</sub>	→ CH <sub>3</sub> O + SO <sub>2</sub>	$1.5 \times 10^{-12} \exp(360.0/T)$	JPL	200-300	Low Temperature
R91	CH <sub>4</sub> + C <sub>2</sub> H	→ C <sub>2</sub> H <sub>2</sub> + CH <sub>3</sub>	$3.0 \times 10^{-12} \exp(-250.0/T)$	NIST	300-2500	
R92	CH <sub>4</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>3</sub> + CH <sub>3</sub>	$5.0 \times 10^{-13} \exp(-2479.0/T)$	NIST	290-310	Low Temperature
R93	CH <sub>4</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + CH <sub>3</sub>	$2.13 \times 10^{-14} (T/298.0)^{4.02} \exp(-2479.0/T)$	NIST	300-2500	
R94	CH <sub>4</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + CH <sub>3</sub>	$2.51 \times 10^{-15} (T/298.0)^{4.14} \exp(-6320.0/T)$	NIST	300-2500	
R95	CH <sub>4</sub> + CH <sub>3</sub>	→ H <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	$1.66 \times 10^{-11} \exp(-11600.0/T)$	NIST	1950-2770	
R96	CH <sub>4</sub> + CH <sub>3</sub> O	→ CH <sub>4</sub> O + CH <sub>3</sub>	$2.61 \times 10^{-13} \exp(-4450.0/T)$	NIST	300-2500	
R97	CH <sub>4</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>3</sub> + CH <sub>4</sub> O <sub>2</sub>	$3.0 \times 10^{-13} \exp(-9299.5/T)$	NIST	300-2500	
R98	CH <sub>4</sub> + CHO	→ CH <sub>2</sub> O + CH <sub>3</sub>	$1.36 \times 10^{-13} (T/298.0)^{2.85} \exp(-11300.0/T)$	NIST	300-2500	
R99	CH <sub>4</sub> + CN	→ HCN + CH <sub>3</sub>	$5.11 \times 10^{-13} (T/298.0)^{2.64} \exp(150.3/T)$	NIST	290-1500	
R100	CH <sub>4</sub> + CNO	→ CH <sub>3</sub> + HCNO	$1.62 \times 10^{-11} \exp(-4090.5/T)$	NIST	512-1100	
R101	CH <sub>4</sub> O + CN	→ HCN + CH <sub>3</sub> O	$1.2 \times 10^{-10}$	NIST	294	
R102	CH <sub>4</sub> S + CN	→ HCN + CH <sub>3</sub> S	$2.19 \times 10^{-10}$	NIST	293	
R103	CH <sub>4</sub> S + H	→ CH <sub>3</sub> + H <sub>2</sub> S	$1.15 \times 10^{-11} \exp(-840.0/T)$	NIST	313-454	Low Temperature
R104	CH <sub>4</sub> S + H	→ H <sub>2</sub> + CH <sub>3</sub> S	$4.82 \times 10^{-11} \exp(-1309.8/T)$	NIST	313-454	Low Temperature
R105	CH <sub>4</sub> S + NO <sub>3</sub>	→ CH <sub>3</sub> S + HNO <sub>3</sub>	$4.4 \times 10^{-13} \exp(210.0/T)$	JPL	200-300	Low Temperature
R106	CH <sub>4</sub> S + O	→ CH <sub>3</sub> + HSO	$3.45 \times 10^{-14} (T/298.0)^{4.7} \exp(1210.0/T)$	NIST	254-495	Low Temperature
R107	CH <sub>4</sub> S + OH	→ H <sub>2</sub> O + CH <sub>3</sub> S	$9.9 \times 10^{-12} \exp(360.0/T)$	JPL	200-300	Low Temperature
R108	CHO + C <sub>2</sub> H	→ C <sub>2</sub> H <sub>2</sub> + CO	$1.0 \times 10^{-10}$	NIST	300-2500	
R109	CHO + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + CO	$1.5 \times 10^{-10}$	NIST	300-2500	
R110	CHO + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>4</sub> O + CO	$1.5 \times 10^{-11}$	NIST	300-2500	
R111	CHO + C <sub>2</sub> H <sub>4</sub> O	→ CH <sub>4</sub> + CO + CHO	$1.33 \times 10^{-11} \exp(-523.0/T)$	NIST	415-670	Low Temperature
R112	CHO + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + CO	$2.0 \times 10^{-10}$	NIST	300-2500	
R113	CHO + CH <sub>3</sub> O	→ CH <sub>4</sub> O + CO	$1.5 \times 10^{-10}$	NIST	300-2500	
R114	CHO + CH <sub>3</sub> O	→ CH <sub>2</sub> O + CH <sub>2</sub> O	$3.0 \times 10^{-10}$	NIST	300-2500	
R115	CHO + CH <sub>4</sub> O	→ CH <sub>2</sub> O + CH <sub>3</sub> O	$2.41 \times 10^{-13} (T/298.0)^{2.9} \exp(-6600.0/T)$	NIST	300-2500	
R116	CHO + CN	→ HCN + CO	$1.0 \times 10^{-10}$	NIST	500-2500	
R117	CHO + CNO	→ HCNO + CO	$6.0 \times 10^{-11}$	NIST	500-2500	
R118	CHO + O <sub>2</sub>	→ CO + HO <sub>2</sub>	$5.2 \times 10^{-12}$	JPL	200-400	Low Temperature
R119	CN + HCNO	→ HCN + CNO	$1.1 \times 10^{-10}$	NIST	298	
R120	CO + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H + CHO	$8.0 \times 10^{-10} \exp(-53641.4/T)$	NIST	300-2500	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R121	CO + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>3</sub> + CHO	$2.5 \times 10^{-10} \exp(-45583.2/T)$	NIST	300-2500	
R122	CO + CH <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + OH	$6.3 \times 10^{-11} \exp(-30428.9/T)$	NIST	1500-1900	
R123	CO <sub>2</sub> + CH <sub>2</sub>	→ CH <sub>2</sub> O + CO	$3.9 \times 10^{-14}$	NIST	300-2500	
R124	CO <sub>2</sub> + CN	→ CNO + CO	$1.35 \times 10^{-12} (T/298.0)^{2.16} \exp(-13470.5/T)$	NIST	300-3000	
R125	CS + O	→ CO + S	$2.7 \times 10^{-10} \exp(-760.0/T)$	JPL	200-300	Low Temperature
R126	CS + O <sub>3</sub>	→ O <sub>2</sub> + OCS	$3.0 \times 10^{-16}$	NIST	298	
R127	H + C <sub>2</sub> H	→ C <sub>2</sub> H <sub>2</sub>	$3.0 \times 10^{-10}$	NIST	300-2500	
R128	H + C <sub>2</sub> H	→ H <sub>2</sub> + C <sub>2</sub>	$6.0 \times 10^{-11} \exp(-14192.0/T)$	NIST	300-2500	
R129	H + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H + H <sub>2</sub>	$1.0 \times 10^{-10} \exp(-11200.0/T)$	NIST	300-2500	
R130	H + C <sub>2</sub> H <sub>2</sub> O	→ CO + CH <sub>3</sub>	$5.0 \times 10^{-12} (T/298.0)^{1.45} \exp(-1398.8/T)$	NIST	200-2500	
R131	H + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub>	$2.02 \times 10^{-10} (T/298.0)^{0.2}$	NIST	200-2000	
R132	H + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub>	$2.0 \times 10^{-11}$	NIST	300-2500	
R133	H + C <sub>2</sub> H <sub>3</sub> O	→ CHO + CH <sub>3</sub>	$2.2 \times 10^{-11}$	NIST	298	
R134	H + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>2</sub> O + H <sub>2</sub>	$1.2 \times 10^{-11}$	NIST	298	
R135	H + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>3</sub> + H <sub>2</sub>	$4.0 \times 10^{-12} (T/298.0)^{2.53} \exp(-6160.0/T)$	NIST	300-2500	
R136	H + C <sub>2</sub> H <sub>4</sub> O	→ C <sub>2</sub> H <sub>5</sub> O	$1.33 \times 10^{-11} \exp(-3221.0/T)$	NIST	298-2000	
R137	H + C <sub>2</sub> H <sub>4</sub> O	→ C <sub>2</sub> H <sub>3</sub> O + H <sub>2</sub>	$6.64 \times 10^{-11} \exp(-2120.4/T)$	NIST	300-2000	
R138	H + C <sub>2</sub> H <sub>4</sub> O	→ CH <sub>4</sub> + CHO	$1.08 \times 10^{-10} \exp(-2120.4/T)$	NIST	300-2000	
R139	H + N <sub>2</sub> O	→ N <sub>2</sub> + OH	$1.60 \times 10^{-10} \exp(-7600.0/T)$	NIST	700-2500	High Temperature
R140	H + C <sub>2</sub> H <sub>5</sub>	→ CH <sub>3</sub> + CH <sub>3</sub>	$6.0 \times 10^{-11}$	NIST	300-2000	
R141	H + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub>	$3.0 \times 10^{-12}$	NIST	300-2500	
R142	H + C <sub>2</sub> H <sub>5</sub> O	→ C <sub>2</sub> H <sub>4</sub> O + H <sub>2</sub>	$3.32 \times 10^{-11}$	NIST	295	
R143	H + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + H <sub>2</sub>	$1.23 \times 10^{-11} (T/298.0)^{1.5} \exp(-3729.6/T)$	NIST	300-2000	
R144	H + C <sub>2</sub> HO	→ CO + CH <sub>2</sub>	$4.98 \times 10^{-11}$	NIST	1000-2500	High Temperature
R145	H + CH	→ C + H <sub>2</sub>	$1.31 \times 10^{-10} \exp(-85.6/T)$	NIST	300-2000	
R146	H + CH <sub>2</sub>	→ CH + H <sub>2</sub>	$1.0 \times 10^{-11} \exp(900.0/T)$	NIST	300-3000	
R147	H + CH <sub>2</sub> O	→ CH <sub>3</sub> O	$4.0 \times 10^{-11} \exp(-2068.7/T)$	NIST	290-2000	
R148	H + CH <sub>2</sub> O	→ H <sub>2</sub> + CHO	$2.14 \times 10^{-12} (T/298.0)^{1.62} \exp(-1090.0/T)$	NIST	300-1700	
R149	H + CH <sub>3</sub>	→ CH <sub>2</sub> + H <sub>2</sub>	$1.0 \times 10^{-10} \exp(-7600.0/T)$	NIST	300-2500	
R150	H + CH <sub>3</sub> NO <sub>2</sub>	→ CH <sub>4</sub> O + NO	$2.0 \times 10^{-13} \exp(-956.2/T)$	NIST	223-398	Low Temperature
R151	H + CH <sub>3</sub> NO <sub>2</sub>	→ CH <sub>3</sub> + HNO <sub>2</sub>	$5.28 \times 10^{-9} \exp(-7920.0/T)$	NIST	1000-1100	High Temperature
R152	H + CH <sub>3</sub> O	→ CH <sub>4</sub> O	$2.89 \times 10^{-10} (T/298.0)^{0.04}$	NIST	300-2500	
R153	H + CH <sub>3</sub> O	→ CH <sub>3</sub> + OH	$1.6 \times 10^{-10}$	NIST	300-2500	
R154	H + CH <sub>3</sub> O	→ CH <sub>2</sub> O + H <sub>2</sub>	$1.0 \times 10^{-11}$	NIST	300-2500	
R155	H + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + OH	$1.6 \times 10^{-10}$	NIST	300-2500	
R156	H + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>4</sub> + O <sub>2</sub>	$1.17 \times 10^{-11} (T/298.0)^{1.02} \exp(-8352.9/T)$	NIST	273-2000	
R157	H + CH <sub>4</sub>	→ CH <sub>3</sub> + H <sub>2</sub>	$5.83 \times 10^{-13} (T/298.0)^{3.0} \exp(-4040.0/T)$	NIST	300-2500	
R158	H + CH <sub>4</sub> O	→ CH <sub>3</sub> + H <sub>2</sub> O	$3.32 \times 10^{-10} \exp(-2670.0/T)$	NIST	1370-1840	High Temperature
R159	H + CH <sub>4</sub> O	→ CH <sub>3</sub> O + H <sub>2</sub>	$2.42 \times 10^{-12} (T/298.0)^{2.0} \exp(-2270.0/T)$	NIST	300-2500	
R160	H + CH <sub>4</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + H <sub>2</sub> O	$1.21 \times 10^{-13} \exp(-936.0/T)$	NIST	250-358	Low Temperature
R161	H + CH <sub>4</sub> O <sub>2</sub>	→ H <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	$1.46 \times 10^{-13} \exp(-936.0/T)$	NIST	250-358	Low Temperature
R162	H + CHO	→ CO + H <sub>2</sub>	$1.50 \times 10^{-10}$	NIST	300-2500	
R163	H + CNO	→ CO + NH	$8.9 \times 10^{-11}$	NIST	500-2500	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R164	H + CNO	→ HCN + O	$1.86 \times 10^{-11} (T/298.0)^{0.9} \exp(-2920.2/T)$	NIST	500-2500	
R165	H + CO <sub>2</sub>	→ CO + OH	$2.51 \times 10^{-10} \exp(-13350.0/T)$	NIST	300-2500	
R166	H + H <sub>2</sub> O	→ H <sub>2</sub> + OH	$6.82 \times 10^{-12} (T/298.0)^{1.6} \exp(-9720.0/T)$	NIST	300-2500	
R167	H + H <sub>2</sub> O <sub>2</sub>	→ OH + H <sub>2</sub> O	$1.69 \times 10^{-11} \exp(-1800.0/T)$	NIST	300-1000	
R168	H + H <sub>2</sub> O <sub>2</sub>	→ H <sub>2</sub> + HO <sub>2</sub>	$2.81 \times 10^{-12} \exp(-1890.0/T)$	NIST	300-1000	
R169	H + HCNO	→ H <sub>2</sub> + CNO	$1.91 \times 10^{-12} (T/298.0)^{1.66} \exp(-7000.0/T)$	NIST	500-2500	
R170	H + HCNO	→ CN + H <sub>2</sub> O	$1.66 \times 10^{-12}$	NIST	1800-2600	High Temperature
R171	H + HCNO	→ CO + NH <sub>2</sub>	$5.0 \times 10^{-11} \exp(-2300.0/T)$	NIST	500-2500	
R172	H + HNO	→ H <sub>2</sub> + NO	$3.0 \times 10^{-11} \exp(-500.0/T)$	NIST	298-2000	
R173	H + HNO	→ OH + NH	$2.41 \times 10^{-9} (T/298.0)^{-0.5} \exp(-9010.0/T)$	NIST	350-3000	
R174	H + HNO	→ NH <sub>2</sub> + O	$1.05 \times 10^{-9} (T/298.0)^{-0.3} \exp(-14673.2/T)$	NIST	550-3000	
R175	H + HNO <sub>2</sub>	→ OH + HNO	$1.26 \times 10^{-11} (T/298.0)^{0.86} \exp(-2500.0/T)$	NIST	300-2500	
R176	H + HNO <sub>2</sub>	→ H <sub>2</sub> + NO <sub>2</sub>	$2.0 \times 10^{-11} \exp(-3700.0/T)$	NIST	300-2500	
R177	H + HNO <sub>2</sub>	→ H <sub>2</sub> O + NO	$6.39 \times 10^{-13} (T/298.0)^{1.89} \exp(-1940.0/T)$	NIST	300-2500	
R178	H + HNO <sub>3</sub>	→ H <sub>2</sub> O + NO <sub>2</sub>	$1.39 \times 10^{-14} (T/298.0)^{3.29} \exp(-3160.0/T)$	NIST	300-3000	
R179	H + HNO <sub>3</sub>	→ H <sub>2</sub> + NO <sub>3</sub>	$5.65 \times 10^{-12} (T/298.0)^{1.53} \exp(-8250.0/T)$	NIST	300-3000	
R180	H + HO <sub>2</sub>	→ OH + OH	$7.2 \times 10^{-11}$	JPL	298	
R181	H + HO <sub>2</sub>	→ O + H <sub>2</sub> O	$1.6 \times 10^{-12}$	JPL	298	
R182	H + HO <sub>2</sub>	→ H <sub>2</sub> + O <sub>2</sub>	$6.9 \times 10^{-12}$	JPL	298	
R183	H + N <sub>2</sub> O	→ NO + NH	$5.03 \times 10^{-7} (T/298.0)^{-2.16} \exp(-18642.2/T)$	NIST	300-4000	
R184	H + NH	→ H <sub>2</sub> + N	$1.69 \times 10^{-11}$	NIST	1500-2500	High Temperature
R185	H + NH <sub>2</sub>	→ H <sub>2</sub> + NH	$1.05 \times 10^{-10} \exp(-4450.1/T)$	NIST	1100-1800	High Temperature
R186	H + NH <sub>3</sub>	→ H <sub>2</sub> + NH <sub>2</sub>	$7.80 \times 10^{-13} (T/298.0)^{2.4} \exp(-4990.1/T)$	NIST	490-1780	
R187	H + NO	→ NH + O	$9.3 \times 10^{-10} (T/298.0)^{-0.1} \exp(-35240.0/T)$	NIST	1300-3000	
R188	H + NO	→ OH + N	$3.6 \times 10^{-10} \exp(-24896.0/T)$	NIST	1500-4500	
R189	H + NO <sub>2</sub>	→ OH + NO	$4.0 \times 10^{-10} \exp(-340.0/T)$	JPL	200-300	Low Temperature
R190	H + NO <sub>3</sub>	→ OH + NO <sub>2</sub>	$9.4 \times 10^{-11}$	NIST	298	
R191	H + O <sub>2</sub>	→ O + OH	$6.73 \times 10^{-10} (T/298.0)^{-0.59} \exp(-8152.0/T)$	NIST	800-3500	High Temperature
R192	H + O <sub>3</sub>	→ OH + O <sub>2</sub>	$1.4 \times 10^{-10} \exp(-470.0/T)$	JPL	200-300	Low Temperature
R193	H <sub>2</sub> + C	→ CH + H	$6.64 \times 10^{-10} \exp(-11700.0/T)$	NIST	1520-2540	
R194	H <sub>2</sub> + C <sub>2</sub>	→ C <sub>2</sub> H + H	$1.1 \times 10^{-10} \exp(-4000.0/T)$	NIST	2580-4650	High Temperature
R195	H <sub>2</sub> + C <sub>2</sub> H	→ C <sub>2</sub> H <sub>2</sub> + H	$8.95 \times 10^{-13} (T/298.0)^{2.57} \exp(-130.0/T)$	NIST	200-2000	
R196	H <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>4</sub>	$5.0 \times 10^{-13} \exp(-19604.4/T)$	NIST	300-2500	
R197	H <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + H	$1.61 \times 10^{-13} (T/298.0)^{2.63} \exp(-4300.0/T)$	NIST	300-2500	
R198	H <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + H	$4.12 \times 10^{-15} (T/298.0)^{3.6} \exp(-4250.0/T)$	NIST	300-2500	
R199	H <sub>2</sub> + C <sub>2</sub> HO	→ C <sub>2</sub> H <sub>3</sub> O	$1.0 \times 10^{-11} \exp(-2000.0/T)$	NIST	438-761	
R200	H <sub>2</sub> + C <sub>2</sub> HO	→ CH <sub>3</sub> + CO	$1.2 \times 10^{-11} \exp(-2000.0/T)$	NIST	438-761	
R201	NH + NO	→ OH + N <sub>2</sub>	$5.86 \times 10^{-12} (T/298.0)^{-0.5} \exp(-60.0/T)$	NIST	300-4000	
R202	H <sub>2</sub> + CH	→ CH <sub>2</sub> + H	$3.75 \times 10^{-10} \exp(-1660.0/T)$	NIST	327-397	Low Temperature
R203	H <sub>2</sub> + CH <sub>3</sub>	→ CH <sub>4</sub> + H	$6.86 \times 10^{-14} (T/298.0)^{2.74} \exp(-4740.0/T)$	NIST	300-2500	
R204	H <sub>2</sub> + CH <sub>3</sub> O	→ CH <sub>4</sub> O + H	$9.96 \times 10^{-14} (T/298.0)^2 \exp(-6720.0/T)$	NIST	300-2500	
R205	H <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>4</sub> O <sub>2</sub> + H	$5.0 \times 10^{-11} \exp(-13110.0/T)$	NIST	300-2500	
R206	H <sub>2</sub> + CHO	→ CH <sub>2</sub> O + H	$2.66 \times 10^{-13} (T/298.0)^{2.0} \exp(-8970.0/T)$	NIST	300-2500	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R207	H <sub>2</sub> + CN	→ HCN + H	$5.65 \times 10^{-13} (T/298.0)^{2.45} \exp(-1131.0/T)$	NIST	300-2500	
R208	H <sub>2</sub> + HNO	→ NH + H <sub>2</sub> O	$1.66 \times 10^{-10} \exp(-8059.4/T)$	NIST	1300-1900	High Temperature
R209	H <sub>2</sub> + HO <sub>2</sub>	→ H <sub>2</sub> O <sub>2</sub> + H	$5.0 \times 10^{-11} \exp(-13110.0/T)$	NIST	300-2500	
R210	H <sub>2</sub> + N <sub>2</sub> O	→ H <sub>2</sub> O + N <sub>2</sub>	$5.73 \times 10^{-12} (T/298.0)^{0.5}$	NIST	1700-3000	High Temperature
R211	H <sub>2</sub> + NH	→ NH <sub>2</sub> + H	$3.5 \times 10^{-11} \exp(-7758.0/T)$	NIST	833-1432	High Temperature
R212	H <sub>2</sub> + NH <sub>2</sub>	→ NH <sub>3</sub> + H	$6.75 \times 10^{-14} (T/298.0)^{2.6} \exp(-3006.8/T)$	NIST	400-2200	
R213	H <sub>2</sub> + NO <sub>2</sub>	→ H + HNO <sub>2</sub>	$4.0 \times 10^{-11} \exp(-14553.0/T)$	NIST	760-1000	
R214	H <sub>2</sub> O + C	→ CH + OH	$1.3 \times 10^{-12} \exp(-19845.0/T)$	NIST	1000-4000	
R215	H <sub>2</sub> O + C <sub>2</sub> H	→ C <sub>2</sub> H <sub>2</sub> + OH	$7.74 \times 10^{-14} (T/298.0)^{3.05} \exp(-376.0/T)$	NIST	300-2000	
R216	HSO + O <sub>3</sub>	→ HSO <sub>2</sub> + O <sub>2</sub>	$3.0 \times 10^{-14}$	JPL	298	
R217	H <sub>2</sub> O + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + OH	$2.06 \times 10^{-14} (T/298.0)^{1.44} \exp(-10200.0/T)$	NIST	300-2500	
R218	H <sub>2</sub> O + CH	→ CH <sub>3</sub> O	$9.48 \times 10^{-12} \exp(380.0/T)$	NIST	298-669	Low Temperature
R219	H <sub>2</sub> O + CN	→ HCN + OH	$1.3 \times 10^{-11} \exp(-3760.0/T)$	NIST	500-2500	
R220	H <sub>2</sub> O + CNO	→ HCNO + OH	$9.13 \times 10^{-14} (T/298.0)^{2.17} \exp(-3050.0/T)$	NIST	500-2500	
R221	H <sub>2</sub> O <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + HO <sub>2</sub>	$2.0 \times 10^{-14} \exp(300.0/T)$	NIST	300-2500	
R222	H <sub>2</sub> O <sub>2</sub> + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>4</sub> O + HO <sub>2</sub>	$3.0 \times 10^{-13} \exp(-4140.0/T)$	NIST	300-2500	
R223	H <sub>2</sub> O <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + HO <sub>2</sub>	$1.45 \times 10^{-14} \exp(-490.0/T)$	NIST	300-2500	
R224	H <sub>2</sub> O <sub>2</sub> + CH <sub>3</sub>	→ CH <sub>4</sub> + HO <sub>2</sub>	$2.0 \times 10^{-14} \exp(300.0/T)$	NIST	300-2500	
R225	H <sub>2</sub> O <sub>2</sub> + CH <sub>3</sub> O	→ CH <sub>4</sub> O + HO <sub>2</sub>	$5.0 \times 10^{-15} \exp(-1300.0/T)$	NIST	300-2500	
R226	H <sub>2</sub> O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>4</sub> O <sub>2</sub> + HO <sub>2</sub>	$4.0 \times 10^{-12} \exp(-5000.0/T)$	NIST	300-2500	
R227	H <sub>2</sub> O <sub>2</sub> + CHO	→ CH <sub>2</sub> O + HO <sub>2</sub>	$1.69 \times 10^{-13} \exp(-3490.0/T)$	NIST	300-2500	
R228	H <sub>2</sub> S + CH	→ HS + CH <sub>2</sub>	$2.8 \times 10^{-10}$	NIST	330	
R229	H <sub>2</sub> S + CH <sub>2</sub>	→ HS + CH <sub>3</sub>	$2.0 \times 10^{-12}$	NIST	295	
R230	H <sub>2</sub> S + H	→ H <sub>2</sub> + HS	$3.66 \times 10^{-12} (T/298.0)^{1.94} \exp(-454.6/T)$	NIST	190-2237	
R231	H <sub>2</sub> S + O	→ OH + HS	$9.2 \times 10^{-12} \exp(-1800.0/T)$	JPL	200-300	Low Temperature
R232	H <sub>2</sub> S + OH	→ H <sub>2</sub> O + HS	$6.1 \times 10^{-12} \exp(-75.0/T)$	JPL	200-300	Low Temperature
R233	HCN + CNO	→ HCNO + CN	$2.0 \times 10^{-11} \exp(-4460.0/T)$	NIST	500-2500	
R234	HNO + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + NO	$1.66 \times 10^{-12}$	NIST	883-953	High Temperature
R235	HNO + CH <sub>3</sub>	→ CH <sub>4</sub> + NO	$1.85 \times 10^{-11} (T/298.0)^{0.76} \exp(-175.6/T)$	NIST	298-2500	
R236	HNO + CH <sub>3</sub> O	→ CH <sub>4</sub> O + NO	$5.0 \times 10^{-11}$	NIST	298	
R237	HNO + CHO	→ CH <sub>2</sub> O + NO	$1.0 \times 10^{-12} \exp(-1000.0/T)$	NIST	300-2500	
R238	HNO + CN	→ HCN + NO	$3.0 \times 10^{-11}$	NIST	500-2500	
R239	HNO + CNO	→ HCNO + NO	$3.0 \times 10^{-11}$	NIST	500-2500	
R240	HNO + CO	→ CO <sub>2</sub> + NH	$3.3 \times 10^{-12} \exp(-6190.0/T)$	NIST	1200-1900	High Temperature
R241	HNO <sub>2</sub> + CH <sub>3</sub>	→ CH <sub>4</sub> + NO <sub>2</sub>	$3.55 \times 10^{-7} \exp(-10100.0/T)$	NIST	1000-1100	High Temperature
R242	HNO <sub>2</sub> + CN	→ HCN + NO <sub>2</sub>	$2.0 \times 10^{-11}$	NIST	500-2500	
R243	HNO <sub>2</sub> + CNO	→ HCNO + NO <sub>2</sub>	$6.0 \times 10^{-12}$	NIST	500-2500	
R244	HO <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>3</sub> + O <sub>2</sub>	$5.0 \times 10^{-14} (T/298.0)^{1.61} \exp(-7129.7/T)$	NIST	300-2500	
R245	HO <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>2</sub> O + OH	$1.0 \times 10^{-14} \exp(-4000.3/T)$	NIST	300-2500	
R246	HO <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	→ OH + CH <sub>3</sub> + CO	$5.0 \times 10^{-11}$	NIST	300-2500	
R247	HO <sub>2</sub> + C <sub>2</sub> H <sub>3</sub> O	→ OH + CH <sub>3</sub> + CO <sub>2</sub>	$5.0 \times 10^{-11}$	NIST	300-2500	
R248	HO <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>4</sub> O + OH	$1.0 \times 10^{-14} \exp(-4000.3/T)$	NIST	300-2500	
R249	HO <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> O	→ C <sub>2</sub> H <sub>3</sub> O + H <sub>2</sub> O <sub>2</sub>	$5.0 \times 10^{-12} \exp(-6000.4/T)$	NIST	900-1200	High Temperature

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R250	HO <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	5.0 × 10 <sup>-13</sup>	NIST	300-2500	
R251	HO <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + O <sub>2</sub>	5.0 × 10 <sup>-13</sup>	NIST	300-2500	
R252	HO <sub>2</sub> + CH <sub>2</sub> O	→ CHO + H <sub>2</sub> O <sub>2</sub>	3.3 × 10 <sup>-12</sup> exp(-5870.5/T)	NIST	300-2500	
R253	HO <sub>2</sub> + CH <sub>2</sub> O	→ CH <sub>3</sub> O + O <sub>2</sub>	5.63 × 10 <sup>-12</sup> exp(-9620.6/T)	NIST	1200-1800	High Temperature
R254	HO <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>4</sub> O <sub>2</sub> + O <sub>2</sub>	4.1 × 10 <sup>-13</sup> exp(750.0/T)	JPL	200-300	Low Temperature
R255	HO <sub>2</sub> + CH <sub>4</sub> O	→ CH <sub>3</sub> O + H <sub>2</sub> O <sub>2</sub>	1.6 × 10 <sup>-13</sup> exp(-6330.0/T)	NIST	300-2500	
R256	HO <sub>2</sub> + CNO	→ HCNO + O <sub>2</sub>	3.32 × 10 <sup>-11</sup>	NIST	623-773	High Temperature
R257	HO <sub>2</sub> + HO <sub>2</sub>	→ H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	3.5 × 10 <sup>-13</sup> exp(430.0/T)	JPL	200-300	Low Temperature
R258	HO <sub>2</sub> + NH <sub>2</sub>	→ NH <sub>3</sub> + O <sub>2</sub>	3.4 × 10 <sup>-11</sup>	JPL	298	
R259	HO <sub>2</sub> + NO	→ OH + NO <sub>2</sub>	3.5 × 10 <sup>-12</sup> exp(250.0/T)	JPL	200-300	Low Temperature
R260	HO <sub>2</sub> + NO <sub>3</sub>	→ OH + NO <sub>2</sub> + O <sub>2</sub>	3.5 × 10 <sup>-12</sup>	JPL	298	
R261	HO <sub>2</sub> + O <sub>3</sub>	→ OH + O <sub>2</sub> + O <sub>2</sub>	1.0 × 10 <sup>-14</sup> exp(-490.0/T)	JPL	200-300	Low Temperature
R262	HS + CH <sub>3</sub>	→ CH <sub>4</sub> S	1.66 × 10 <sup>-11</sup>	NIST	681-723	High Temperature
R263	HS + HO <sub>2</sub>	→ OH + HSO	1.0 × 10 <sup>-11</sup>	NIST	298	
R264	HS + HS	→ S + H <sub>2</sub> S	1.5 × 10 <sup>-11</sup>	NIST	298	
R265	HS + NO <sub>2</sub>	→ NO + HSO	2.9 × 10 <sup>-11</sup> exp(240.0/T)	JPL	220-420	Low Temperature
R266	HS + O	→ H + SO	1.6 × 10 <sup>-10</sup>	NIST	298	
R267	HS + CHO	→ H <sub>2</sub> S + CO	5.0 × 10 <sup>-11</sup>	Kasting (1990)	298	
R268	HS + O <sub>2</sub>	→ SO + OH	4.0 × 10 <sup>-19</sup>	NIST	298	
R269	HS + O <sub>3</sub>	→ O <sub>2</sub> + HSO	9.0 × 10 <sup>-12</sup> exp(-280.0/T)	JPL	200-300	Low Temperature
R270	HSO + NO <sub>2</sub>	→ HSO <sub>2</sub> + NO	9.6 × 10 <sup>-12</sup>	JPL	298	
R271	HSO + O <sub>3</sub>	→ HS + O <sub>2</sub> + O <sub>2</sub>	7.0 × 10 <sup>-14</sup>	JPL	298	
R272	HS + CH <sub>2</sub> O	→ H <sub>2</sub> S + CHO	1.7 × 10 <sup>-11</sup> exp(-800.0/T)	JPL	200-300	Low Temperature
R273	HSO <sub>2</sub> + O <sub>2</sub>	→ HO <sub>2</sub> + SO <sub>2</sub>	3.0 × 10 <sup>-13</sup>	JPL	298	
R274	HSO <sub>3</sub> + O	→ OH + SO <sub>3</sub>	1.0 × 10 <sup>-11</sup>	Kasting (1990)	298	
R275	HSO <sub>3</sub> + O <sub>2</sub>	→ HO <sub>2</sub> + SO <sub>3</sub>	1.3 × 10 <sup>-12</sup> exp(-330.0/T)	JPL	200-300	Low Temperature
R276	N + C <sub>2</sub>	→ CN + C	2.8 × 10 <sup>-11</sup>	NIST	298	
R277	N + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> N + H	6.2 × 10 <sup>-11</sup>	NIST	298	
R278	N + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + NH	1.2 × 10 <sup>-11</sup>	NIST	298	
R279	N + C <sub>2</sub> H <sub>4</sub>	→ HCN + CH <sub>3</sub>	4.2 × 10 <sup>-14</sup>	NIST	298	
R280	N + CH	→ C + NH	3.0 × 10 <sup>-11</sup> (T/298.0) <sup>0.65</sup> exp(-1203.0/T)	NIST	990-1010	High Temperature
R281	N + CH	→ CN + H	1.66 × 10 <sup>-10</sup> (T/298.0) <sup>-0.09</sup>	NIST	216-584	Low Temperature
R282	N + CH <sub>3</sub>	→ H <sub>2</sub> + HCN	4.3 × 10 <sup>-10</sup> exp(-420.0/T)	NIST	200-423	Low Temperature
R283	N + CH <sub>4</sub> O	→ CH <sub>3</sub> + HNO	4.0 × 10 <sup>-10</sup> exp(-4330.0/T)	NIST	309-409	Low Temperature
R284	N + CN	→ C + N <sub>2</sub>	3.0 × 10 <sup>-10</sup>	NIST	300-2500	
R285	N + CNO	→ CO + N <sub>2</sub>	3.3 × 10 <sup>-11</sup>	NIST	1100-1400	High Temperature
R286	N + CNO	→ CN + NO	1.66 × 10 <sup>-12</sup>	NIST	1400-2000	High Temperature
R287	N + H <sub>2</sub> O	→ OH + NH	6.03 × 10 <sup>-11</sup> (T/298.0) <sup>1.2</sup> exp(-19243.6/T)	NIST	800-3000	
R288	N + HCNO	→ NH + CNO	3.85 × 10 <sup>-5</sup> exp(-26460.0/T)	NIST	1000-3000	
R289	N + NH	→ N <sub>2</sub> + H	1.95 × 10 <sup>-11</sup> (T/298.0) <sup>0.51</sup> exp(-9.6/T)	NIST	300-2500	
R290	N + NH <sub>2</sub>	→ NH + NH	3.0 × 10 <sup>-13</sup> exp(-7600.0/T)	NIST	1000-4000	High Temperature
R291	N + NO	→ O + N <sub>2</sub>	2.1 × 10 <sup>-11</sup> exp(100.0/T)	JPL	200-300	Low Temperature
R292	N + NO <sub>2</sub>	→ N <sub>2</sub> O + O	5.8 × 10 <sup>-12</sup> exp(220.0/T)	JPL	200-300	Low Temperature

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R293	N + O <sub>2</sub>	→ NO + O	$1.5 \times 10^{-11} \exp(-3600.0/T)$	JPL	200-300	Low Temperature
R294	N + O <sub>3</sub>	→ NO + O <sub>2</sub>	$2.0 \times 10^{-16}$	JPL	298	
R295	N + OH	→ NO + H	$4.7 \times 10^{-11}$	NIST	300-2500	
R296	N <sub>2</sub> O + C	→ CO + N <sub>2</sub>	$8.0 \times 10^{-12}$	NIST	298	
R297	N <sub>2</sub> O + CH	→ HCN + NO	$3.1 \times 10^{-11} \exp(257.4/T)$	NIST	200-1250	
R298	N <sub>2</sub> O + CN	→ N <sub>2</sub> + CNO	$2.0 \times 10^{-12}$	NIST	297	
R299	N <sub>2</sub> O + HCN	→ HCNO + N <sub>2</sub>	$2.0 \times 10^{-11}$	NIST	1400-1800	High Temperature
R300	NH + NH <sub>3</sub>	→ NH <sub>2</sub> + NH <sub>2</sub>	$5.25 \times 10^{-10} \exp(-13470.0/T)$	NIST	1300-1700	
R301	NH + NO	→ N <sub>2</sub> O + H	$1.17 \times 10^{-10} (T/298.0)^{-1.03} \exp(-420.0/T)$	NIST	300-4000	
R302	NH + NO <sub>2</sub>	→ NO + HNO	$2.1 \times 10^{-13} \exp(1140.2/T)$	NIST	200-300	
R303	NH + NO <sub>2</sub>	→ OH + N <sub>2</sub> O	$1.4 \times 10^{-13} \exp(1140.2/T)$	NIST	200-300	Low Temperature
R304	NH + O	→ NO + H	$1.16 \times 10^{-10}$	NIST	250-3000	
R305	NH + O	→ OH + N	$1.16 \times 10^{-11}$	NIST	250-3000	
R306	NH + O <sub>2</sub>	→ OH + NO	$6.74 \times 10^{-14} (T/298.0)^{0.79} \exp(-601.4/T)$	NIST	298-2200	
R307	NH + O <sub>2</sub>	→ O + HNO	$6.79 \times 10^{-14} (T/298.0)^{2.0} \exp(-3270.2/T)$	NIST	300-3300	
R308	NH + OH	→ H + HNO	$3.32 \times 10^{-11}$	NIST	298-3000	
R309	NH + OH	→ H <sub>2</sub> O + N	$3.1 \times 10^{-12} (T/298.0)^{1.2}$	NIST	298-3000	
R310	NH <sub>2</sub> + C	→ CH + NH	$9.61 \times 10^{-13} \exp(-10500.0/T)$	NIST	1000-4000	
R311	NH <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H + NH <sub>3</sub>	$8.2 \times 10^{-13} \exp(-2780.0/T)$	NIST	340-510	Low Temperature
R312	NH <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>3</sub> + NH <sub>3</sub>	$3.42 \times 10^{-14} \exp(-1320.6/T)$	NIST	250-465	Low Temperature
R313	NH <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> O	→ C <sub>2</sub> H <sub>3</sub> O + NH <sub>3</sub>	$3.5 \times 10^{-13} \exp(-1250.0/T)$	NIST	297-453	Low Temperature
R314	NH <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + NH	$5.1 \times 10^{-12} \exp(-4678.6/T)$	NIST	300-2000	
R315	NH <sub>2</sub> + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + NH <sub>3</sub>	$2.74 \times 10^{-14} (T/298.0)^{3.46} \exp(-2820.0/T)$	NIST	300-2000	
R316	NH <sub>2</sub> + CH <sub>3</sub>	→ CH <sub>4</sub> + NH	$8.4 \times 10^{-10} \exp(-4834.9/T)$	NIST	300-2000	
R317	NH <sub>2</sub> + CH <sub>4</sub>	→ CH <sub>3</sub> + NH <sub>3</sub>	$8.77 \times 10^{-15} (T/298.0)^3 \exp(-2130.0/T)$	NIST	300-2000	
R318	NH <sub>2</sub> + CNO	→ HCNO + NH	$1.71 \times 10^{-11} (T/298.0)^{1.91} \exp(1039.0/T)$	NIST	1000-3000	High Temperature
R319	NH <sub>2</sub> + H <sub>2</sub> O	→ OH + NH <sub>3</sub>	$2.1 \times 10^{-13} (T/298.0)^{1.9} \exp(-5725.0/T)$	NIST	300-3000	
R320	NH <sub>2</sub> + NO	→ H <sub>2</sub> O + N <sub>2</sub>	$4.0 \times 10^{-12} \exp(450.0/T)$	JPL	200-300	Low Temperature
R321	NH <sub>2</sub> + NO <sub>2</sub>	→ H <sub>2</sub> O + N <sub>2</sub> O	$2.1 \times 10^{-12} \exp(650.0/T)$	JPL	200-300	Low Temperature
R322	NH <sub>2</sub> + O	→ H + HNO	$7.47 \times 10^{-11}$	NIST	298-3000	
R323	NH <sub>2</sub> + O	→ OH + NH	$1.16 \times 10^{-11}$	NIST	298-3000	
R324	NH <sub>2</sub> + O	→ H <sub>2</sub> + NO	$8.3 \times 10^{-12}$	NIST	298-3000	
R325	NH <sub>2</sub> + O <sub>3</sub>	→ H <sub>2</sub> O + NO <sub>2</sub>	$4.3 \times 10^{-12} \exp(-930.0/T)$	JPL	200-300	
R326	NH <sub>2</sub> + OH	→ H <sub>2</sub> O + NH	$7.69 \times 10^{-13} (T/298.0)^{1.5} \exp(-230.0/T)$	NIST	250-3000	
R327	NH <sub>3</sub> + CH	→ HCN + H <sub>2</sub> + H	$7.24 \times 10^{-11} \exp(317.0/T)$	NIST	300-1300	
R328	NH <sub>3</sub> + CH <sub>3</sub>	→ CH <sub>4</sub> + NH <sub>2</sub>	$9.55 \times 10^{-14} \exp(-4895.0/T)$	NIST	350-600	Low Temperature
R329	NH <sub>3</sub> + CN	→ HCN + NH <sub>2</sub>	$1.66 \times 10^{-11}$	NIST	300-700	Low Temperature
R330	NH <sub>3</sub> + CNO	→ CO + N <sub>2</sub> H <sub>3</sub>	$6.29 \times 10^{-14} (T/298.0)^{2.48} \exp(-493.0/T)$	NIST	295-882	
R331	NO + C	→ CO + N	$3.49 \times 10^{-11} (T/298.0)^{-0.02}$	NIST	200-5000	
R332	NO + C	→ CN + O	$5.57 \times 10^{-11} (T/298.0)^{-0.32}$	NIST	200-5000	
R333	NO + C <sub>2</sub> H	→ HCN + CO	$3.6 \times 10^{-11}$	NIST	298	
R334	NO + C <sub>2</sub> H <sub>3</sub>	→ CH <sub>2</sub> O + HCN	$5.0 \times 10^{-11} (T/298.0)^{-3.38} \exp(-516.0/T)$	NIST	200-2000	
R335	NO + C <sub>2</sub> H <sub>5</sub> O	→ C <sub>2</sub> H <sub>4</sub> O + HNO	$1.3 \times 10^{-11}$	NIST	298	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R336	NO + C <sub>2</sub> H <sub>2</sub> O	→ CO + HCNO	$1.4 \times 10^{-11} \exp(320.0/T)$	NIST	296-2000	
R337	NO + C <sub>2</sub> H <sub>2</sub> O	→ HCN + CO <sub>2</sub>	$6.12 \times 10^{-12} (T/298.0)^{-0.72} \exp(200.0/T)$	NIST	296-2000	
R338	NO + CH	→ N + CHO	$1.33 \times 10^{-11}$	NIST	298	
R339	NO + CH	→ H + CNO	$4.0 \times 10^{-11}$	NIST	298	
R340	NO + CH	→ CO + NH	$2.5 \times 10^{-10}$	NIST	298	
R341	NO + CH	→ O + HCN	$1.37 \times 10^{-10}$	NIST	298	
R342	NO + CH	→ CN + OH	$1.4 \times 10^{-10}$	NIST	289	
R343	NO + CH <sub>2</sub>	→ HCNO + H	$4.17 \times 10^{-12} \exp(-3007.0/T)$	NIST	1100-2600	High Temperature
R344	NO + CH <sub>2</sub>	→ HCN + OH	$8.32 \times 10^{-13} \exp(-1443.0/T)$	NIST	1100-2600	High Temperature
R345	NO + CH <sub>3</sub>	→ HCN + H <sub>2</sub> O	$4.0 \times 10^{-12} \exp(-7900.0/T)$	NIST	1300-2080	High Temperature
R346	NO + CH <sub>3</sub> O	→ CH <sub>2</sub> O + HNO	$4.0 \times 10^{-12} (T/298.0)^{-0.7}$	NIST	200-400	Low Temperature
R347	NO + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + NO <sub>2</sub>	$2.8 \times 10^{-12} \exp(300.0/T)$	JPL	200-300	Low Temperature
R348	NO + CHO	→ CO + HNO	$1.2 \times 10^{-11}$	NIST	295-2500	
R349	NO + CN	→ CO + N <sub>2</sub>	$1.79 \times 10^{-10} \exp(-4040.0/T)$	NIST	687-1500	High Temperature
R350	NO + CNO	→ CO + N <sub>2</sub> O	$5.15 \times 10^{-11} (T/298.0)^{-1.34} \exp(-360.0/T)$	NIST	300-3000	
R351	NO + CNO	→ CO <sub>2</sub> + N <sub>2</sub>	$1.29 \times 10^{-10} (T/298.0)^{-1.97} \exp(-560.0/T)$	NIST	300-3000	
R352	NO + CNO	→ CO + N <sub>2</sub> + O	$2.78 \times 10^{-11} (T/298.0)^{-1.73} \exp(-380.0/T)$	NIST	300-3000	
R353	NO + NO <sub>3</sub>	→ NO <sub>2</sub> + NO <sub>2</sub>	$1.5 \times 10^{-11} \exp(170.0/T)$	JPL	200-300	Low Temperature
R354	NO + O <sub>3</sub>	→ NO <sub>2</sub> + O <sub>2</sub>	$3.0 \times 10^{-12} \exp(-1500.0/T)$	JPL	200-300	Low Temperature
R355	NO <sub>2</sub> + C	→ CO + NO	$1.1 \times 10^{-10}$	NIST	300	
R356	NO <sub>2</sub> + C <sub>2</sub> H	→ C <sub>2</sub> H <sub>2</sub> O + NO	$7.6 \times 10^{-11} \exp(130.0/T)$	NIST	288-800	
R357	NO <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>3</sub> O + NO	$4.21 \times 10^{-11} (T/298.0)^{-0.6}$	NIST	220-336	Low Temperature
R358	NO <sub>2</sub> + C <sub>2</sub> H <sub>3</sub> O	→ CO <sub>2</sub> + CH <sub>3</sub> + NO	$7.3 \times 10^{-11} \exp(80.6/T)$	NIST	298-328	Low Temperature
R359	NO <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> O	→ C <sub>2</sub> H <sub>4</sub> O + HNO <sub>2</sub>	$1.3 \times 10^{-11} (T/298.0)^{-1.0}$	NIST	200-300	Low Temperature
R360	NO <sub>2</sub> + C <sub>2</sub> HO	→ CO <sub>2</sub> + HCNO	$9.72 \times 10^{-12} \exp(171.0/T)$	NIST	298-423	Low Temperature
R361	NO <sub>2</sub> + C <sub>2</sub> HO	→ CO + CHO + NO	$1.46 \times 10^{-11} \exp(171.0/T)$	NIST	298-423	Low Temperature
R362	NO <sub>2</sub> + CH	→ CHO + NO	$1.45 \times 10^{-10}$	NIST	298	
R363	NO <sub>2</sub> + CH <sub>2</sub>	→ CH <sub>2</sub> O + NO	$6.91 \times 10^{-11}$	NIST	295	
R364	NO <sub>2</sub> + CH <sub>3</sub>	→ CH <sub>3</sub> O + NO	$2.26 \times 10^{-11}$	NIST	233-1700	
R365	NO <sub>2</sub> + CH <sub>3</sub>	→ CH <sub>2</sub> O + HNO	$5.4 \times 10^{-12}$	NIST	298	
R366	NO <sub>2</sub> + CH <sub>3</sub> O	→ CH <sub>2</sub> O + HNO <sub>2</sub>	$1.1 \times 10^{-11} \exp(-1200.0/T)$	JPL	200-300	Low Temperature
R367	NO <sub>2</sub> + CH <sub>4</sub>	→ HNO <sub>2</sub> + CH <sub>3</sub>	$1.58 \times 10^{-9} \exp(-19364.0/T)$	NIST	600-1100	
R368	NO <sub>2</sub> + CHO	→ NO + CHO <sub>2</sub>	$2.71 \times 10^{-11}$	NIST	296	
R369	NO <sub>2</sub> + CHO	→ NO + CO + OH	$4.0 \times 10^{-11}$	NIST	298	
R370	NO <sub>2</sub> + CHO	→ NO + CO <sub>2</sub> + H	$1.94 \times 10^{-10} (T/298.0)^{-0.75} \exp(-970.0/T)$	NIST	294-1650	
R371	NO <sub>2</sub> + CN	→ NO + CNO	$4.0 \times 10^{-11} \exp(186.0/T)$	NIST	500-2500	
R372	NO <sub>2</sub> + CN	→ CO + N <sub>2</sub> O	$7.11 \times 10^{-12}$	NIST	298	
R373	NO <sub>2</sub> + CN	→ CO <sub>2</sub> + N <sub>2</sub>	$5.2 \times 10^{-12}$	NIST	298	
R374	NO <sub>2</sub> + CNO	→ CO <sub>2</sub> + N <sub>2</sub> O	$1.64 \times 10^{-11}$	NIST	296	
R375	NO <sub>2</sub> + CNO	→ CO + NO + NO	$1.3 \times 10^{-12}$	NIST	296	
R376	NO <sub>2</sub> + NO <sub>3</sub>	→ NO + NO <sub>2</sub> + O <sub>2</sub>	$4.5 \times 10^{-14} \exp(-1260.0/T)$	JPL	200-300	Low Temperature
R377	NO <sub>2</sub> + O <sub>3</sub>	→ NO <sub>3</sub> + O <sub>2</sub>	$1.2 \times 10^{-13} \exp(-2450.0/T)$	JPL	200-300	Low Temperature
R378	NO <sub>3</sub> + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>2</sub> O + HNO <sub>3</sub>	$2.5 \times 10^{-11}$	NIST	298	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R379	$\text{NO}_3 + \text{C}_2\text{H}_4\text{O}$	$\longrightarrow \text{C}_2\text{H}_3\text{O} + \text{HNO}_3$	$1.4 \times 10^{-12} \exp(-1900.0/T)$	JPL	200-300	Low Temperature
R380	$\text{NO}_3 + \text{C}_2\text{H}_5$	$\longrightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2$	$4.0 \times 10^{-11}$	NIST	298	
R381	$\text{NO}_3 + \text{CH}_3$	$\longrightarrow \text{CH}_3\text{O} + \text{NO}_2$	$3.5 \times 10^{-11}$	NIST	298	
R382	$\text{NO}_3 + \text{CH}_3\text{O}$	$\longrightarrow \text{CH}_3\text{O}_2 + \text{NO}_2$	$1.8 \times 10^{-12}$	NIST	298	
R383	$\text{NO}_3 + \text{CH}_3\text{O}$	$\longrightarrow \text{CH}_2\text{O} + \text{HNO}_3$	$1.5 \times 10^{-12}$	NIST	298	
R384	$\text{NO}_3 + \text{CH}_3\text{O}_2$	$\longrightarrow \text{CH}_3\text{O} + \text{NO}_2 + \text{O}_2$	$1.3 \times 10^{-12}$	NIST	298	
R385	$\text{NO}_3 + \text{CH}_4\text{O}$	$\longrightarrow \text{CH}_3\text{O} + \text{HNO}_3$	$9.4 \times 10^{-13} \exp(-2646.0/T)$	NIST	258-367	Low Temperature
R386	$\text{NO}_3 + \text{HCNO}$	$\longrightarrow \text{CO}_2 + \text{NO} + \text{HNO}$	$1.66 \times 10^{-12} \exp(-5027.0/T)$	NIST	623-773	High Temperature
R387	$\text{NO}_3 + \text{NO}_3$	$\longrightarrow \text{NO}_2 + \text{NO}_2 + \text{O}_2$	$8.5 \times 10^{-13} \exp(-2450.0/T)$	JPL	200-300	Low Temperature
R388	$\text{O} + \text{C}_2$	$\longrightarrow \text{CO} + \text{C}$	$6.0 \times 10^{-10}$	NIST	8000	High Temperature
R389	$\text{O} + \text{C}_2\text{H}$	$\longrightarrow \text{CO} + \text{CH}$	$1.7 \times 10^{-11}$	NIST	300-2500	
R390	$\text{O} + \text{C}_2\text{H}_2$	$\longrightarrow \text{H} + \text{C}_2\text{HO}$	$1.5 \times 10^{-11} \exp(-2280.0/T)$	NIST	300-2500	
R391	$\text{O} + \text{C}_2\text{H}_2$	$\longrightarrow \text{CO} + \text{CH}_2$	$3.49 \times 10^{-12} (T/298.0)^{1.5} \exp(-850.0/T)$	NIST	300-2500	
R392	$\text{O} + \text{C}_2\text{H}_2\text{N}$	$\longrightarrow \text{CH}_2\text{O} + \text{CN}$	$8.49 \times 10^{-11} (T/298.0)^{0.64}$	NIST	253-353	Low Temperature
R393	$\text{O} + \text{C}_2\text{H}_3$	$\longrightarrow \text{C}_2\text{H}_3\text{O}$	$5.5 \times 10^{-11} (T/298.0)^{0.2} \exp(215.0/T)$	NIST	200-2500	
R394	$\text{O} + \text{C}_2\text{H}_3$	$\longrightarrow \text{C}_2\text{H}_2 + \text{OH}$	$5.5 \times 10^{-11} (T/298.0)^{0.2} \exp(215.0/T)$	NIST	200-2500	
R395	$\text{O} + \text{C}_2\text{H}_3$	$\longrightarrow \text{C}_2\text{H}_2\text{O} + \text{H}$	$1.6 \times 10^{-10}$	NIST	300-2500	
R396	$\text{O} + \text{C}_2\text{H}_4$	$\longrightarrow \text{C}_2\text{H}_3\text{O} + \text{H}$	$3.85 \times 10^{-13} (T/298.0)^{1.88} \exp(-91.4/T)$	NIST	300-2000	
R397	$\text{O} + \text{C}_2\text{H}_4$	$\longrightarrow \text{C}_2\text{H}_3 + \text{OH}$	$1.33 \times 10^{-12} (T/298.0)^{1.91} \exp(-1880.0/T)$	NIST	290-1510	
R398	$\text{O} + \text{C}_2\text{H}_4$	$\longrightarrow \text{CH}_3 + \text{CHO}$	$1.5 \times 10^{-12} (T/298.0)^{1.55} \exp(-215.0/T)$	NIST	300-2500	
R399	$\text{O} + \text{C}_2\text{H}_4$	$\longrightarrow \text{C}_2\text{H}_2\text{O} + \text{H}_2$	$5.5 \times 10^{-14} (T/298.0)^{1.88} \exp(-91.4/T)$	NIST	300-2000	
R400	$\text{O} + \text{C}_2\text{H}_4$	$\longrightarrow \text{CH}_2\text{O} + \text{CH}_2$	$8.3 \times 10^{-12} \exp(-754.0/T)$	NIST	226-380	Low Temperature
R401	$\text{O} + \text{C}_2\text{H}_4\text{O}$	$\longrightarrow \text{C}_2\text{H}_3\text{O} + \text{OH}$	$1.8 \times 10^{-11} \exp(-1100.0/T)$	JPL	200-300	Low Temperature
R402	$\text{O} + \text{C}_2\text{H}_5$	$\longrightarrow \text{C}_2\text{H}_5\text{O}$	$6.3 \times 10^{-11} (T/298.0)^{0.03} \exp(198.45/T)$	NIST	200-2500	
R403	$\text{O} + \text{C}_2\text{H}_5$	$\longrightarrow \text{C}_2\text{H}_4\text{O} + \text{H}$	$1.33 \times 10^{-10}$	NIST	300-2500	
R404	$\text{O} + \text{C}_2\text{H}_5$	$\longrightarrow \text{C}_2\text{H}_4 + \text{OH}$	$6.3 \times 10^{-12} (T/298.0)^{0.03} \exp(198.45/T)$	NIST	200-2500	
R405	$\text{O} + \text{C}_2\text{H}_5$	$\longrightarrow \text{CH}_2\text{O} + \text{CH}_3$	$2.67 \times 10^{-11}$	NIST	300-2500	
R406	$\text{O} + \text{C}_2\text{H}_6$	$\longrightarrow \text{C}_2\text{H}_5 + \text{OH}$	$8.54 \times 10^{-12} (T/298.0)^{1.5} \exp(-2920.0/T)$	NIST	300-1200	
R407	$\text{O} + \text{CH}$	$\longrightarrow \text{OH} + \text{C}$	$2.52 \times 10^{-11} \exp(-2380.0/T)$	NIST	10-6000	
R408	$\text{O} + \text{CH}$	$\longrightarrow \text{CO} + \text{H}$	$6.6 \times 10^{-11}$	NIST	300-2000	
R409	$\text{O} + \text{CH}_2$	$\longrightarrow \text{CH} + \text{OH}$	$7.2 \times 10^{-12}$	NIST	300-2500	
R410	$\text{O} + \text{CH}_2$	$\longrightarrow \text{CHO} + \text{H}$	$5.0 \times 10^{-11}$	NIST	1200-1800	High Temperature
R411	$\text{O} + \text{CH}_2$	$\longrightarrow \text{CO} + \text{H} + \text{H}$	$1.2 \times 10^{-10}$	NIST	300-2500	
R412	$\text{O} + \text{CH}_2$	$\longrightarrow \text{CO} + \text{H}_2$	$7.3 \times 10^{-11}$	NIST	300-2500	
R413	$\text{O} + \text{CH}_2\text{O}$	$\longrightarrow \text{CHO} + \text{OH}$	$1.78 \times 10^{-11} (h[i]/298.0, 0.57) \exp(-1390.0/T)$	NIST	250-2200	
R414	$\text{O} + \text{CH}_3$	$\longrightarrow \text{CH}_3\text{O}$	$7.51 \times 10^{-14} (T/298.0)^{-2.12} \exp(-314.0/T)$	NIST	300-2500	
R415	$\text{O} + \text{CH}_3$	$\longrightarrow \text{CH}_2\text{O} + \text{H}$	$1.4 \times 10^{-10}$	NIST	300-2500	
R416	$\text{O} + \text{CH}_3$	$\longrightarrow \text{CO} + \text{H}_2 + \text{H}$	$5.72 \times 10^{-11}$	NIST	290-900	
R417	$\text{O} + \text{CH}_3\text{NO}_2$	$\longrightarrow \text{OH} + \text{CH}_2\text{O} + \text{NO}$	$2.32 \times 10^{-11} \exp(-2620.0/T)$	NIST	300-410	Low Temperature
R418	$\text{O} + \text{CH}_3\text{NO}_3$	$\longrightarrow \text{OH} + \text{CH}_2\text{O} + \text{NO}_2$	$2.49 \times 10^{-11} \exp(-2650.0/T)$	NIST	294-473	Low Temperature
R419	$\text{O} + \text{CH}_3\text{O}$	$\longrightarrow \text{CH}_2\text{O} + \text{OH}$	$7.0 \times 10^{-11}$	NIST	300-2500	
R420	$\text{O} + \text{CH}_3\text{O}$	$\longrightarrow \text{CH}_3 + \text{O}_2$	$2.5 \times 10^{-11}$	NIST	298	
R421	$\text{O}_3 + \text{C}_2\text{H}_2$	$\longrightarrow \text{CO} + \text{CH}_2\text{O}_2$	$1.0 \times 10^{-14} \exp(-4100/T)$	JPL	200-300	Low Temperature

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R422	O + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + O <sub>2</sub>	8.3 × 10 <sup>-11</sup>	NIST	300-2000	
R423	O + CH <sub>4</sub>	→ CH <sub>3</sub> + OH	2.26 × 10 <sup>-12</sup> (T/298.0) <sup>2.2</sup> exp(-3820.0/T)	NIST	420-1520	
R424	O + CH <sub>4</sub> O	→ CH <sub>3</sub> O + OH	1.66 × 10 <sup>-11</sup> exp(-2360.0/T)	NIST	300-1000	
R425	O + CH <sub>4</sub> O <sub>2</sub>	→ CH <sub>3</sub> O <sub>2</sub> + OH	3.3 × 10 <sup>-11</sup> exp(-2390.0/T)	NIST	300-1000	
R426	O + CHO	→ CO + OH	5.0 × 10 <sup>-11</sup>	NIST	300-2500	
R427	O + CHO	→ CO <sub>2</sub> + H	5.0 × 10 <sup>-11</sup>	NIST	300-2500	
R428	O + CHO <sub>2</sub>	→ CO <sub>2</sub> + OH	1.44 × 10 <sup>-11</sup>	JPL	298	
R429	O + CN	→ C + NO	5.37 × 10 <sup>-11</sup> exp(-13711.0/T)	NIST	200-5000	
R430	O + CN	→ CO + N	3.4 × 10 <sup>-11</sup> exp(-210.0/T)	NIST	500-2500	
R431	O + CNO	→ CO + NO	7.5 × 10 <sup>-11</sup>	NIST	500-2500	
R432	O + CNO	→ CN + O <sub>2</sub>	4.05 × 10 <sup>-10</sup> (T/298.0) <sup>-1.43</sup> exp(-3500.0/T)	NIST	500-2500	
R433	O + H <sub>2</sub>	→ H + OH	3.44 × 10 <sup>-13</sup> (T/298.0) <sup>2.67</sup> exp(-3160.0/T)	NIST	300-2500	
R434	O + H <sub>2</sub> O <sub>2</sub>	→ OH + HO <sub>2</sub>	1.4 × 10 <sup>-12</sup> exp(-2000.0/T)	JPL	200-300	Low Temperature
R435	O + HCN	→ H + CNO	7.0 × 10 <sup>-12</sup> exp(-4000.0/T)	JPL	470-900	
R436	O + HCN	→ CO + NH	3.0 × 10 <sup>-12</sup> exp(-4000.0/T)	JPL	470-900	
R437	O + HCNO	→ CNO + OH	6.16 × 10 <sup>-13</sup> (T/298.0) <sup>2.11</sup> exp(-5750.0/T)	NIST	500-2500	
R438	O + HCNO	→ CO <sub>2</sub> + NH	4.93 × 10 <sup>-13</sup> (T/298.0) <sup>1.41</sup> exp(-4290.0/T)	NIST	500-2500	
R439	O + HNO	→ OH + NO	6.0 × 10 <sup>-11</sup>	NIST	300-2500	
R440	O + HNO <sub>4</sub>	→ HNO <sub>3</sub> + O <sub>2</sub>	7.8 × 10 <sup>-11</sup> exp(-3400.0/T)	JPL	200-300	Low Temperature
R441	O + HO <sub>2</sub>	→ OH + O <sub>2</sub>	3.0 × 10 <sup>-11</sup> exp(200.0/T)	JPL	200-300	Low Temperature
R442	O + NO <sub>2</sub>	→ NO + O <sub>2</sub>	5.1 × 10 <sup>-12</sup> exp(210.0/T)	JPL	200-300	Low Temperature
R443	O + NO <sub>3</sub>	→ NO <sub>2</sub> + O <sub>2</sub>	1.0 × 10 <sup>-11</sup>	JPL	200-300	Low Temperature
R444	O + O <sub>3</sub>	→ O <sub>2</sub> + O <sub>2</sub>	8.0 × 10 <sup>-12</sup> exp(-2060.0/T)	JPL	200-300	Low Temperature
R445	O + OH	→ O <sub>2</sub> + H	2.2 × 10 <sup>-11</sup> exp(120.0/T)	JPL	200-300	Low Temperature
R446	O + S <sub>2</sub>	→ S + SO	1.66 × 10 <sup>-11</sup>	NIST	298	
R447	O( <sup>1</sup> D) + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>3</sub> + OH	2.19 × 10 <sup>-10</sup>	NIST	298	
R448	O( <sup>1</sup> D) + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + OH	6.29 × 10 <sup>-10</sup>	NIST	300	
R449	O( <sup>1</sup> D) + CH <sub>4</sub>	→ CH <sub>3</sub> O + H	3.5 × 10 <sup>-11</sup>	JPL	200-300	Low Temperature
R450	O( <sup>1</sup> D) + CH <sub>4</sub>	→ CH <sub>3</sub> + OH	1.31 × 10 <sup>-10</sup>	JPL	200-300	Low Temperature
R451	O( <sup>1</sup> D) + CH <sub>4</sub>	→ CH <sub>2</sub> O + H <sub>2</sub>	9.0 × 10 <sup>-12</sup>	JPL	200-300	Low Temperature
R452	O( <sup>1</sup> D) + CH <sub>4</sub> O	→ CH <sub>3</sub> O <sub>2</sub> + H	9.0 × 10 <sup>-11</sup>	NIST	300	
R453	O( <sup>1</sup> D) + CH <sub>4</sub> O	→ CH <sub>3</sub> O + OH	4.2 × 10 <sup>-10</sup>	NIST	300	
R454	O( <sup>1</sup> D) + CO <sub>2</sub>	→ CO <sub>2</sub> + O	7.5 × 10 <sup>-11</sup> exp(115.0/T)	JPL	200-300	Low Temperature
R455	O( <sup>1</sup> D) + H <sub>2</sub>	→ H + OH	1.2 × 10 <sup>-10</sup>	JPL	200-300	Low Temperature
R456	O( <sup>1</sup> D) + H <sub>2</sub> O	→ OH + OH	1.63 × 10 <sup>-10</sup> exp(60.0/T)	JPL	200-300	Low Temperature
R457	O( <sup>1</sup> D) + HCNO	→ CO <sub>2</sub> + NH	4.6 × 10 <sup>-11</sup>	NIST	298	
R458	O( <sup>1</sup> D) + N <sub>2</sub>	→ O + N <sub>2</sub>	2.15 × 10 <sup>-11</sup> exp(110.0/T)	JPL	200-300	Low Temperature
R459	O( <sup>1</sup> D) + N <sub>2</sub> O	→ O <sub>2</sub> + N <sub>2</sub>	4.63 × 10 <sup>-11</sup> exp(20.0/T)	JPL	200-300	Low Temperature
R460	O( <sup>1</sup> D) + N <sub>2</sub> O	→ NO + NO	7.25 × 10 <sup>-11</sup> exp(20.0/T)	JPL	200-300	Low Temperature
R461	O( <sup>1</sup> D) + NH <sub>3</sub>	→ OH + NH <sub>2</sub>	2.5 × 10 <sup>-10</sup>	JPL	200-300	Low Temperature
R462	O( <sup>1</sup> D) + NO	→ O <sub>2</sub> + N	8.5 × 10 <sup>-11</sup>	NIST	300	
R463	O( <sup>1</sup> D) + NO <sub>2</sub>	→ O <sub>2</sub> + NO	3.0 × 10 <sup>-10</sup>	NIST	300	
R464	O( <sup>1</sup> D) + O <sub>2</sub>	→ O + O <sub>2</sub>	3.3 × 10 <sup>-11</sup> exp(55.0/T)	JPL	200-300	Low Temperature

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R465	O( <sup>1</sup> D) + O <sub>3</sub>	→ O <sub>2</sub> + O <sub>2</sub>	1.2 × 10 <sup>-10</sup>	JPL	200-300	Low Temperature
R466	O( <sup>1</sup> D) + O <sub>3</sub>	→ O <sub>2</sub> + O + O	1.2 × 10 <sup>-10</sup>	JPL	200-300	Low Temperature
R467	O( <sup>1</sup> D) + OCS	→ CO + SO	3.0 × 10 <sup>-10</sup>	NIST	300	
R468	O <sub>3</sub> + C <sub>2</sub> H <sub>4</sub>	→ CH <sub>2</sub> O + CH <sub>2</sub> O <sub>2</sub>	1.2 × 10 <sup>-14</sup> exp(-2630.0/T)	JPL	178-360	Low Temperature
R469	O <sub>3</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>5</sub> O + O <sub>2</sub>	3.32 × 10 <sup>-14</sup>	NIST	298	
R470	O <sub>3</sub> + CH <sub>3</sub>	→ CH <sub>3</sub> O + O <sub>2</sub>	5.4 × 10 <sup>-12</sup> exp(-220.0/T)	JPL	200-300	Low Temperature
R471	O <sub>3</sub> + CH <sub>3</sub> O	→ CH <sub>3</sub> O <sub>2</sub> + O <sub>2</sub>	2.53 × 10 <sup>-14</sup>	NIST	298	
R472	O <sub>3</sub> + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + O <sub>2</sub> + O <sub>2</sub>	2.9 × 10 <sup>-16</sup> exp(-1000.0/T)	JPL	200-300	Low Temperature
R473	OCS + OH	→ CO <sub>2</sub> + HS	1.1 × 10 <sup>-13</sup> exp(-1200.0/T)	JPL	200-300	Low Temperature
R474	OCS + CH	→ CHO + CS	2.0 × 10 <sup>-10</sup> exp(190.0/T)	NIST	297-667	Low Temperature
R475	OCS + O	→ CO + SO	2.1 × 10 <sup>-11</sup> exp(-2200.0/T)	JPL	200-300	Low Temperature
R476	OH + C <sub>2</sub>	→ CO + CH	8.3 × 10 <sup>-12</sup>	NIST	2200	High Temperature
R477	OH + C <sub>2</sub> H	→ CO + CH <sub>2</sub>	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R478	OH + C <sub>2</sub> H	→ C <sub>2</sub> H <sub>2</sub> + O	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R479	OH + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>2</sub> O + H	4.12 × 10 <sup>-13</sup> (T/298.0) <sup>2.3</sup> exp(-6790.0/T)	NIST	500-2500	
R480	OH + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H + H <sub>2</sub> O	1.03 × 10 <sup>-13</sup> (T/298.0) <sup>2.68</sup> exp(-6060.0/T)	NIST	300-2500	
R481	OH + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> HO + H <sub>2</sub>	1.91 × 10 <sup>-13</sup>	NIST	295	
R482	OH + C <sub>2</sub> H <sub>2</sub>	→ CO + CH <sub>3</sub>	6.34 × 10 <sup>-18</sup> (T/298.0) <sup>4.0</sup> exp(1010.0/T)	NIST	500-2500	
R483	OH + C <sub>2</sub> H <sub>2</sub> O	→ CO + CH <sub>3</sub> O	1.0 × 10 <sup>-11</sup>	NIST	298	
R484	OH + C <sub>2</sub> H <sub>2</sub> O	→ CO <sub>2</sub> + CH <sub>3</sub>	4.98 × 10 <sup>-12</sup>	NIST	800-1200	High Temperature
R485	OH + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> O	5.0 × 10 <sup>-11</sup>	NIST	300-2500	
R486	OH + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> O	5.0 × 10 <sup>-11</sup>	NIST	300-2500	
R487	OH + C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>2</sub> O + H <sub>2</sub> O	2.0 × 10 <sup>-11</sup>	NIST	300-2500	
R488	OH + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>3</sub> + H <sub>2</sub> O	1.66 × 10 <sup>-13</sup> (T/298.0) <sup>2.75</sup> exp(-2100.0/T)	NIST	300-2500	
R489	OH + C <sub>2</sub> H <sub>4</sub> O	→ C <sub>2</sub> H <sub>3</sub> O + H <sub>2</sub> O	4.4 × 10 <sup>-12</sup> exp(364.0/T)	NIST	200-350	Low Temperature
R490	OH + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>4</sub> + H <sub>2</sub> O	4.0 × 10 <sup>-11</sup>	NIST	300-2500	
R491	OH + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + H <sub>2</sub> O	8.7 × 10 <sup>-12</sup> exp(-1070.0/T)	JPL	200-300	Low Temperature
R492	OH + CH <sub>2</sub>	→ CH <sub>2</sub> O + H	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R493	OH + CH <sub>2</sub> O	→ CHO + H <sub>2</sub> O	5.5 × 10 <sup>-12</sup> exp(125.0/T)	JPL	200-300	Low Temperature
R494	OH + CH <sub>2</sub> O <sub>2</sub>	→ CHO <sub>2</sub> + H <sub>2</sub> O	4.0 × 10 <sup>-13</sup>	JPL	200-300	Low Temperature
R495	OH + CH <sub>3</sub>	→ CH <sub>3</sub> O + H	6.45 × 10 <sup>-13</sup> (T/298.0) <sup>1</sup> exp(-6012.0/T)	NIST	300-3000	
R496	OH + CH <sub>3</sub>	→ CH <sub>2</sub> + H <sub>2</sub> O	1.2 × 10 <sup>-10</sup> exp(-1400.0/T)	NIST	300-1000	
R497	OH + CH <sub>3</sub>	→ CH <sub>2</sub> O + H <sub>2</sub>	2.59 × 10 <sup>-13</sup> (T/298.0) <sup>-0.53</sup> exp(-5440.0/T)	NIST	600-2500	High Temperature
R498	OH + CH <sub>3</sub> NO <sub>3</sub>	→ CH <sub>2</sub> O + NO <sub>2</sub> + H <sub>2</sub> O	8.0 × 10 <sup>-13</sup> exp(-1000.0/T)	JPL	200-300	Low Temperature
R499	OH + CH <sub>3</sub> O	→ CH <sub>2</sub> O + H <sub>2</sub> O	3.0 × 10 <sup>-11</sup>	NIST	300-2500	
R500	OH + CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>4</sub> O + O <sub>2</sub>	1.0 × 10 <sup>-10</sup>	NIST	300-2500	
R501	OH + CH <sub>4</sub>	→ CH <sub>3</sub> + H <sub>2</sub> O	2.45 × 10 <sup>-12</sup> exp(-1775.0/T)	JPL	200-300	Low Temperature
R502	OH + CH <sub>4</sub> O	→ CH <sub>3</sub> O + H <sub>2</sub> O	2.9 × 10 <sup>-12</sup> exp(-345.0/T)	JPL	200-300	Low Temperature
R503	OH + CH <sub>4</sub> O <sub>2</sub>	→ CH <sub>3</sub> O <sub>2</sub> + H <sub>2</sub> O	3.8 × 10 <sup>-12</sup> exp(200.0/T)	JPL	200-300	Low Temperature
R504	OH + CHO	→ CO + H <sub>2</sub> O	1.69 × 10 <sup>-10</sup>	NIST	300-2500	
R505	OH + CHO <sub>2</sub>	→ CO <sub>2</sub> + H <sub>2</sub> O	1.0 × 10 <sup>-10</sup>	NIST	300	
R506	OH + CN	→ H + CNO	7.0 × 10 <sup>-11</sup>	NIST	500-2500	
R507	OH + CN	→ O + HCN	1.0 × 10 <sup>-11</sup> exp(-1000.0/T)	NIST	500-2500	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R508	OH + CNO	→ CHO + NO	$4.0 \times 10^{-13}$	NIST	1500	High Temperature
R509	OH + CNO	→ HCNO + O	$5.38 \times 10^{-14} (T/298.0)^{2.27} \exp(-497.0/T)$	NIST	500-2500	
R510	OH + CNO	→ CO + NO + H	$9.3 \times 10^{-15}$	NIST	1000	High Temperature
R511	OH + CO	→ CO <sub>2</sub> + H	$5.4 \times 10^{-14} (T/298.0)^{1.5} \exp(250.0/T)$	NIST	300-2000	
R512	OH + H <sub>2</sub>	→ H <sub>2</sub> O + H	$2.8 \times 10^{-12} \exp(-1800.0/T)$	JPL	200-300	Low Temperature
R513	OH + H <sub>2</sub> O <sub>2</sub>	→ H <sub>2</sub> O + HO <sub>2</sub>	$2.9 \times 10^{-12} \exp(-160.0/T)$	JPL	200-300	Low Temperature
R514	OH + HCN	→ HCNO + H	$4.65 \times 10^{-11} \exp(-1860.0/T)$	NIST	1500-2400	High Temperature
R515	OH + HCN	→ CO + NH <sub>2</sub>	$1.1 \times 10^{-13} \exp(-5890.0/T)$	NIST	500-2500	
R516	OH + HCN	→ CN + H <sub>2</sub> O	$1.84 \times 10^{-13} (T/298.0)^{1.5} \exp(-3890.0/T)$	NIST	298-2840	
R517	OH + HCNO	→ CNO + H <sub>2</sub> O	$9.43 \times 10^{-14} (T/298.0)^2 \exp(-1290.0/T)$	NIST	500-2500	
R518	OH + HCNO	→ CO <sub>2</sub> + NH <sub>2</sub>	$1.54 \times 10^{-14} (T/298.0)^{1.5} \exp(-1810.0/T)$	NIST	1250-1860	High Temperature
R519	OH + HNO	→ H <sub>2</sub> O + NO	$8.0 \times 10^{-11} \exp(-500.0/T)$	NIST	300-2000	
R520	OH + HNO <sub>2</sub>	→ H <sub>2</sub> O + NO <sub>2</sub>	$1.8 \times 10^{-11} \exp(-390.0/T)$	JPL	200-300	Low Temperature
R521	OH + HNO <sub>4</sub>	→ H <sub>2</sub> O + NO <sub>2</sub> + O <sub>2</sub>	$1.3 \times 10^{-12} \exp(380.0/T)$	JPL	200-300	Low Temperature
R522	OH + HO <sub>2</sub>	→ H <sub>2</sub> O + O <sub>2</sub>	$4.8 \times 10^{-11} \exp(250.0/T)$	JPL	200-300	Low Temperature
R523	OH + NH <sub>3</sub>	→ H <sub>2</sub> O + NH <sub>2</sub>	$1.7 \times 10^{-12} \exp(-710.0/T)$	JPL	200-300	Low Temperature
R524	OH + NO <sub>3</sub>	→ HO <sub>2</sub> + NO <sub>2</sub>	$2.0 \times 10^{-11}$	NIST	298	
R525	OH + O <sub>3</sub>	→ HO <sub>2</sub> + O <sub>2</sub>	$1.7 \times 10^{-12} \exp(-940.0/T)$	JPL	200-300	Low Temperature
R526	OH + OH	→ H <sub>2</sub> O + O	$1.8 \times 10^{-12}$	JPL	200-300	Low Temperature
R527	OH + S	→ H + SO	$6.6 \times 10^{-11}$	JPL	298	
R528	OH + SO	→ SO <sub>2</sub> + H	$2.7 \times 10^{-11} \exp(355.0/T)$	JPL	200-300	Low Temperature
R529	S + C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + HS	$2.04 \times 10^{-10} \exp(-7420.0/T)$	NIST	880-1150	High Temperature
R530	S + CH <sub>4</sub>	→ CH <sub>3</sub> + HS	$3.4 \times 10^{-10} \exp(-10000.0/T)$	NIST	1140-1480	High Temperature
R531	S + H <sub>2</sub>	→ H + HS	$2.24 \times 10^{-10} \exp(-9710.0/T)$	NIST	910-1660	High Temperature
R532	S + H <sub>2</sub> S	→ HS + HS	$1.38 \times 10^{-10} \exp(-3720.0/T)$	NIST	1050-1540	High Temperature
R533	S + HS	→ H + S <sub>2</sub>	$4.0 \times 10^{-11}$	NIST	295	
R534	S + NO	→ SO + N	$1.75 \times 10^{-10} \exp(-20206.0/T)$	NIST	2420-3870	
R535	S + NO <sub>2</sub>	→ NO + SO	$4.9 \times 10^{-11} \exp(84.2/T)$	NIST	296-410	Low Temperature
R536	S + O <sub>2</sub>	→ SO + O	$2.3 \times 10^{-12}$	JPL	200-300	Low Temperature
R537	S + O <sub>3</sub>	→ O <sub>2</sub> + SO	$1.2 \times 10^{-11}$	JPL	298	
R538	S + OCS	→ CO + S <sub>2</sub>	$1.5 \times 10^{-12} \exp(-1260.0/T)$	NIST	300-2570	
R539	S + SO <sub>2</sub>	→ SO + SO	$9.77 \times 10^{-12} \exp(-4546.0/T)$	NIST	1120-1540	High Temperature
R540	CS + O <sub>2</sub>	→ OCS + O	$2.9 \times 10^{-19}$	JPL	298	
R541	SO + NO <sub>2</sub>	→ SO <sub>2</sub> + NO	$1.4 \times 10^{-11}$	JPL	200-300	Low Temperature
R542	CS + NO <sub>2</sub>	→ OCS + NO	$7.6 \times 10^{-17}$	JPL	298	
R543	SO + CHO	→ HSO + CO	$5.5 \times 10^{-11} (T)^{-0.4}$	Kasting (1990)		Low Temperature
R544	SO + O <sub>2</sub>	→ SO <sub>2</sub> + O	$1.25 \times 10^{-13} \exp(-2190.0/T)$	JPL	200-300	Low Temperature
R545	SO + O <sub>3</sub>	→ SO <sub>2</sub> + O <sub>2</sub>	$3.4 \times 10^{-12} \exp(-1100.0/T)$	JPL	200-300	Low Temperature
R546	SO <sub>2</sub> + C <sub>2</sub> H	→ CO + OCS + H	$1.1 \times 10^{-11}$	NIST	298	
R547	SO <sub>2</sub> + CH	→ CHO + SO	$1.32 \times 10^{-10} \exp(250.0/T)$	NIST	295-665	Low Temperature
R548	SO <sub>2</sub> + CH <sub>2</sub>	→ CH <sub>2</sub> O + SO	$4.9 \times 10^{-12}$	NIST	295	
R549	SO <sub>2</sub> + CN	→ CNO + SO	$4.4 \times 10^{-12}$	NIST	298	
R550	SO <sub>2</sub> + H	→ OH + SO	$4.58 \times 10^{-8} (T/298.0)^{-2.3} \exp(-15635.0/T)$	NIST	900-1800	High Temperature

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R551	SO <sub>2</sub> + HO <sub>2</sub>	→ HSO <sub>2</sub> + O <sub>2</sub>	$8.6 \times 10^{-10} \exp(-5230.0/T)$	NIST	400-2000	
R552	SO <sub>2</sub> + NO <sub>2</sub>	→ SO <sub>3</sub> + NO	$1.05 \times 10^{-11} \exp(-13591.0/T)$	NIST	703-1850	
R553	SO <sub>2</sub> + O	→ SO + O <sub>2</sub>	$8.3 \times 10^{-12} \exp(-9800.0/T)$	NIST	440-3000	
R554	SO <sub>3</sub> + H	→ OH + SO <sub>2</sub>	$1.46 \times 10^{-11} (T/298.0)^{1.22} \exp(-1672.0/T)$	NIST	700-2000	
R555	SO <sub>3</sub> + O	→ SO <sub>2</sub> + O <sub>2</sub>	$1.06 \times 10^{-13} (T/298.0)^{2.57} \exp(-14673.0/T)$	NIST	1000-2000	
R556	SO <sub>3</sub> + OH	→ HO <sub>2</sub> + SO <sub>2</sub>	$9.73 \times 10^{-14} (T/298.0)^{2.46} \exp(-13711.0/T)$	NIST	800-2000	
R557	SO <sub>3</sub> + SO	→ SO <sub>2</sub> + SO <sub>2</sub>	$2.0 \times 10^{-15}$	NIST	298	
R558	HSO + O <sub>2</sub>	→ OH + SO <sub>2</sub>	$1.69 \times 10^{-15}$	NIST	298	
R559	SO + SO	→ SO <sub>2</sub> + S	$3.5 \times 10^{-15}$	NIST	298	
R560	HS + H	→ H <sub>2</sub> + S	$2.16 \times 10^{-11}$	NIST	295	
R561	CHO + CHO	→ CH <sub>2</sub> O + CO	$3.0 \times 10^{-11}$	NIST	300-2500	
R562	SO <sub>2</sub> <sup>1</sup> + O <sub>2</sub>	→ O + SO <sub>3</sub>	$1.0 \times 10^{-16}$	Turco et al. (1982)		Low Temperature
R563	SO <sub>2</sub> <sup>1</sup> + SO <sub>2</sub>	→ SO + SO <sub>3</sub>	$4.0 \times 10^{-12}$	Turco et al. (1982)		Low Temperature
R564	SO <sub>2</sub> <sup>3</sup> + SO <sub>2</sub>	→ SO + SO <sub>3</sub>	$7.0 \times 10^{-14}$	Turco et al. (1982)		Low Temperature
R565	SO <sub>3</sub> + H <sub>2</sub> O	→ H <sub>2</sub> SO <sub>4</sub>	$1.2 \times 10^{-15}$	NIST	298	
R566	HSO <sub>3</sub> + OH	→ H <sub>2</sub> O + SO <sub>3</sub>	$1.0 \times 10^{-11}$	Kasting (1990)		Low Temperature
R567	HSO <sub>3</sub> + H	→ H <sub>2</sub> + SO <sub>3</sub>	$1.0 \times 10^{-11}$	Kasting (1990)		Low Temperature
R568	NO <sub>2</sub> + CHO	→ CO + HNO <sub>2</sub>	$3.49 \times 10^{-24} (T/298.0)^{3.29} \exp(-1180.0/T)$	NIST	294-1650	
R569	S + CHO	→ HS + CO	$5.0 \times 10^{-11}$	Kasting (1990)		Low Temperature
R570	S + HO <sub>2</sub>	→ HS + O <sub>2</sub>	$1.5 \times 10^{-11}$	Kasting (1990)		Low Temperature
R571	S + HO <sub>2</sub>	→ SO + OH	$1.5 \times 10^{-11}$	Kasting (1990)		Low Temperature
R572	S + CO <sub>2</sub>	→ SO + CO	$1.0 \times 10^{-20}$	Yung & Demore (1999)		Low Temperature
R573	HSO + NO	→ HNO + SO	$3.7 \times 10^{-12} \exp(250.0/T)$	Kasting (1990)		Low Temperature
R574	HSO + OH	→ H <sub>2</sub> O + SO	$4.8 \times 10^{-11} \exp(250.0/T)$	Kasting (1990)		Low Temperature
R575	HSO + H	→ HS + OH	$7.29 \times 10^{-11}$	Kasting (1990)		Low Temperature
R576	HSO + H	→ H <sub>2</sub> + SO	$6.48 \times 10^{-12}$	Kasting (1990)		Low Temperature
R577	HSO + HS	→ H <sub>2</sub> S + SO	$1.0 \times 10^{-12}$	Kasting (1990)		Low Temperature
R578	HSO + O	→ OH + SO	$3.0 \times 10^{-11} \exp(200.0/T)$	Kasting (1990)		Low Temperature
R579	HSO + S	→ HS + SO	$1.0 \times 10^{-11}$	Kasting (1990)		Low Temperature
R580	H + C <sub>3</sub> H <sub>4</sub> <sup>2</sup>	→ H + C <sub>3</sub> H <sub>4</sub> <sup>1</sup>	$1.0 \times 10^{-11} \exp(-1000.0/T)$	Yung & Demore (1999)		Low Temperature
R581	H + C <sub>3</sub> H <sub>5</sub>	→ C <sub>3</sub> H <sub>4</sub> <sup>1</sup> + H <sub>2</sub>	$6.0 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R582	H + C <sub>3</sub> H <sub>5</sub>	→ C <sub>3</sub> H <sub>4</sub> <sup>2</sup> + H <sub>2</sub>	$6.0 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R583	H + C <sub>3</sub> H <sub>5</sub>	→ CH <sub>4</sub> + C <sub>2</sub> H <sub>2</sub>	$6.0 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R584	H + C <sub>3</sub> H <sub>6</sub>	→ C <sub>3</sub> H <sub>5</sub> + H <sub>2</sub>	$4.4 \times 10^{-13} (T/298.0)^{2.5} \exp(-1250.0/T)$	NIST	300-2500	
R585	H + C <sub>3</sub> H <sub>7</sub>	→ C <sub>3</sub> H <sub>6</sub> + H <sub>2</sub>	$5.0 \times 10^{-11}$	Yung & Demore (1999)		Low Temperature
R586	H + C <sub>3</sub> H <sub>7</sub>	→ C <sub>2</sub> H <sub>5</sub> + CH <sub>3</sub>	$6.0 \times 10^{-11}$	Yung & Demore (1999)		Low Temperature
R587	H + C <sub>4</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	$3.3 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R588	H + C <sub>4</sub> H <sub>3</sub>	→ C <sub>4</sub> H <sub>2</sub> + H <sub>2</sub>	$6.0 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R589	H + C <sub>4</sub> H <sub>5</sub>	→ C <sub>4</sub> H <sub>4</sub> + H <sub>2</sub>	$6.0 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R590	H + C <sub>4</sub> H <sub>9</sub>	→ C <sub>4</sub> H <sub>8</sub> + H <sub>2</sub>	$1.5 \times 10^{-12}$	NIST	300-2500	
R591	H + C <sub>6</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>4</sub> H <sub>2</sub>	$3.3 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R592	H + C <sub>6</sub> H <sub>3</sub>	→ C <sub>6</sub> H <sub>2</sub> + H <sub>2</sub>	$6.0 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R593	CH + C <sub>2</sub> H <sub>2</sub>	→ C <sub>3</sub> H <sub>2</sub> + H	$3.5 \times 10^{-10} \exp(61.0/T)$	Yung & Demore (1999)		Low Temperature

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R594	CH + C <sub>2</sub> H <sub>4</sub>	→ C <sub>3</sub> H <sub>4</sub> <sup>2</sup> + H	2.23 × 10 <sup>-10</sup> exp (173.0/T)	Yung & Demore (1999)		Low Temperature
R595	CH + C <sub>2</sub> H <sub>6</sub>	→ C <sub>3</sub> H <sub>6</sub> + H	1.8 × 10 <sup>-10</sup> exp (132.0/T)	Yung & Demore (1999)		Low Temperature
R596	CH <sub>21</sub> + H <sub>2</sub>	→ CH <sub>2</sub> + H <sub>2</sub>	1.26 × 10 <sup>-11</sup>	Yung & Demore (1999)		Low Temperature
R597	CH <sub>21</sub> + H <sub>2</sub>	→ CH <sub>3</sub> + H	9.24 × 10 <sup>-11</sup>	Yung & Demore (1999)		Low Temperature
R598	CH <sub>21</sub> + CH <sub>4</sub>	→ CH <sub>2</sub> + CH <sub>4</sub>	1.2 × 10 <sup>-11</sup>	Yung & Demore (1999)		Low Temperature
R599	CH <sub>21</sub> + CH <sub>4</sub>	→ CH <sub>3</sub> + CH <sub>3</sub>	5.9 × 10 <sup>-11</sup>	Yung & Demore (1999)		Low Temperature
R600	CH <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>3</sub> H <sub>2</sub> + H <sub>2</sub>	1.0 × 10 <sup>-10</sup> exp (-3332.0/T)	Yung & Demore (1999)		Low Temperature
R601	CH <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>3</sub> H <sub>3</sub> + H	1.0 × 10 <sup>-10</sup> exp (-3332.0/T)	Yung & Demore (1999)		Low Temperature
R602	CH <sub>3</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>3</sub> H <sub>5</sub> + H	6.5 × 10 <sup>-13</sup>	Yung & Demore (1999)		Low Temperature
R603	CH <sub>3</sub> + C <sub>3</sub> H <sub>5</sub>	→ CH <sub>4</sub> + C <sub>3</sub> H <sub>4</sub> <sup>1</sup>	6.5 × 10 <sup>-13</sup>	Yung & Demore (1999)		Low Temperature
R604	CH <sub>3</sub> + C <sub>3</sub> H <sub>5</sub>	→ CH <sub>4</sub> + C <sub>3</sub> H <sub>4</sub> <sup>2</sup>	6.5 × 10 <sup>-13</sup>	Yung & Demore (1999)		Low Temperature
R605	CH <sub>3</sub> + C <sub>3</sub> H <sub>7</sub>	→ CH <sub>4</sub> + C <sub>3</sub> H <sub>6</sub>	1.85 × 10 <sup>-12</sup> exp (339.0/T)	Yung & Demore (1999)		Low Temperature
R606	CH <sub>3</sub> + C <sub>3</sub> H <sub>8</sub>	→ CH <sub>4</sub> + C <sub>3</sub> H <sub>7</sub>	1.3 × 10 <sup>-24</sup> (T) <sup>4.0</sup> exp (-4175.0/T)	Yung & Demore (1999)		Low Temperature
R607	CH <sub>3</sub> + C <sub>4</sub> H <sub>5</sub>	→ CH <sub>4</sub> + C <sub>4</sub> H <sub>4</sub>	6.5 × 10 <sup>-13</sup>	Yung & Demore (1999)		Low Temperature
R608	C <sub>2</sub> + CH <sub>4</sub>	→ C <sub>2</sub> H + CH <sub>3</sub>	5.5 × 10 <sup>-11</sup> exp (-297.0/T)	Yung & Demore (1999)		Low Temperature
R609	C <sub>2</sub> H + C <sub>2</sub> H <sub>2</sub>	→ C <sub>4</sub> H <sub>2</sub> + H	1.25 × 10 <sup>-10</sup> (T/298.0) <sup>0.24</sup> exp (37.3/T)	NIST	200-2000	
R610	C <sub>2</sub> H + C <sub>2</sub> H <sub>4</sub>	→ C <sub>4</sub> H <sub>4</sub> + H	2.0 × 10 <sup>-11</sup>	NIST	300-2500	
R611	NO + CN	→ CNO + N	1.6 × 10 <sup>-10</sup> exp (-21168.0/T)	NIST	500-2500	
R612	C <sub>2</sub> H + C <sub>3</sub> H <sub>8</sub>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>3</sub> H <sub>7</sub>	6.0 × 10 <sup>-12</sup>	NIST	300-2500	
R613	C <sub>2</sub> H + C <sub>4</sub> H <sub>2</sub>	→ C <sub>6</sub> H <sub>2</sub> + H	1.5 × 10 <sup>-10</sup>	Yung & Demore (1999)		Low Temperature
R614	C <sub>2</sub> H + C <sub>4</sub> H <sub>10</sub>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>4</sub> H <sub>9</sub>	1.0 × 10 <sup>-11</sup>	NIST	300-2500	
R615	C <sub>2</sub> H + C <sub>6</sub> H <sub>2</sub>	→ C <sub>8</sub> H <sub>2</sub> + H	3.75 × 10 <sup>-12</sup>	Yung & Demore (1999)		Low Temperature
R616	C <sub>2</sub> H + C <sub>8</sub> H <sub>2</sub>	→ Haze	3.75 × 10 <sup>-12</sup>	Yung & Demore (1999)		Low Temperature
R617	C <sub>2</sub> H <sub>3</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>2</sub>	1.8 × 10 <sup>-11</sup>	Yung & Demore (1999)		Low Temperature
R618	C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>4</sub>	1.2 × 10 <sup>-11</sup> exp (-540.0/T)	Yung & Demore (1999)		Low Temperature
R619	C <sub>3</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>4</sub> H <sub>2</sub> + CH <sub>2</sub>	5.0 × 10 <sup>-13</sup>	Yung & Demore (1999)		Low Temperature
R620	C <sub>3</sub> H <sub>3</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>4</sub> H <sub>2</sub> + CH <sub>3</sub>	2.0 × 10 <sup>-13</sup>	Yung & Demore (1999)		Low Temperature
R621	C <sub>3</sub> H <sub>5</sub> + H <sub>2</sub>	→ C <sub>3</sub> H <sub>6</sub> + H	1.39 × 10 <sup>-13</sup> (T/298.0) <sup>2.38</sup> exp (-9560.0/T)	NIST	300-2500	
R622	C <sub>3</sub> H <sub>7</sub> + H <sub>2</sub>	→ C <sub>3</sub> H <sub>8</sub> + H	3.19 × 10 <sup>-14</sup> (T/298.0) <sup>2.84</sup> exp (-4600.0/T)	NIST	300-2500	
R623	C <sub>4</sub> H + H <sub>2</sub>	→ C <sub>4</sub> H <sub>2</sub> + H	6.3 × 10 <sup>-12</sup> exp (-1450.0/T)	Yung & Demore (1999)		Low Temperature
R624	C <sub>4</sub> H + CH <sub>4</sub>	→ C <sub>4</sub> H <sub>2</sub> + CH <sub>3</sub>	9.0 × 10 <sup>-12</sup> exp (-250.0/T)	Yung & Demore (1999)		Low Temperature
R625	C <sub>4</sub> H + C <sub>2</sub> H <sub>2</sub>	→ C <sub>6</sub> H <sub>2</sub> + H	1.5 × 10 <sup>-10</sup>	Yung & Demore (1999)		Low Temperature
R626	C <sub>4</sub> H + C <sub>2</sub> H <sub>6</sub>	→ C <sub>4</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	2.1 × 10 <sup>-11</sup>	Yung & Demore (1999)		Low Temperature
R627	C <sub>4</sub> H + C <sub>4</sub> H <sub>2</sub>	→ C <sub>8</sub> H <sub>2</sub> + H	3.75 × 10 <sup>-12</sup>	Yung & Demore (1999)		Low Temperature
R628	C <sub>4</sub> H + C <sub>6</sub> H <sub>2</sub>	→ Haze	3.75 × 10 <sup>-12</sup>	Yung & Demore (1999)		Low Temperature
R629	C <sub>4</sub> H + C <sub>8</sub> H <sub>2</sub>	→ Haze	3.75 × 10 <sup>-12</sup>	Yung & Demore (1999)		Low Temperature
R630	C <sub>4</sub> H <sub>5</sub> + H <sub>2</sub>	→ C <sub>4</sub> H <sub>6</sub> <sup>1</sup> + H	1.8 × 10 <sup>-11</sup> exp (-1699/T)	Yung & Demore (1999)		Low Temperature
R631	C <sub>4</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>6</sub> H <sub>6</sub> + H	3.0 × 10 <sup>-12</sup> exp (-1861/T)	Yung & Demore (1999)		Low Temperature
R632	C <sub>6</sub> H + H <sub>2</sub>	→ C <sub>6</sub> H <sub>2</sub> + H	6.3 × 10 <sup>-12</sup> exp (-1450.0/T)	Yung & Demore (1999)		Low Temperature
R633	C <sub>6</sub> H + CH <sub>4</sub>	→ C <sub>6</sub> H <sub>2</sub> + CH <sub>3</sub>	9.0 × 10 <sup>-12</sup> exp (-250.0/T)	Yung & Demore (1999)		Low Temperature
R634	C <sub>6</sub> H + C <sub>2</sub> H <sub>2</sub>	→ C <sub>8</sub> H <sub>2</sub> + H	3.75 × 10 <sup>-12</sup>	Yung & Demore (1999)		Low Temperature
R635	C <sub>6</sub> H + C <sub>2</sub> H <sub>6</sub>	→ C <sub>6</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>5</sub>	2.1 × 10 <sup>-11</sup>	Yung & Demore (1999)		Low Temperature
R636	C <sub>6</sub> H + C <sub>4</sub> H <sub>2</sub>	→ Haze	3.75 × 10 <sup>-12</sup>	Yung & Demore (1999)		Low Temperature

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
R637	C <sub>6</sub> H + C <sub>6</sub> H <sub>2</sub>	→ Haze	$3.75 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R638	C <sub>6</sub> H + C <sub>8</sub> H <sub>2</sub>	→ Haze	$3.75 \times 10^{-12}$	Yung & Demore (1999)		Low Temperature
R639	N <sub>2</sub> H <sub>4</sub> + H	→ N <sub>2</sub> H <sub>3</sub> + H <sub>2</sub>	$1.17 \times 10^{-11} \exp(-1260.0/T)$	NIST	222-657	Low Temperature
R640	NO <sub>2</sub> + CH <sub>3</sub>	→ CH <sub>3</sub> NO <sub>2</sub>	$3.44 \times 10^{-11} (T/298.0)^{-0.6}$	NIST	300-1400	
R641	N <sub>2</sub> H <sub>3</sub> + H	→ NH <sub>2</sub> + NH <sub>2</sub>	$2.66 \times 10^{-12}$	NIST	300	
R642	N <sub>2</sub> H <sub>3</sub> + N <sub>2</sub> H <sub>3</sub>	→ N <sub>2</sub> H <sub>4</sub> + N <sub>2</sub> H <sub>2</sub>	$1.9 \times 10^{-11}$	NIST	298	
R643	N <sub>2</sub> H <sub>3</sub> + N <sub>2</sub> H <sub>3</sub>	→ NH <sub>3</sub> + NH <sub>3</sub> + N <sub>2</sub>	$5.0 \times 10^{-12}$	NIST	423	
R644	NH <sub>2</sub> + OH	→ NH <sub>3</sub> + O	$3.32 \times 10^{-13} (T/298.0)^{0.4} \exp(-250.2/T)$	NIST	250-3000	
R645	O <sub>2</sub> + CHO <sub>2</sub>	→ HO <sub>2</sub> + CO <sub>2</sub>	$2.0 \times 10^{-12}$	NIST	220-430	Low Temperature
M1	C + C	→ C <sub>2</sub>	$5.46 \times 10^{-31} (T/298.0)^{-1.6} \times N$	NIST	5000-6000	High Temperature
M2	C + H <sub>2</sub>	→ CH <sub>2</sub>	$6.89 \times 10^{-32} \times N$	NIST	300	
M3	CH <sub>3</sub> + CH <sub>3</sub>	→ C <sub>2</sub> H <sub>6</sub>	$1.68 \times 10^{-24} (T/298.0)^{-7.0} \exp(-1390.0/T) \times N$	NIST	300-2000	
M4	CH <sub>3</sub> + O <sub>2</sub>	→ CH <sub>3</sub> O <sub>2</sub>	$k_0 = 1.2 \times 10^{-12} (T/300.0)^{1.1}$ $k_\infty = 4.0 \times 10^{-31} (T/300.0)^{-3.6}$	JPL	200-300	Low Temperature
M5	CO + CH	→ C <sub>2</sub> HO	$4.1 \times 10^{-30} (T/298.0)^{-2.1} \times N$	NIST	53-584	Low Temperature
M6	CO + CH <sub>3</sub>	→ C <sub>2</sub> H <sub>3</sub> O	$7.83 \times 10^{-29} (T/298.0)^{-7.56} \exp(-5490.0/T) \times N$	NIST	300-1700	
M7	H + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>3</sub>	$3.31 \times 10^{-30} \exp(-740.0/T) \times N$	NIST	200-400	Low Temperature
M8	H + C <sub>2</sub> H <sub>2</sub> O	→ C <sub>2</sub> H <sub>3</sub> O	$1.38 \times 10^{-30} \times N$	NIST	1000-1700	High Temperature
M9	H + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>5</sub>	$7.69 \times 10^{-30} \exp(-380.0/T) \times N$	NIST	300-800	
M10	H + CHO	→ CH <sub>2</sub> O	$3.21 \times 10^{-30} (T/298.0)^{-2.57} \exp(-215.0/T) \times N$	NIST	1560-2270	
M11	H + CN	→ HCN	$9.35 \times 10^{-30} (T/298.0)^{-2.0} \exp(-521.0/T) \times N$	NIST	500-2500	
M12	H + CO	→ CHO	$5.29 \times 10^{-34} \exp(-370.0/T) \times N$	NIST	300-2500	
M13	H + H	→ H <sub>2</sub>	$6.04 \times 10^{-33} (T/298.0)^{-1.0} \times N$	NIST	300-2500	
M14	H + NH <sub>2</sub>	→ NH <sub>3</sub>	$3.0 \times 10^{-30} \times N$	NIST	298	
M15	H + NO	→ HNO	$k_0 = 2.44 \times 10^{-10} (T/298.0)^{-0.41}$ $k_\infty = 1.34 \times 10^{-31} (T/298.0)^{-1.32} \exp(-370.5/T)$	NIST	230-4200	
M16	H + O	→ OH	$4.36 \times 10^{-32} (T/298.0)^{-1.0} \times N$	NIST	300-2500	
M17	H + O <sub>2</sub>	→ HO <sub>2</sub>	$k_0 = 7.5 \times 10^{-11} (T/300.0)^{0.2}$ $k_\infty = 4.4 \times 10^{-32} (T/300.0)^{-1.3}$	JPL	200-300	Low Temperature
M18	H + OH	→ H <sub>2</sub> O	$6.87 \times 10^{-31} (T/298.0)^{-2.0} \times N$	NIST	300-3000	
M19	HO <sub>2</sub> + HO <sub>2</sub>	→ H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	$1.7 \times 10^{-33} \exp(1000.0/T) \times N$	JPL	200-300	Low Temperature
M20	HO <sub>2</sub> + NO <sub>2</sub>	→ HNO <sub>4</sub>	$k_0 = 2.9 \times 10^{-12} (T/300.0)^{-1.1}$ $k_\infty = 2.0 \times 10^{-31} (T/300.0)^{-3.4}$	JPL	200-300	Low Temperature
M21	HS + O <sub>2</sub>	→ HSO <sub>2</sub>	$9.18 \times 10^{-34} (T/298.0)^{-1.69} \times N$	NIST	200-400	Low Temperature
M22	N + C	→ CN	$9.4 \times 10^{-33} \times N$	NIST	298	
M23	N + H	→ NH	$5.0 \times 10^{-32} \times N$	NIST	298	
M24	N + H <sub>2</sub>	→ NH <sub>2</sub>	$1.0 \times 10^{-36} \times N$	NIST	298	
M25	N + N	→ N <sub>2</sub>	$1.38 \times 10^{-33} \exp(502.7/T) \times N$	JPL	90-6400	
M26	N + O	→ NO	$5.46 \times 10^{-33} (T/298.0)^{-1.29} \times N$	NIST	196-297	Low Temperature
M27	NO + CH <sub>3</sub> O	→ CH <sub>3</sub> NO <sub>2</sub>	$k_0 = 3.8 \times 10^{-11} (T/300.0)^{-0.6}$ $k_\infty = 2.3 \times 10^{-29} (T/300.0)^{-2.8}$	JPL	200-300	Low Temperature
M28	NO <sub>2</sub> + CH <sub>3</sub> O	→ CH <sub>3</sub> NO <sub>3</sub>	$k_0 = 1.9 \times 10^{-11} (T/300.0)^{-1.8}$ $k_\infty = 5.3 \times 10^{-29} (T/300.0)^{-4.4}$	JPL	200-300	Low Temperature

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
M29	NO <sub>2</sub> + NO <sub>3</sub>	→ N <sub>2</sub> O <sub>5</sub>	$k_0 = 1.4 \times 10^{-12} (T/300.0)^{-0.7}$ $k_\infty = 2.0 \times 10^{-30} (T/300.0)^{-4.4}$	JPL	200-300	Low Temperature
M30	O + C	→ CO	$2.0 \times 10^{-34} \times N$	NIST	8000	High Temperature
M31	O + CO	→ CO <sub>2</sub>	$1.7 \times 10^{-33} \exp(-1509.0/T) \times N$	NIST	300-2500	
M32	O + NO	→ NO <sub>2</sub>	$k_0 = 3.0 \times 10^{-11}$ $k_\infty = 9.0 \times 10^{-32} (T/300)^{-1.5}$	JPL	200-300	Low Temperature
M33	O + NO <sub>2</sub>	→ NO <sub>3</sub>	$k_0 = 2.2 \times 10^{-11} (T/300.0)^{-0.7}$ $k_\infty = 2.5 \times 10^{-31} (T/300.0)^{-1.8}$	JPL	200-300	Low Temperature
M34	O + O	→ O <sub>2</sub>	$5.21 \times 10^{-35} \exp(900.0/T) \times N$	NIST	200-4000	
M35	O + O <sub>2</sub>	→ O <sub>3</sub>	$6.0 \times 10^{-34} (T/300.0)^{-2.4} \times N$	JPL	200-300	Low Temperature
M36	O( <sup>1</sup> D) + N <sub>2</sub>	→ N <sub>2</sub> O	$2.8 \times 10^{-36} (T/300.0)^{-0.9} \times N$	JPL	200-300	Low Temperature
M37	OH + C <sub>2</sub> H <sub>2</sub>	→ C <sub>2</sub> H <sub>3</sub> O	$k_0 = 8.3 \times 10^{-13} (T/300.0)^{2.0}$ $k_\infty = 5.5 \times 10^{-30}$	JPL	200-300	Low Temperature
M38	OH + C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>5</sub> O	$k_0 = 7.5 \times 10^{-12} (T/300.0)^{-0.85}$ $k_\infty = 1.0 \times 10^{-28} (T/300.0)^{-4.5}$	JPL	200-300	Low Temperature
M39	NH <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>5</sub> N	$1.8 \times 10^{-27} (T/298.0)^{-3.85} \times N$		200-400	Low Temperature
M40	OH + HNO <sub>3</sub>	→ H <sub>2</sub> O + NO <sub>3</sub>	$k_0 = 2.4 \times 10^{-14} \exp(460.0/T)$ $k_2 = 2.7 \times 10^{-17} \exp(2199.0/T)$ $k_3 = 6.5 \times 10^{-34} \exp(1355.0/T)$	JPL	200-300	Low Temperature
M41	OH + NO	→ HNO <sub>2</sub>	$k_0 = 3.6 \times 10^{-11} (T/300.0)^{-0.1}$ $k_\infty = 7.0 \times 10^{-31} (T/300.0)^{-2.6}$	JPL	200-300	Low Temperature
M42	OH + NO <sub>2</sub>	→ HNO <sub>3</sub>	$k_0 = 2.8 \times 10^{-11}$ $k_\infty = 1.8 \times 10^{-30} (T/300.0)^{-3.0}$	JPL	200-300	Low Temperature
M43	OH + OH	→ H <sub>2</sub> O <sub>2</sub>	$k_0 = 2.6 \times 10^{-11}$ $k_\infty = 6.9 \times 10^{-31} (T/300.0)^{-1.0}$	JPL	200-300	Low Temperature
M44	S + S	→ S <sub>2</sub>	$5.0 \times 10^{-32} \exp(900.0/T) \times N$	Moses et al. (2002)	100-500	Low Temperature
M45	SO + O	→ SO <sub>2</sub>	$4.82 \times 10^{-31} (T/298.0)^{-2.17} \times N$	NIST	298-3000	
M46	SO + OH	→ HSO <sub>2</sub>	$6.45 \times 10^{-29} (T/298.0)^{-3.48} \exp(-490.0/T) \times N$	NIST	200-2000	
M47	SO <sub>2</sub> + H	→ HSO <sub>2</sub>	$5.61 \times 10^{-30} (T/298.0)^{-5.19} \exp(-2271.0/T) \times N$	NIST	200-1000	
M48	SO <sub>2</sub> + O	→ SO <sub>3</sub>	$k_0 = 4.2 \times 10^{-14} (T/300.0)^{1.8}$ $k_\infty = 1.8 \times 10^{-33} (T/300.0)^{2.0}$	JPL	200-300	Low Temperature
M49	SO <sub>2</sub> + OH	→ HSO <sub>3</sub>	$k_0 = 1.6 \times 10^{-12}$ $k_\infty = 3.3 \times 10^{-31} (T/300.0)^{-4.3}$	JPL	200-300	Low Temperature
M50	H + SO	→ HSO	$k_0 = 7.5 \times 10^{-11}$ $k_\infty = 5.7 \times 10^{-32} (T/300.0)^{-1.6}$	Kasting (1990)		Low Temperature
M51	S + S <sub>2</sub>	→ S <sub>3</sub>	$1.1 \times 10^{-30} (T/300.0)^{-2.0} \times N$	Moses et al. (2002)		Low Temperature
M52	S + S <sub>3</sub>	→ S <sub>4</sub>	$1.1 \times 10^{-30} (T/300.0)^{-2.0} \times N$	Moses et al. (2002)		Low Temperature
M53	S <sub>2</sub> + S <sub>2</sub>	→ S <sub>4</sub>	$4.0 \times 10^{-31} \exp(900.0/T) \times N$	Moses et al. (2002)		Low Temperature
M54	S <sub>4</sub> + S <sub>4</sub>	→ S <sub>8</sub> (A)	$4.0 \times 10^{-31} \exp(900.0/T) \times N$	Moses et al. (2002)		Low Temperature
M55	H + CH <sub>2</sub>	→ CH <sub>3</sub>	$k_0 = 2.37 \times 10^{-12} \exp(523.0/T)$ $k_\infty = 5.8 \times 10^{-30} \exp(355.0/T)$	Yung & Demore (1999)		Low Temperature
M56	H + CH <sub>3</sub>	→ CH <sub>4</sub>	$6.2 \times 10^{-29} (T/298.0)^{-1.8} \times N$	NIST	300-1000	
M57	H + C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>6</sub>	$k_0 = 1.5 \times 10^{-10}$			

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
			$k_\infty = 5.5 \times 10^{-23} (T)^{-2.0} \exp(-1040/T)$	Yung & Demore (1999)		Low Temperature
M58	H + C <sub>3</sub> H <sub>2</sub>	→ C <sub>3</sub> H <sub>3</sub>	$4.42 \times 10^{-10} (T/298.0)^{0.22} \exp(43.0/T)$	NIST	200-2000	
M59	H + C <sub>3</sub> H <sub>3</sub>	→ C <sub>3</sub> H <sub>4</sub> <sup>1</sup>	$1.9 \times 10^{-10} (T/298.0)^{0.1} \exp(16.0/T)$	NIST	200-2000	
M60	H + C <sub>3</sub> H <sub>3</sub>	→ C <sub>3</sub> H <sub>4</sub> <sup>2</sup>	$1.1 \times 10^{-10} (T/298.0)^{0.21} \exp(86.6/T)$	NIST	200-2000	
M61	H + C <sub>3</sub> H <sub>4</sub> <sup>1</sup>	→ CH <sub>3</sub> + C <sub>2</sub> H <sub>2</sub>	$9.49 \times 10^{-12} (T/298.0)^{1.74} \exp(3872.8/T)$	NIST	200-3000	
M62	H + C <sub>3</sub> H <sub>4</sub> <sup>1</sup>	→ C <sub>3</sub> H <sub>5</sub>	$9.61 \times 10^{-12} \exp(-1560.0/T)$	NIST	195-503	Low Temperature
M63	H + C <sub>3</sub> H <sub>4</sub> <sup>2</sup>	→ CH <sub>3</sub> + C <sub>2</sub> H <sub>2</sub>	$9.49 \times 10^{-12} (T/298.0)^{1.74} \exp(3872.8/T)$	NIST	200-3000	
M64	H + C <sub>3</sub> H <sub>4</sub> <sup>2</sup>	→ C <sub>3</sub> H <sub>5</sub>	$1.01 \times 10^{-11} (T/298.0)^{0.69} \exp(1509.0/T)$	NIST	350-1200	
M65	H + C <sub>3</sub> H <sub>5</sub>	→ C <sub>3</sub> H <sub>6</sub>	$2.64 \times 10^{-10} (T/298.0)^{0.18} \exp(62.5/T)$	NIST	200-2000	
M66	H + C <sub>3</sub> H <sub>6</sub>	→ C <sub>3</sub> H <sub>7</sub>	$7.59 \times 10^{-12} (T/298.0)^{0.51} \exp(-1318.2/T)$	NIST	298-2000	
M67	H + C <sub>3</sub> H <sub>7</sub>	→ C <sub>3</sub> H <sub>8</sub>	$3.32 \times 10^{-11}$	NIST	300-2000	
M68	H + C <sub>3</sub> H <sub>8</sub>	→ C <sub>3</sub> H <sub>7</sub> + H <sub>2</sub>	$4.23 \times 10^{-12} (T/298.0)^{2.54} \exp(-3400/T)$	NIST	298-2500	
M69	H + C <sub>4</sub> H <sub>2</sub>	→ C <sub>4</sub> H <sub>3</sub>	$k_0 = 1.39 \times 10^{-10} \exp(-1184/T)$ $k_\infty = 1.0 \times 10^{-28}$	Yung & Demore (1999)		Low Temperature
M70	H + C <sub>4</sub> H <sub>5</sub>	→ C <sub>4</sub> H <sub>6</sub> <sup>1</sup>	$6.68 \times 10^{-11} (T/298.0)^{0.31} \exp(93.8/T)$	NIST	200-2000	
M71	H + C <sub>6</sub> H <sub>2</sub>	→ C <sub>6</sub> H <sub>3</sub>	$k_0 = 1.39 \times 10^{-10} \exp(-1184/T)$ $k_\infty = 1.0 \times 10^{-28}$	Yung & Demore (1999)		Low Temperature
M72	CH + H <sub>2</sub>	→ CH <sub>3</sub>	$k_0 = 2.37 \times 10^{-12} \exp(523.0/T)$ $k_\infty = 5.8 \times 10^{-30} \exp(355.0/T)$	Yung & Demore (1999)		Low Temperature
M73	CH <sub>3</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>3</sub> H <sub>6</sub>	$1.2 \times 10^{-10}$	NIST	298	
M74	CH <sub>3</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>3</sub> H <sub>8</sub>	$5.6 \times 10^{-11}$	NIST	300-2000	
M75	CH <sub>3</sub> + C <sub>3</sub> H <sub>3</sub>	→ C <sub>4</sub> H <sub>6</sub> <sup>1</sup>	$8.3 \times 10^{-12}$	NIST	1200-1500	High Temperature
M76	CH <sub>3</sub> + C <sub>3</sub> H <sub>3</sub>	→ C <sub>4</sub> H <sub>6</sub> <sup>2</sup>	$8.3 \times 10^{-12}$	NIST	1200-1500	High Temperature
M77	CH <sub>3</sub> + C <sub>3</sub> H <sub>5</sub>	→ C <sub>4</sub> H <sub>8</sub>	$2.72 \times 10^{-11} (T/298.0)^{-0.32} \exp(66.1/T)$	NIST	300-2500	
M78	CH <sub>3</sub> + C <sub>3</sub> H <sub>6</sub>	→ C <sub>4</sub> H <sub>9</sub>	$1.27 \times 10^{-14} (T/298.0)^{2.67} \exp(-3447.0/T)$	NIST	298-2000	
M79	CH <sub>3</sub> + C <sub>3</sub> H <sub>7</sub>	→ C <sub>4</sub> H <sub>10</sub>	$5.16 \times 10^{-11} (T/298.0)^{-0.32}$	NIST	300-2500	
M80	C <sub>2</sub> H <sub>3</sub> + C <sub>2</sub> H <sub>2</sub>	→ C <sub>4</sub> H <sub>5</sub>	$2.09 \times 10^{-14} (T/298.0)^{1.9} \exp(-1060/T)$	NIST	300-1500	
M81	C <sub>2</sub> H <sub>3</sub> + C <sub>2</sub> H <sub>3</sub>	→ C <sub>4</sub> H <sub>6</sub> <sup>3</sup>	$k_0 = 8.2 \times 10^{-11}$ $k_\infty = 8.76 \times 10^{-6} (T)^{-7.03} \exp(-1390/T)$	Yung & Demore (1999)		Low Temperature
M82	C <sub>2</sub> H <sub>3</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>4</sub> H <sub>8</sub>	$6.5 \times 10^{-11}$	NIST	298	
M83	C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>5</sub>	→ C <sub>4</sub> H <sub>10</sub>	$1.9 \times 10^{-11}$	NIST	300-1200	
M84	NH <sub>2</sub> + NH <sub>2</sub>	→ N <sub>2</sub> H <sub>4</sub>	$1.96 \times 10^{-29} (T/298.0)^{-3.9} \times N$	NIST	200-400	Low Temperature
M85	NH <sub>2</sub> + CH <sub>3</sub>	→ CH <sub>5</sub> N	$1.8 \times 10^{-27} (T/298.0)^{-3.85} \times N$	NIST	200-400	Low Temperature
T1	O <sub>3</sub>	→ O <sub>2</sub> + O	$7.16 \times 10^{-10} \exp(-11200.0/T) \times N$	NIST	300-3000	
T2	HO <sub>2</sub>	→ O <sub>2</sub> + H	$2.41 \times 10^{-8} (T/298.0)^{-1.18} \exp(-24415.0/T) \times N$	NIST	200-2000	
T3	H <sub>2</sub> O <sub>2</sub>	→ OH + OH	$2.01 \times 10^{-7} \exp(-22852.0/T) \times N$	NIST	700-1500	
T4	N <sub>2</sub> O	→ N <sub>2</sub> + O	$7.07 \times 10^{-9} \exp(-29467.0/T) \times N$	NIST	900-2000	
T5	NO <sub>2</sub>	→ NO + O	$1.88 \times 10^{-4} (T/298.0)^{-3.37} \exp(-37645.0/T) \times N$	NIST	1400-2500	
T6	NO <sub>3</sub>	→ NO + O <sub>2</sub>	$2.5 \times 10^6 \exp(-6100.0/T)$	NIST	298-934	
T7	N <sub>2</sub> O <sub>5</sub>	→ NO <sub>2</sub> + NO <sub>3</sub>	$1.0 \times 10^{-3} (T/298.0)^{-3.5} \exp(-11000.0/T) \times N$	NIST	200-400	Low Temperature
T8	HNO	→ H + NO	$5.48 \times 10^{-7} (T/298.0)^{-1.24} \exp(-25312.0/T) \times N$	NIST	300-2500	
T9	HNO <sub>2</sub>	→ OH + NO	$1.98 \times 10^{-3} (T/298.0)^{-3.8} \exp(-25257.0/T) \times N$	NIST	300-2500	
T10	HNO <sub>3</sub>	→ OH + NO <sub>2</sub>	$1.15 \times 10^{-6} \exp(-23092.0/T) \times N$	NIST	300-2000	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
T11	HNO <sub>3</sub>	→ HO <sub>2</sub> + NO	$8.0 \times 10^{-2} (T/298.0)^{-6.55} \exp(-26099.0/T) \times N$	NIST	295-1200	
T12	HNO <sub>4</sub>	→ O <sub>2</sub> + HNO <sub>2</sub>	$6.31 \times 10^{17} \exp(-13110.0/T)$	NIST	245-328	Low Temperature
T13	HNO <sub>4</sub>	→ HO <sub>2</sub> + NO <sub>2</sub>	$4.10 \times 10^{-5} \exp(-10600.0/T) \times N$	NIST	260-300	Low Temperature
T14	CH <sub>2</sub> O	→ CO + H <sub>2</sub>	$7.7 \times 10^{-9} \exp(-33075.0/T) \times N$	NIST	1400-3200	
T15	CH <sub>2</sub> O <sub>2</sub>	→ CO <sub>2</sub> + H <sub>2</sub>	$2.49 \times 10^{-8} \exp(-28745.0/T) \times N$	NIST	1280-2030	
T16	CH <sub>2</sub> O <sub>2</sub>	→ CO + H <sub>2</sub> O	$3.47 \times 10^{-10} \exp(-20326.0/T) \times N$	NIST	1370-2000	
T17	CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>2</sub> O + OH	$5.0 \times 10^4$	NIST	249	Low Temperature
T18	CH <sub>3</sub> O <sub>2</sub>	→ CH <sub>2</sub> O <sub>2</sub> + H	$1.0 \times 10^{14} \exp(-7500.0/T)$	NIST	298-343	Low Temperature
T19	CH <sub>4</sub> O	→ CH <sub>3</sub> O + H	$2.16 \times 10^{-8} \exp(-33556.0/T) \times N$	NIST	1400-2500	
T20	CH <sub>4</sub> O	→ CH <sub>3</sub> + OH	$1.1 \times 10^{-7} \exp(-33075.0/T) \times N$	NIST	1000-2000	
T21	CH <sub>4</sub> O	→ CH <sub>2</sub> O + H <sub>2</sub>	$2.12 \times 10^{13} (T/298.0)^{1.22} \exp(-43539.0/T)$	NIST	300-2500	
T22	CH <sub>4</sub> O	→ CH <sub>2</sub> + H <sub>2</sub> O	$9.51 \times 10^{15} (T/298.0)^{-1.02} \exp(-46185.0/T)$	NIST	1000-3000	
T23	CH <sub>4</sub> O <sub>2</sub>	→ CH <sub>3</sub> O + OH	$6.0 \times 10^{14} \exp(-21288.0/T)$	NIST	500-800	
T24	CH <sub>4</sub> O <sub>2</sub>	→ CH <sub>2</sub> O + H <sub>2</sub> O	$4.15 \times 10^{13} \exp(-22731.0/T)$	NIST	300-1000	
T25	C <sub>2</sub> H <sub>3</sub>	→ C <sub>2</sub> H <sub>2</sub> + H	$0.19 (T/298.0)^{-7.5} \exp(-22852.0/T) \times N$	NIST	500-2500	
T26	C <sub>2</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub>	$5.8 \times 10^{-8} \exp(-35961.0/T) \times N$	NIST	1500-3200	
T27	C <sub>2</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>4</sub> + H	$1.69 \times 10^{-6} \exp(-16838.0/T) \times N$	NIST	700-900	
T28	C <sub>2</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>5</sub> + H	$8.11 \times 10^{17} (T/298.0)^{-1.23} \exp(-51356.0/T)$	NIST	200-2500	
T29	C <sub>2</sub> HO	→ CO + CH	$1.08 \times 10^{-8} \exp(-29828.0/T) \times N$	NIST	1500-2500	
T30	C <sub>2</sub> H <sub>2</sub> O	→ CO + CH <sub>2</sub>	$5.98 \times 10^{-9} \exp(-29828.0/T) \times N$	NIST	1000-2000	
T31	C <sub>2</sub> H <sub>3</sub> O	→ C <sub>2</sub> H <sub>2</sub> + OH	$2.2 \times 10^{12} \exp(-15154.0/T)$	NIST	627-713	
T32	C <sub>2</sub> H <sub>3</sub> O	→ CO + CH <sub>3</sub>	$6.82 \times 10^{-3} (T/298.0)^{-8.62} \exp(-11300.0/T) \times N$	NIST	500-2500	
T33	C <sub>2</sub> H <sub>4</sub> O	→ CHO + CH <sub>3</sub>	$2.0 \times 10^{15} \exp(-39810.0/T)$	NIST	500-2000	
T34	C <sub>2</sub> H <sub>4</sub> O	→ C <sub>2</sub> H <sub>2</sub> O + H <sub>2</sub>	$3.0 \times 10^{14} \exp(-42216.0/T)$	NIST	1000-1700	
T35	C <sub>2</sub> H <sub>4</sub> O	→ CH <sub>4</sub> + CO	$1.0 \times 10^{15} \exp(-42817.0/T)$	NIST	1000-1700	
T36	C <sub>2</sub> H <sub>5</sub> O	→ CH <sub>2</sub> O + CH <sub>3</sub>	$1.33 \times 10^{15} (T/298.0)^{-2.02} \exp(-12749.0/T)$	NIST	298-2000	
T37	C <sub>2</sub> H <sub>5</sub> O	→ C <sub>2</sub> H <sub>4</sub> + OH	$6.19 \times 10^{11} \exp(-11900.0/T)$	NIST	544-673	
T38	C <sub>2</sub> H <sub>5</sub> O	→ C <sub>2</sub> H <sub>4</sub> O + H	$1.07 \times 10^{14} (T/298.0)^{-0.69} \exp(-11187.0/T)$	NIST	298-2000	
T39	HCNO	→ CN + OH	$1.66 \times 10^{-9} \exp(-64.0/T) \times N$	NIST	1420-1750	High Temperature
T40	CNO	→ CO + N	$1.69 \times 10^{-9} \exp(-23453.0/T) \times N$	NIST	1450-2600	
T41	SO <sub>3</sub>	→ SO <sub>2</sub> + O	$9.47 \times 10^{-7} \exp(-40051.0/T) \times N$	NIST	1273-1348	
T42	HSO	→ SO + H	$1.4 \times 10^{-8} \exp(-29467.0/T) \times N$	NIST	1100-2000	
T43	HSO <sub>2</sub>	→ SO <sub>2</sub> + H	$4.16 \times 10^{-7} (T/298.0)^{-3.29} \exp(-9610.0/T) \times N$	NIST	200-2000	
T44	HSO <sub>2</sub>	→ O + HSO	$4.61 \times 10^{-4} (T/298.0)^{-5.87} \exp(-15635.4/T) \times N$	NIST	200-2000	
T45	HSO <sub>2</sub>	→ O <sub>2</sub> + HS	$2.73 \times 10^{-8} (T/298.0)^{-2.82} \exp(3750.0/T) \times N$	NIST	200-2000	
T46	CHO	→ CO + H	$6.0 \times 10^{-11} \exp(-7721.0/T) \times N$	NIST	298-1229	
T47	CH <sub>3</sub> O	→ CH <sub>2</sub> O + H	$1.69 \times 10^{14} (T/298.0)^{-0.39} \exp(-13230.0/T)$	NIST	298-2000	
T48	CHO <sub>2</sub>	→ CO + OH	$7.67 \times 10^{-6} (T/298.0)^{-1.89} \exp(-17800.0/T) \times N$	NIST	200-2200	
T49	CHO <sub>2</sub>	→ CO <sub>2</sub> + H	$1.25 \times 10^{-5} (T/298.0)^{-3.02} \exp(-17560.0/T) \times N$	NIST	200-2200	
T50	CH <sub>3</sub> NO <sub>2</sub>	→ CH <sub>3</sub> O + NO	$1.32 \times 10^{-6} \exp(-17199.0/T) \times N$	NIST	680-955	
T51	CH <sub>3</sub> NO <sub>2</sub>	→ CH <sub>2</sub> O + HNO	$3.98 \times 10^{13} \exp(-19364.0/T)$	NIST	440-473	
T52	CH <sub>3</sub> NO <sub>3</sub>	→ CH <sub>3</sub> O + NO <sub>2</sub>	$1.0 \times 10^{13} \exp(-16838.0/T)$	NIST	700-1200	
T53	HSO <sub>3</sub>	→ OH + SO <sub>2</sub>	$3.16 \times 10^{-4} (T/298.0)^{-4.72} \exp(-13591.0/T) \times N$	NIST	150-1500	

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No.	Reactants	Products	Reaction Rate	Reference	Temperature	Note
T54	SO <sub>2</sub> <sup>1</sup>	→ SO <sub>2</sub> <sup>3</sup>	$1.0 \times 10^{-12} \times N + 1.5 \times 10^3$	Turco et al. (1982)		Low Temperature
T55	SO <sub>2</sub> <sup>1</sup>	→ SO <sub>2</sub>	$1.0 \times 10^{-11} \times N + 2.2 \times 10^4$	Turco et al. (1982)		Low Temperature
T56	SO <sub>2</sub> <sup>3</sup>	→ SO <sub>2</sub>	$1.5 \times 10^{-13} \times N + 1.13 \times 10^3$	Turco et al. (1982)		Low Temperature
T57	HCN	→ H + CN	$1.93 \times 10^{-4} (T/298.0)^{-2.44} \exp(-62782.1/T) \times N$	NIST	1800-5000	
T58	H <sub>2</sub> S	→ H <sub>2</sub> + S	$3.16 \times 10^{-10} \exp(-32954.6/T) \times N$	NIST	1890-2890	
T59	H <sub>2</sub> S	→ HS + H	$2.92 \times 10^{-8} \exp(-33315.4/T) \times N$	NIST	873-1470	
T60	OCS	→ CO + S	$4.07 \times 10^{-10} \exp(-30910.0/T) \times N$	NIST	1900-3230	
T61	C <sub>3</sub> H <sub>5</sub>	→ C <sub>3</sub> H <sub>4</sub> <sup>1</sup> + H	$3.98 \times 10^{12} \exp(-18402.0/T)$	NIST	300-2500	
T62	C <sub>3</sub> H <sub>5</sub>	→ C <sub>3</sub> H <sub>4</sub> <sup>2</sup> + H	$1.40 \times 10^{13} \exp(-30188.3/T)$	NIST	300-2500	
T63	C <sub>3</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>2</sub> + CH <sub>3</sub>	$1.26 \times 10^{13} \exp(-16838.0/T)$	NIST	300-2500	
T64	C <sub>3</sub> H <sub>6</sub>	→ C <sub>2</sub> H <sub>3</sub> + CH <sub>3</sub>	$1.18 \times 10^{18} (T/298.0)^{-1.2} \exp(-49191.0/T)$	NIST	300-2500	
T65	C <sub>3</sub> H <sub>6</sub>	→ C <sub>3</sub> H <sub>5</sub> + H	$2.50 \times 10^{15} \exp(-43659.0/T)$	NIST	300-2500	
T66	C <sub>3</sub> H <sub>6</sub>	→ C <sub>3</sub> H <sub>4</sub> <sup>2</sup> + H <sub>2</sub>	$4.00 \times 10^{13} \exp(-40291.0/T)$	NIST	1200-1800	
T67	C <sub>3</sub> H <sub>7</sub>	→ C <sub>3</sub> H <sub>6</sub> + H	$1.09 \times 10^{13} (T/298.0)^{0.17} \exp(-17921.6/T)$	NIST	298-2000	
T68	C <sub>3</sub> H <sub>7</sub>	→ C <sub>2</sub> H <sub>4</sub> + CH <sub>3</sub>	$1.31 \times 10^{13} (T/298.0)^{0.87} \exp(-15274.6/T)$	NIST	298-1000	
T69	C <sub>3</sub> H <sub>8</sub>	→ C <sub>3</sub> H <sub>7</sub> + H	$1.58 \times 10^{16} \exp(-49071.0/T)$	NIST	300-2500	
T70	C <sub>3</sub> H <sub>8</sub>	→ C <sub>2</sub> H <sub>5</sub> + CH <sub>3</sub>	$1.07 \times 10^{12} (T/298.0)^{-15.74} \exp(-49672.0/T) \times N$	NIST	600-1653	
T71	C <sub>3</sub> H <sub>8</sub>	→ C <sub>3</sub> H <sub>6</sub> + H <sub>2</sub>	$3.38 \times 10^{10}$	NIST	3392	High Temperature
T72	C <sub>4</sub> H <sub>3</sub>	→ C <sub>4</sub> H <sub>2</sub> + H	$1.66 \times 10^{-8} \exp(-29707.0/T) \times N$	NIST	1900-2500	
T73	C <sub>4</sub> H <sub>4</sub>	→ C <sub>4</sub> H <sub>3</sub> + H	$6.3 \times 10^{13} \exp(-43779.0/T)$	NIST	1170-1690	
T74	C <sub>4</sub> H <sub>4</sub>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>2</sub>	$1.15 \times 10^{15} \exp(-43539.0/T)$	NIST	1700-2400	
T75	C <sub>4</sub> H <sub>5</sub>	→ C <sub>4</sub> H <sub>4</sub> + H	$1.6 \times 10^{14} \exp(-20807.0/T)$	NIST	900-1100	
T76	C <sub>4</sub> H <sub>5</sub>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	$3.57 \times 10^{-8} (T/298.0)^{0.7} \exp(-21288.0/T) \times N$	NIST	300-1500	
T77	C <sub>4</sub> H <sub>6</sub> <sup>1</sup>	→ C <sub>4</sub> H <sub>5</sub> + H	$7.7 \times 10^{14} \exp(-44260.0/T)$	NIST	1100-1600	
T78	C <sub>4</sub> H <sub>6</sub> <sup>2</sup>	→ C <sub>3</sub> H <sub>3</sub> + CH <sub>3</sub>	$5.0 \times 10^{15} \exp(-38126.0/T)$	NIST	300-2500	
T79	C <sub>4</sub> H <sub>6</sub> <sup>2</sup>	→ C <sub>4</sub> H <sub>5</sub> + H	$2.0 \times 10^{15} \exp(-43178.0/T)$	NIST	300-2500	
T80	C <sub>4</sub> H <sub>6</sub> <sup>2</sup>	→ C <sub>3</sub> H <sub>3</sub> + CH <sub>3</sub>	$2.0 \times 10^{15} \exp(-37645.0/T)$	NIST	1100-1600	
T81	C <sub>4</sub> H <sub>6</sub> <sup>3</sup>	→ C <sub>4</sub> H <sub>5</sub> + H	$1.58 \times 10^{16} \exp(-55445.0/T)$	NIST	300-2500	
T82	C <sub>4</sub> H <sub>6</sub> <sup>3</sup>	→ C <sub>2</sub> H <sub>3</sub> + C <sub>2</sub> H <sub>3</sub>	$1.8 \times 10^{13} \exp(-42817.0/T)$	NIST	1560-2210	
T83	C <sub>4</sub> H <sub>6</sub> <sup>3</sup>	→ C <sub>2</sub> H <sub>2</sub> + C <sub>2</sub> H <sub>4</sub>	$1.0 \times 10^{14} \exp(-37645.0/T)$	NIST	1100-1600	
T84	C <sub>4</sub> H <sub>8</sub>	→ CH <sub>3</sub> + C <sub>3</sub> H <sub>5</sub>	$1.0 \times 10^{16} \exp(-36683.0/T)$	NIST	300-2500	
T85	C <sub>4</sub> H <sub>9</sub>	→ H + C <sub>4</sub> H <sub>8</sub>	$1.1 \times 10^{13} (T/298.0)^{0.25} \exp(-17921.6/T)$	NIST	298-2000	
T86	C <sub>4</sub> H <sub>9</sub>	→ CH <sub>3</sub> + C <sub>3</sub> H <sub>6</sub>	$7.7 \times 10^{13} (T/298.0)^{0.77} \exp(-15394.8/T)$	NIST	298-2000	
T87	C <sub>4</sub> H <sub>10</sub>	→ H + C <sub>4</sub> H <sub>9</sub>	$1.58 \times 10^{16} \exp(-49312.0/T)$	NIST	300-2500	
T88	C <sub>4</sub> H <sub>10</sub>	→ CH <sub>3</sub> + C <sub>3</sub> H <sub>7</sub>	$1.0 \times 10^{17} \exp(-42576.0/T)$	NIST	300-2500	
T89	C <sub>4</sub> H <sub>10</sub>	→ C <sub>2</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>5</sub>	$7.94 \times 10^{16} \exp(-40411.0/T)$	NIST	300-2500	
T90	C <sub>6</sub> H <sub>6</sub>	→ C <sub>3</sub> H <sub>3</sub> + C <sub>3</sub> H <sub>3</sub>	$6.31 \times 10^{14} \exp(-31151.0/T)$	NIST	300-2500	
T91	N <sub>2</sub> H <sub>4</sub>	→ NH <sub>2</sub> + NH <sub>2</sub>	$6.61 \times 10^{-9} \exp(-20567.0/T) \times N$	NIST	1280-1580	
T92	CH <sub>5</sub> N	→ CH <sub>4</sub> + NH	$2.66 \times 10^{-11} \exp(-24295.0/T) \times N$	NIST	1750-2450	
T93	CH <sub>5</sub> N	→ CH <sub>3</sub> + NH <sub>2</sub>	$1.36 \times 10^{-7} \exp(-30669.0/T) \times N$	NIST	1530-1980	