Modeling the hydrolysis of perfluorinated compounds containing carboxylic and phosphoric acid ester functions, alkyl iodides, and sulfonamide groups

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ABSTRACT

Temperature dependent rate constants were estimated for the acid- and base-catalyzed and neutral hydrolysis reactions of perfluorinated telomer acrylates (FTAcrs) and phosphate esters (FTPEs), and the S_N1 and S_N2 hydrolysis reactions of fluorotelomer iodides (FTIs). Under some environmental conditions, hydrolysis of monomeric FTAcrs could be rapid (half-lives of several years in marine systems and as low as several days in some landfills) and represent a dominant portion of their overall degradation. Abiotic hydrolysis of monomeric FTAcrs may be a significant contributor to current environmental loadings of fluorotelomer alcohols (FTOHs) and perfluoroalkyl carboxylic acids (PFCAs). Polymeric FTAcrs are expected to be hydrolyzed more slowly, with estimated half-lives in soil and natural waters ranging between several centuries to several millenia absent additional surface area limitations on reactivity. Poor agreement was found between the limited experimental data on

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FTPE hydrolysis and computational estimates, requiring more detailed experimental data before any further modeling can occur on these compounds or their perfluoroalkyl sulfonamidoethanol phosphate ester (PFSamPE) analogs. FTIs are expected to have hydrolytic half-lives of about 130 days in most natural waters, suggesting they may be contributing to substantial FTOH and PFCA inputs in aquatic systems. Perfluoroalkyl sulfonamides (PFSams) appear unlikely to undergo abiotic hydrolysis at the S-N, C-S, or N-C linkages under environmentally relevant conditions, although potentially facile S-N hydrolysis via intramolecular catalysis by ethanol and acetic acid amide substituents warrants further investigation.

Keywords: Hydrolysis; perfluorinated acid precursors; environmental fate; water and waste water treatment; fluorotelomers; acrylates; phosphate esters; iodides; perfluoroalkyl sulfonamides

INTRODUCTION

The fate of perfluorinated compounds (PFCs) in natural and engineered systems is of current interest.[1-3] Early research efforts were primarily focused on documenting the presence of perfluoroalkyl carboxylic acids (PFCAs) and sulfonic acids (PFSAs) in environmental matrices and their possible biological effects.[4-7] Recent studies have begun to develop a more comprehensive picture regarding the sources and fate of PFCAs and PFSAs.[8, 9] In particular, a number of works have investigated precursor PFCs, such as fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamides (PFSams), hydrofluorocarbons (HFCs), and polytetrafluoroethylene (PTFE) based polymers, that can be degraded abiotically and/or biotically to the more recalcitrant PFCAs and PFSAs (see, e.g., ref. [10, 10-23]). However, no works have explored in detail the potential abiotic hydrolysis of any FTOH, PFCA, or PFSA precursor compounds under the wide range of solution conditions that can be found in aquatic systems. Among the various possible precursors, the perfluorinated telomer acrylates (FTAcrs), phosphate esters (FTPEs), iodides (FTIs), PFSams, and perfluoroalkyl sulfonamidoethanol phosphate esters (PFSamPEs) (Fig. 1) have functional groups that may be susceptible to hydrolytic cleavage. In addition to their direct releases into the environment near production and processing facilities, these compounds may also be released from consumer products, where they can be present at concentrations up to the low percent by weight.[24]

Of these precursors, the FTAcrs are reported to be the largest category of commercial polyfluorinated products,[25] and have been found in atmospheric, rain water, and surface water samples at concentrations up to 3 pg L^{-1}, 0.5 ng L^{-1}, and 0.2 ng L^{-1}, respectively, with concentrations that are strongly correlated with point sources.[26-30] FTPEs are exploited for their hydro- and oleo-phobic nature in food packaging, and can migrate into food products.[31, 32] In addition, these compounds are

also approved as additives in pesticide mixtures,[32] are found in human sera, consumer products, and waste water sludge [33] - indicating they are widely present in environmental systems - and can be biologically converted into FTOHs and ultimately oxidized to PFCAs.[32] PFSams are widely employed in various industries, and their occurrence in the environment has been documented, but not to the extent of that for PFCAs and PFSAs.[4, 6, 7] PFSamPEs were also used in food packaging applications until the early 2000s, but have since been phased out.[34] However, reservoirs of PFSamPEs in discarded consumer products may still represent a continuing source of PFSams into the environment via various degradation processes. FTIs are used in the synthesis of various fluorotelomer products, including FTOHs and fluorotelomer olefins (FTOls). The general emission quantity of FTIs is unknown, but total production masses of FTIs and related fluorotelomer products are in the millions of kilograms per year.[35]

To better understand the potential abiotic hydrolysis of PFCA and PFSA precursors in natural and engineering systems, the current study critically examines the limited direct information available on selected PFCs, integrates the broader relevant literature on similar compound classes, and uses various computational approaches to estimate the hydrolytic behavior of FTAcrs, FTPEs, PFSamPEs, FTIs, and PFSams.

MATERIALS AND METHODS

Acid- (k_A) and base- (k_B) catalyzed and neutral (k_N) hydrolysis rate constants for carboxylic and phosphoric acid esters were estimated using the SPARC software program (http://ibmlc2.chem.uga.edu/sparc/; August 2007 release w4.0.1219-s4.0.1219).[36-38] S_N1 hydrolysis rate constants of fluorotelomer iodides were estimated with the HYDROWIN module of the EPI Suite software program (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm; EPI Suite v.4.00). Inputs to both the SPARC and EPI Suite programs used the SMILES molecular formula language.[39, 40]

RESULTS AND DISCUSSION

Fluorotelomer Acrylates

To better understand the potential hydrolytic behavior of both monomeric and polymeric FTAcrs and their derivatives, we estimated the acid-catalyzed (k_A), neutral (k_N), and base-catalyzed (k_B) rate constants (Fig. 2) of the 2:2 through 12:2 acrylate monomers (**1**), 2:2 through 12:2 fluorotelomer methacrylate monomers (**2**), and the model 8:2 fluorotelomer polymer segments **3** and **4** (Fig. 3; structures for **3** and **4** adapted from ref. [12, 24, 25]) using the SPARC software program (Table 1). The estimated rate constants of **1** and **2** are generally insensitive to perfluoroalkyl chain length with ≥4 perfluorocarbons, but exhibit about a 5-fold reduction in k_A, a 1.6-fold reduction in k_N, and a 3.6-fold reduction in k_B on moving from two to four perfluorocarbons. The addition of the α-methyl group in the fluorotelomer methacrylates has an insignificant effect on k_N values relative to chain length equivalent acrylates, but reduces the k_A and k_B values by about 1.6 and 1.8, respectively, on a chain length equivalent basis. This k_A and k_B rate reduction for the α-methylated methacrylate **2** is likely due

to steric hindrance that inhibits the rate-limiting attack of water and hydroxide ions, respectively, at the carbonyl carbon. The model 8:2 fluorotelomer acrylate polymer segments **3** and **4** have smaller k_A and k_B values relative to the monomers, by up to two orders of magnitude, but the polymer segments have corresponding k_N values up to more than two orders of magnitude higher than their monomeric counterparts.

By determining the SPARC estimated k_A, k_N, and k_B values at 0°C and 100°C for each 8:2 fluorotelomer member of structures **1** to **4**, the following activation energies (E_a) were derived: **1**, k_A=83.2 kJ mol^{-1}, k_N=61.2 kJ mol^{-1}, and k_B=19.8 kJ mol^{-1}; **2**, k_A=83.3 kJ mol^{-1}, k_N=61.1 kJ mol^{-1}, and k_B=20.1 kJ mol^{-1}; **3**, k_A=75.8 kJ mol^{-1}, k_N=49.3 kJ mol^{-1}, and k_B=20.6 kJ mol^{-1}; and **4**, k_A=76.4 kJ mol^{-1}, k_N=45.3 kJ mol^{-1}, and k_B=17.6 kJ mol^{-1}. When these activation energies were used to estimate the corresponding rate constants at 25°C, the differences between the values obtained using direct SPARC calculation at 25°C and the use of our E_a values from either temperature end member (i.e., 0°C or 100°C) was <5%. There is little difference in the E_a values of all three mechanisms between the acrylate and methacrylate monomers, but the model polymer segments **3** and **4** have lower E_a values for the k_A (about 7 to 8 kJ mol^{-1} lower) and k_N (up to 16 kJ mol^{-1} lower) mechanisms compared to the monomers. The purely hydrocarbon polymer linkage model **3** has a base-catalyzed E_a about equal to that of the two monomers **1** and **2**, but the addition of the four electron withdrawing γ-chlorine atoms in **4** substantially increases the partial positive charge on the carbonyl carbon, making it more susceptible to attack from hydroxide ions, resulting in an activation energy for base-catalyzed hydrolysis up to 3 kJ mol^{-1} lower than the other three compounds.

With these estimated k_A, k_N, and k_B values for **1** to **4**, and the corresponding E_a estimates, we have mapped the estimated hydrolytic half-lives ($t_{1/2,hydr}$) for these compounds at pH values between 0 and

14 and temperatures ranging from 0°C to 100°C (Fig. 4) using the following equations,

$$t_{1/2,hydr} = \ln 2/k_{hydr} \quad \ldots (1)$$

$$k_{hydr} = k_A[H_3O^+] + k_N[H_2O] + k_B[OH^-] \quad \ldots (2)$$

$$\ln(k_{A,T}) = \ln(k_{A,298.15K}) + \Delta E_{a,kA}/R \times (1/298.15 - 1/T) \quad \ldots (3)$$

$$\ln(k_{N,T}) = \ln(k_{N,298.15K}) + \Delta E_{a,kN}/R \times (1/298.15 - 1/T) \quad \ldots (4)$$

$$\ln(k_{B,T}) = \ln(k_{B,298.15K}) + \Delta E_{a,kB}/R \times (1/298.15 - 1/T) \ldots (5)$$

$$[H_3O^+] = 10^{-pH} \ldots (6)$$

$$[OH^-] = 10^{-pKw}/10^{-pH} \quad \ldots (7)$$

$$pK_w = 36.9 - 0.120 \times T + 0.000144 \times T^2 \quad \ldots (8)$$

where $k_{A,T}/k_{N,T}/k_{B,T}$ and $k_{A,298.15K}/k_{N,298.15K}/k_{B,298.15}$ are the corresponding rate constants at the temperature of interest and at 298.15 K, respectively, $\Delta E_{a,kA}/\Delta E_{a,kN}/\Delta E_{a,kB}$ are the activation energies for the respective reactions, $[H_3O^+]$ and $[OH^-]$ are the concentrations of hydronium and hydroxide ions, respectively, the concentration of water ($[H_2O]$) is assumed constant at 55.5 mol L^{-1} under all conditions, pK_w is the negative logarithm (base ten) of the water ionization constant (equation 8 is valid between 0 and 100°C), and T is the temperature in kelvin.

As is generally expected for the hydrolysis of carboxylic acid esters, the half-lives decrease rapidly with changes in solution pH for the monomeric models **1** and **2** on either side of the "saddle" existing between pH 3 and 5, where the pK_a of the carboxylic acid leaving group plays a substantial role in determining the dominant mechanistic pathway and associated rate. As the solution becomes more acidic or basic outside of this range, the $t_{1/2,hydr}$ declines rapidly as the acid- and base-catalyzed mechanisms become more important. For the model polymeric segments **3** and **4**, the width of this "saddle" is significantly larger, from about pH 3 to 7 for **3** and about pH 2 to 8 for **4**, reflecting the larger relative values of k_N compared to k_A and k_B for the polymeric models versus the monomers. With all compounds, increasing the temperature from 0 to 100°C reduces the $t_{1/2,hydr}$ by up to several orders of magnitude, as expected given the endothermic nature of hydrolysis reactions. The findings show generally strong temperature and solution pH dependence on the hydrolytic half-lives of all FTAcrs, necessitating a more detailed consideration of this degradation pathway in aquatic systems.

Under some environmental conditions, hydrolysis of both monomeric and polymeric FTAcrs could be rapid and represent a dominant portion of their overall degradation. At 15°C and pH 8.1 (i.e., possible marine conditions), the monomeric models **1** and **2** are expected to have half-lives of only 3 and 5 years, respectively, whereas the polymeric models **3** and **4** have much longer corresponding estimated $t_{1/2,hydr}$ of about 170 and 270 years, respectively. Under landfill conditions, with temperatures up to 40 to 50°C and pH values ranging between 4 and 9, the half-lives of the monomeric FTAcrs could be as short as 4 days, with that of the model polymeric segments under similar conditions as low as one year. Consequently, substantial abiotic hydrolytic degradation of fluorotelomer acrylates could be occurring under some saturated landfill conditions, resulting in significant fluxes of FTOHs and their degradation products (including PFCAs) into ground and surface waters. At elevated temperatures and under

moderately alkaline conditions, hydrolysis of monomeric FTAcrs could also be an effective means of degradation. For example, a solution of pH 11 at 100°C is expected to hydrolyze the monomeric FTAcrs with half-lives of 2 to 4 minutes. The corresponding polymeric models have much higher half-lives of between 3 and 13 hours at pH 11 and 100°C, precluding a rapid treatment option unless the pH is raised to highly basic conditions (an estimated polymeric $t_{1/2,hydr}$ at pH 13 and 100°C of 2 to 8 minutes).

We stress that all hydrolytic behavior modeled in our work is based on freely dissolved assumptions for both the monomers and the polymeric segments, and thereby does not reflect any surface area limitations analogous to those reported by Washington et al. [12] in their studies on the soil biodegradation of FTAcr polymers. As a result, actual hydrolysis rates for polymer particles will likely be significantly slower than those predicted by freely dissolved models. However, our results demonstrate a significant potential for FTAcr hydrolysis in aquatic systems, and the need to better understand quantitative weathering and mass-transfer parameters for the physical (i.e., abrasion, freeze-thaw cycling, etc.), chemical (i.e., hydrolysis, photolysis, oxidation/reduction, etc.), and biological pathways that act together to increase the mass-normalized surface areas of these materials as they weather and further degrade the polymeric structure into oligomeric and monomeric segments that may be further decomposed into other PFCs such as FTOHs and PFCAs.

Our computational estimates are also in excellent agreement with the recent experimental FTAcr biodegradation reports by Russell et al. [25] and Washington et al.[12] In their study on the aerobic biodegradation potential of a commercial fluoroacrylate polymer product, Russell et al. [25] reported that the material exhibited no signs of hydrolysis after five days at pH 1.2 (37°C), 4 (50°C), 7 (50°C), and 9 (50°C), and their long-term control samples also did not indicate any substantial abiotic

hydrolysis.[25] Assuming abiotic hydrolysis was negligible under all environmental conditions, these authors estimated an aerobic soil biodegradation half-life of between 1200 to 1700 years. Recently, Washington et al. [12] have questioned the findings of Russell et al.,[25] suggesting that FTAcrs may be much more biologically labile in aerobic soils than previously thought, with surface area limited half-lives for finely grained polymers in the range from 10 to 17 years. Our results support no significant five-day hydrolysis of the polymeric models **3** and **4** expected under any of these conditions (our estimated $t_{1/2,hydr}$ range from 1 to 70 years for pH 1.2 (37°C), 4 (50°C), 7 (50°C), and 9 (50°C)), and hydrolytic half-lives of several centuries are predicted at a soil temperature of 20°C and water content pH 7. Therefore, control samples for soil biodegradation studies conducted at a neutral pH and at room temperature would not be expected to show substantial abiotic hydrolysis of the starting polymeric materials or monomeric/oligomeric intermediates produced within the time frame of trials lasting between several months and a couple of years. However, it does not appear reasonable to assume negligible hydrolysis of either monomeric or polymeric FTAcrs on the timescales of centuries or millenia in aquatic or terrestrial matrices. By comparison, the atmospheric lifetimes of FTAcrs will likely be short (about one day) and determined by reaction with hydroxyl radicals;[41] and thus, atmospheric hydrolysis of FTAcrs in precipitation and aerosols is not expected to be a major loss process.

Rather, under realistic environmental conditions encountered in soils, landfills, and aquatic systems, abiotic hydrolysis of these materials may have half-lives ranging widely between several days and several centuries. Within the polymeric FTAcr biodegradation time frame of one to two decades put forward by Washington et al.,[12] abiotic hydrolysis will not be competitive with biological processes, but hydrolysis may be competitive with (and/or complementary to) biodegradation if the centuries through millenia time frame of Russell et al. [25] is used. Furthermore, the FTAcr monomers are known

to be widely present in environmental systems, and with estimated hydrolytic half-lives ranging from days to decades depending on ambient conditions, abiotic degradation of these compounds appears to be a significant contributor to current environmental loadings of FTOHs and PFCAs. Consequently, both compound specific and site specific effects will be required to properly assess any contributions from abiotic hydrolysis of FTAcrs when conducting fate and degradation modeling.

Fluorotelomer and Perfluoroalkyl Sulfonamidoethanol Phosphate Esters

D'Eon and Mabury have reported that the mono- and di-8:2-FTPEs (**5** and **6**, respectively; Fig. 5) were only slowly hydrolyzed at 50°C and pH 9, with estimated half-lives of >26 years.[32] Although SPARC estimates potentially appropriate acid- and base-catalyzed hydrolysis rate constants for these two compounds at 50°C ($k_{A,mono\text{-}8:2\text{-}FTPE}=5.5\times10^{-6}$; $k_{A,di\text{-}8:2\text{-}FTPE}=4.1\times10^{-5}$; $k_{B,mono\text{-}8:2\text{-}FTPE}=4.3\times10^{-5}$; $k_{B,di\text{-}8:2\text{-}FTPE}=1.4\times10^{-6}$; all units are L mol^{-1} s^{-1}), the corresponding neutral rate constants are too high ($k_{N,mono\text{-}8:2\text{-}FTPE}=2.3\times10^{1}$ and $k_{N,di\text{-}8:2\text{-}FTPE}=1.3\times10^{4}$ L mol^{-1} s^{-1}), yielding half-lives at 50°C and pH 9 of 0.6 ms and 1 μs, respectively, that disagree with the experimental data by 12 to 15 orders of magnitude. Using shorter perfluoroalkyl chains as model compounds does not improve the SPARC results. For example, the di-2:2-FTPE is predicted by SPARC to have a similarly short hydrolytic half-life (about 1 ms at 25°C and pH 9; $k_A=6.9\times10^{-7}$; $k_N=9.8$ and $k_B=3.1\times10^{-6}$ L mol^{-1} s^{-1}). As noted in the SPARC software manual, the program can only be used to reliably estimate k_A and k_B for phosphate esters; and thus, k_N values for these compounds must be approximated by other means.

Using D'Eon and Mabury's [32] minimum estimated $t_{1/2,hydr}$ of 26 years for both the mono- and di-8:2-FTPEs at pH 9 and 50°C, and the corresponding SPARC estimated k_A and k_B values, we made efforts to back-calculate maximum k_N values for these two compounds at these experimental conditions.

However, even assigning both k_A and k_N to zero, the SPARC k_B value for the mono-8:2-FTPE yields a $t_{1/2,hydr}$ of 36 days at pH 9 and 50°C. For the di-8:2-FTPE, a k_N of 1×10^{-11} L mol^{-1} s^{-1} (or 6×10^{-10} s^{-1}) is required to fit a net $t_{1/2,hydr}$ of 26 years (even when assuming a k_A of zero). Such a k_N value would be one to three orders of magnitude below the typical range (10^{-9} to 10^{-7} s^{-1}) reported for phosphate triesters, although the k_B values for the two FTPEs are within the lower end of the literature range often reported for the triester hydrocarbon analogs (10^{-6} to 10^{-1} L mol^{-1} s^{-1}).[42] Consequently, it appears that either the current version of SPARC cannot be used to model the hydrolysis rates of FTPEs, or that the estimated half-lives provided by D'Eon and Mabury [32] are too long by up to several orders of magnitude. Additional rate data are needed for these compounds under different temperature and pH conditions to better assess the true values of k_A, k_B, and k_N, and if necessary, to allow a reparametrization of SPARC to better match observed hydrolytic behavior. In addition, the HYDROWIN module (v.2.00) within EPI Suite cannot estimate the hydrolytic behavior of these compounds.

PFSamPEs were used in food packaging products until recently, and it has been hypothesized that this potential source may be linked to increasing concentrations of PFSam derivatives in human blood between the 1970s and late 1980s.[32, 34] For the mono- (**7**) and di-phosphate (**8**) esters of N-ethylperfluorooctane sulfonamidoethanol (NEtFOSE), SPARC estimates the following hydrolytic rate constants at 25°C (all units are L mol^{-1} s^{-1}): **7**, $k_A=1.7\times10^{-7}$, $k_N=0.19$, and $k_B=2.9\times10^{-5}$; **8**, $k_A=3.1\times10^{-6}$, $k_N=5.7$, and $k_B=4.6\times10^{-6}$. Assuming a k_N of zero (the SPARC estimates are clearly in error), at pH 7 the corresponding $t_{1/2,hydr}$ of **7** and **8** are estimated to be 7,400 years and 29,000 years, respectively. At pH 9 and 50°C, the estimated $t_{1/2,hydr}$ of **7** and **8** are 2.5 and 19 years, respectively. Unfortunately, no experimental data on the hydrolysis of PFSamPEs appears available upon which to benchmark these preliminary estimates.

The results highlight the absence of applicable quantitative structure-reactivity relationships and associated computational tools for assessing key abiotic transformations of these important environmental contaminants. Thus, the current state of the art regarding FTPE and PFSamPE hydrolyses is that while limited experimental work and/or computational estimates suggest these compounds may be hydrolytically stable under moderately alkaline conditions, we have little knowledge regarding their projected behavior under more acidic or highly basic conditions.

Fluorotelomer Iodides

No previous experimental studies have considered the hydrolysis of FTIs. In a related study on alkyl iodides, Glowa and Wren concluded that hydrolysis rates increased from primary to secondary to tertiary substitution, and that the alkyl chain length had little effect on the net rate of reaction.[43] Based on a review of the literature, these authors also reported that the S_N2 mechanism contribution toward hydrolysis of alkyl iodides is expected to be negligible at near neutral pH values, and does not become important until above pH 11. Consequently, Glowa and Wren [43] proposed a uniform S_N1 mechanism (Fig. 6(a)) rate constant (k_{SN1}) of $1.3\pm0.9\times10^{-7}$ s^{-1} at 298 K with an activation energy of 104±10 kJ mol^{-1} for alkyl iodides. Adachi et al. [44] determined the k_{SN2} for the S_N2 reaction (Fig 6(b)) of the hydroxide ion with methyl iodide as 6.6×10^{-5} L mol^{-1} s^{-1} at 298 K, and having an activation energy of 92 kJ mol^{-1}. By comparison, the HYDROWIN module (v.2.00) within EPI Suite estimates a chain length independent k_{SN1} of 7.9×10^{-7} L mol^{-1} s^{-1} for the >3:2 FTIs, with a higher value for the 2:2 FTI (2.2×10^{-6} L mol^{-1} s^{-1}). The current version of SPARC does not estimate k_{SN1} or k_{SN2} hydrolysis rates for alkyl iodides. Assuming k_{SN2} for methyl iodide hydrolysis can be generalized for all alkyl iodides as is the case for k_{SN1}, net hydrolysis rates (k_{hydr}) as functions of both temperature and pH can be estimated for

FTIs using the following equations,

$$k_{hydr} = k_{SN1} + k_{SN2} \times [OH^-] \quad \ldots (9)$$

$$\ln(k_{SN1,T}) = \ln(k_{SN1,298.15K}) + \Delta E_{a,SN1}/R \times (1/298.15 - 1/T) \quad \ldots (10)$$

$$\ln(k_{SN2,T})_T = \ln(k_{SN2,298.15K}) + \Delta E_{a,SN2}/R \times (1/298.15 - 1/T) \quad \ldots (11)$$

where $k_{SN1,T}$ and $k_{SN1,298.15K}$ are the S_N1 rate constants at the temperature of interest and at 298.15 K ($k_{SN1,298.15K}=1.3\times10^{-7}$ s^{-1}), respectively, $\Delta E_{a,SN1}$ is the activation energy for the S_N1 reaction ($\Delta E_{a,SN1}=$ 104 kJ mol^{-1}), $k_{SN2,T}$ and $k_{SN2,298.15K}$ are the S_N2 rate constants at the temperature of interest and at 298.15 K ($k_{SN2,298.15K}=6.6\times10^{-5}$ L mol^{-1} s^{-1}), respectively, and $\Delta E_{a,SN2}$ is the activation energy for the S_N2 reaction ($\Delta E_{a,SN1}=$ 92 kJ mol^{-1}). Equations (1), (6), (7), and (8) given previously are also applicable.

Based on these rate constants and activation energies, two- and three-dimensional reactivity maps for the $t_{1/2,hydr}$ of FTIs as functions of temperature and pH are given in Figure 7. Between pH 0 and 9, the S_N1 reaction dominates and $t_{1/2,hydr}$ is only dependent on temperature. Above pH 9, the contribution from the S_N2 reaction becomes progressively more important as the hydroxide ion increases with increasing pH, resulting in rapid increases in reactivity at all temperatures. For example, at 20°C the $t_{1/2,hydr}$ of a FTI is expected to remain constant at 126 days between pH 0 and 9, and then decrease to 121 days at pH 10, 88 days at pH 11, 12 days at pH 12, 3 days at pH 13, and <7 hours at pH 14. At all pH values, temperature plays a significant role in the hydrolysis rate, with $t_{1/2,hydr}$ at pH 7 decreasing from about 8 years at 0°C to <20 minutes at 100°C. In marine systems, with a pH of about 8.1, the

$t_{1/2,hydr}$ of FTIs decreases from about 8 years at 0°C to about 130 days at 20°C. It appears that hydrolysis of FTIs in aquatic systems may play a significant role in their environmental fate, potentially acting as important precursors of FTOHs, and ultimately, PFCAs. With atmospheric lifetimes toward direct photolysis and reaction with hydroxyl radicals on the order of several days,[35] atmospheric hydrolysis will not be an important degradation pathway for FTIs. As a potential treatment method, hydrolysis of FTIs may be practical at elevated temperatures and under alkaline conditions ($t_{1/2}$=20 min at 100°C and pH 7, decreasing to $t_{1/2}$=8 min at 100°C and pH 10, and $t_{1/2}$<10 seconds at 100°C and pH 12).

Perfluoroalkyl Sulfonamides

In contrast to carboxamido groups, the sulfonamido moiety is widely believed to be both chemically and metabolically stable, and that the alkaline hydrolysis of a sulfonamide function to yield a sulfonic acid and an amine is difficult to achieve, even in hot, concentrated alkali solutions (Fig. 8(a)).[45-48] Where electron withdrawing groups (EWGs) are present on the sulfonyl group, extreme conditions (e.g., fusion in 80% sodium hydroxide) can hydrolyze the C-S linkage (Fig. 8(b)).[49, 50] Dealkylation of the amide group can also occur under strongly alkaline conditions (Fig. 8(c)).[51] For tertiary substituted sulfonamides, reaction with highly basic alkoxide ions (e.g., sodium isoamoxide in isoamyl alcohol) can result in net S-N hydrolysis under high temperatures (>150°C) and extended reaction times (>3 hours) (Fig. 8(d)).[45] Where an amidic proton is present (i.e., primary and secondary substituted sulfonamides), alkoxide mediated hydrolysis is not effective, likely because the proton dissociates in highly basic conditions yielding an amidic anion that is resistant to attack (Fig. 8(e)). Alkyl transfer from the amidic group of sulfonamides to other amines can also occur, and is promoted by EWGs (Fig. 8(f)),[45] potentially raising the question of DNA alkylation by PFSams. In the presence of strong

oxidizing agents (e.g., hot $KMnO_4$), sulfonamides can also be dealkylated (Fig. 8(g)).[45]

A high stability toward acid hydrolysis is also to be expected,[47] given the low pK_a (<-6 on the H_o scale) [52] of the nitrogen atom which is believed to require protonation prior to hydrolysis, although there are reports of acid hydrolysis of the sulfonamide linkage under some conditions (Fig. 8(h)).[46, 48, 53] As early as 1914, Johnson and Ambler [46] reported on earlier studies by the groups of Hinsberg, Marckwald and Huelshoff, Ullman, Schroeter and Eisleb, and Witt and Uermenyi, collectively showing that heating sulfonamides under pressure in concentrated mineral acids, chlorosulfonic acid, or mixtures of inorganic (e.g., sulfuric) and organic (glacial acetic) acids effected hydrolysis. More recent work has further demonstrated that sulfuric:acetic acid mixtures and concentrated sulfuric acid can hydrolyze a range of sulfonamides.[45, 54] The hydrolysis of sulfonamides via heating in the presence of other carboxylic acids has also been reported,[45] resulting in an amidic exchange to yield the corresponding sulfonic acid and carboxylic amide. Under acidic hydrolysis conditions, S-N bond cleavage is usually preferred to N-C cleavage (if an alkyl substituent is present on a secondary or tertiary amide), unless the alkyl group can effectively stabilize a carbocation.[45] Since PFSams generally contain only straight chain alkyl (e.g., methyl, ethyl) or electron withdrawing alcoholic (e.g., ethanol) or carboxylic (e.g., acetic) amide substituents, this mode of N-C cleavage acidic hydrolysis is not likely prominent.

Work in the 1970s and 1980s by Engberts and coworkers [55-58] has also shown that sulfonamide hydrolysis via S-N cleavage can occur through intramolecular nucleophilic acid catalysis mediated by neighboring carboxyl and hydroxyl groups, both mechanisms exhibiting high preferences for five-membered cyclic transition states whereby the carboxyl/hydroxyl oxygen atoms nucleophilically attack the sulfur atom, resulting in expulsion of the amine. Half-lives as short as about 30 seconds in 0.1 M

HCl at 75°C were reported for some α-carboxyl sulfonamide compounds; other α-carboxyl sulfonamides required higher acid concentrations (1 M HCl) and longer reaction times (half-lives ranging up to 200 hours).[57] EWGs (e.g., F, NO_2) and bulky amide substituents lowered the hydrolysis rates. For effective intramolecular α-hydroxyl sulfonamide hydrolysis, secondary or tertiary alcohols were required. While half-lives of <20 minutes at 25°C in 1 M HCl in 1:1 ethanol:water (v/v) were observed for a tertiary alcohol derivative, the half-life increased to >70 hours for the corresponding secondary alcohol. The analogous primary alcohol displayed no hydrolysis even after 7 months in a similar solvent system.[58] Two major classes of perfluoroalkyl sulfonamides, the perfluoroalkyl sulfonamido ethanols (SEs) and acetates (SAAs), are both capable of forming the five-membered cyclic transition state (Fig. 9) pioneered by Engberts and colleagues for intramolecular nucleophilic acid catalysis. Applying the proposed mechanisms given by these researchers for the α-carboxyl and α-hydroxyl reactions to two major commercial SE and SAA derivatives, n-perfluorooctane sulfonamidoethanol (n-PFOSE; Fig. 10(a)) and n-perfluorooctane sulfonamidoacetate (n-PFOSAA; Fig. 10(b)), indicates a potential for these compounds to be hydrolyzed to n-perfluorooctane sulfonate (n-PFOS) via intramolecular acid catalysis. It is important to note that SEs are primary alcohols, and as such, would be expected to have a very low reactivity toward intramolecular acid catalysis.

Based on work primarily dealing with pharmaceutically relevant sulfonamide derivatives, it is generally believed that in vivo or in environmental matrices, the sulfonamide linkage is unlikely to be abiotically hydrolyzed.[59, 60] However, Sukul and Spiteller [53] have cited Boreen et al. [61] as giving an environmentally relevant hydrolysis half-life of only four hours for sulfamoxole (**9**; Fig. 11) at pH 5, but a review of Boreen et al. [61] indicates that while these authors did observe thermal degradation of **1** under such conditions, no products were identified that supported a hydrolytic mechanism. Yang et al. [62] also claimed that sulfadiazine (**10**) hydrolyzed at pH 4.7, but not at pH 7.6, in model aqueous

solutions designed to better understand the fate of this sulfonamide in soils. A review of their data shows that the degradation they reported was not likely due to hydrolysis. At pH 4.7, Yang et al. [62] found a small decrease in sulfadiazine concentration from 9.8 to 8.1 mg L^{-1}, but all degradation took place in the initial 48 hours of exposure, with no significant subsequent degradation up to a total of 336 hours. Such kinetic behaviour is not consistent with the pseudo first order kinetics expected for hydrolysis, whereby Yang et al. [62] should have observed a continuing degradation over time, rather than an initial rapid decline to a marginally lower steady state aqueous concentration that persisted unchanged for an extended period.

Although there appears to be some work that supports possible abiotic hydrolysis of perfluoroalkyl sulfonamides in natural and engineered aquatic systems and in vivo, the most relevant study to date appears to be that of Lehmler et al.[63] These researchers, as part of their synthetic exercises for various perfluoroalkyl sulfonamide derivatives, exposed several commercially relevant compounds to strong acid and base conditions as rigorous as would be expected in vivo or in waste treatment systems (e.g., refluxing concentrated KOH solutions for 3 hours; 1 M HCl exposure for 2 days). Neither dealkylation of the amidic moiety nor hydrolysis of the perfluoroalkyl sulfonamide moiety was reported. These results are consistent, as discussed above, with earlier studies indicating that the presence of EWGs on the sulfonate function reduces the rate and yield of sulfonamide hydrolysis.[45, 64] In addition, Lehmler et al. [63] found significant double bond character in the S-N bond of the N-ethyl and N,N-diethylperfluorooctane sulfonamides, further supporting the likely high resistance to hydrolysis. At present and within this context of limited and sometimes conflicting evidence, it is not possible to assess the potential for PFSam abiotic hydrolysis. Further experimental studies are required that better understand this important question.

CONCLUSIONS

Depending on solution pH and temperature, the abiotic hydrolysis of various perfluorinated compounds with carboxylic and phosphoric acid ester functions and alkyl iodide groups may make a significant contribution toward the overall degradation of these compounds in natural and engineered aquatic systems. In contrast, it appears that even relatively harsh conditions will not effect significant environmental hydrolysis rates for perfluoroalkyl sulfonamide moieties. At present, fluxes of perfluorinated telomer acrylates, phosphate esters, and iodides, as well as perfluoroalkyl sulfonamidoethanol phosphate esters, in environmental systems are poorly constrained. These compounds are generally not included in multimedia modeling efforts for elucidating the sources, fates, and distribution of perfluoroalkyl carboxylic and sulfonic acids and fluorotelomer alcohol precursors. If hydrolysis of these compounds proceeds at the rates expected in various aquatic and terrestrial matrices, the contributions of these precursor compounds - from both direct emissions and the degradation of consumer products - to total environmental loadings of fluorotelomer alcohols and perfluoroalkyl carboxylic and sulfonic acids may be significantly underestimated.

FIGURE CAPTIONS

Figure 1. General structures of fluorotelomer acrylates, fluorotelomer phosphate esters, fluorotelomer iodides, perfluoroalkyl sulfonamides, and perfluoroalkyl sulfonamidoethanol phosphate esters.

Figure 2. General acid- and base-catalyzed and neutral mechanisms for the hydrolysis of fluorotelomer acrylates.

Figure 3. Structures of the fluorotelomer acrylate monomer (**1**), the fluorotelomer methacrylate monomer (**2**), and the model fluorotelomer polymer segments **3** and **4**.

Figure 4. Two-dimensional hydrolysis half-life ($t_{1/2,hydr}$) maps for the fluorotelomer acrylate monomer (**1**), the fluorotelomer methacrylate monomer (**2**), and the model fluorotelomer polymer segments **3** and **4**. $t_{1/2,hydr}$ values for the contour intervals are given adjacent to the x- and y-axes and are in units of days.

Figure 5. Structures of mono-8:2-FTPE (**5**), di-8:2-FTPE (**6**), and the mono- (**7**) and di- (**8**) phosphoric acid esters of N-ethylperfluorooctane sulfonamidoethanol (NEtFOSE).

Figure 6. General mechanisms for the S_N1 and S_N2 hydrolysis of fluorotelomer iodides.

Figure 7. Two- and three-dimensional hydrolysis half-life ($t_{1/2,hydr}$) maps for the fluorotelomer iodides. $t_{1/2,hydr}$ values in days for the contour intervals are given adjacent to the x- and y-axes on the two-dimensional section.

Figure 8. General pathways for the hydrolysis and dealkylation of sulfonamides reported in the literature.

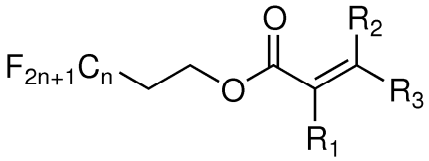
Figure 9. General structures of perfluoroalkyl sulfonamido ethanols (SEs) and acetates (SAAs) capable of forming the five-membered cyclic transition state for intramolecular nucleophilic acid catalysis.

Figure 10. Possible mechanisms for the intramolecular nucleophilic acid catalyzed hydrolysis of (a) n-perfluorooctane sulfonamidoethanol (n-PFOSE) and (b) n-perfluorooctane sulfonamidoacetate (n-PFOSAA).

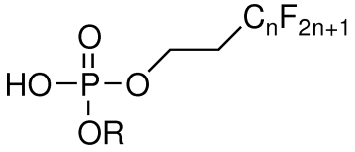
Figure 11. Structures of sulfamoxole (**9**) and sulfadiazine (**10**).

Table 1. SPARC estimated acid-catalyzed (k_A), neutral (k_N), and base-catalyzed (k_B) hydrolysis rate constants at 25°C in pure water for the 2:2 through 12:2 fluorotelomer acrylate monomers (**1**), the 2:2 through 12:2 fluorotelomer methacrylate monomers (**2**), and the model 8:2 fluorotelomer acrylate polymer segments **3** and **4**.

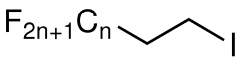
Compound	**k_A (L mol^{-1} s^{-1})**	**k_N (L mol^{-1} s^{-1})**	**k_B (L mol^{-1} s^{-1})**
2:2-**1**	3.5×10^{-7}	1.0×10^{-13}	6.1×10^{-2}
4:2-**1**	7.4×10^{-8}	6.2×10^{-14}	1.7×10^{-2}
6:2-**1**	6.1×10^{-8}	5.8×10^{-14}	1.4×10^{-2}
8:2-**1**	6.0×10^{-8}	5.8×10^{-14}	1.4×10^{-2}
10:2-**1**	6.0×10^{-8}	5.8×10^{-14}	1.4×10^{-2}
12:2-**1**	6.0×10^{-8}	5.8×10^{-14}	1.4×10^{-2}
2:2-**2**	2.1×10^{-7}	8.7×10^{-14}	3.4×10^{-2}
4:2-**2**	4.5×10^{-8}	5.3×10^{-14}	9.4×10^{-3}
6:2-**2**	3.7×10^{-8}	5.0×10^{-14}	8.0×10^{-3}
8:2-**2**	3.6×10^{-8}	5.0×10^{-14}	7.8×10^{-3}
10:2-**2**	3.6×10^{-8}	5.0×10^{-14}	7.8×10^{-3}
12:2-**2**	3.6×10^{-8}	5.0×10^{-14}	7.8×10^{-3}
8:2-**3**	1.7×10^{-8}	1.2×10^{-12}	1.9×10^{-4}
8:2-**4**	9.4×10^{-10}	1.9×10^{-12}	5.1×10^{-5}



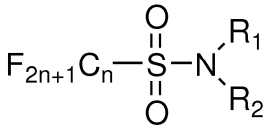
Fluorotelomer acrylates
(FTAcrs)



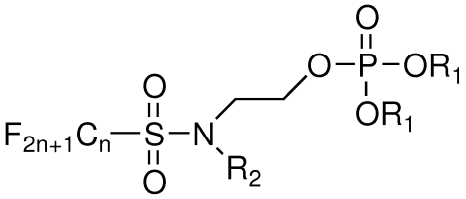
R=H (mono-n:2-FTPE) or $CH_2CH_2C_nF_{2n+1}$ (di-n:2-FTPE)
Fluorotelomer phosphate esters (FTPEs)



Fluorotelomer iodides
(FTIs)



Perfluoroalkyl sulfonamides
(PFSams)



R_1=H or $CH_2CH_2N(R_2)SO_2(C_nF_{2n+1})$
R_2=H, CH_3, CH_2CH_3, alcohols, or acetates, etc.
Perfluoroalkyl sulfonamidoethanol phosphate esters
(PFSamPEs)

Fig. 1

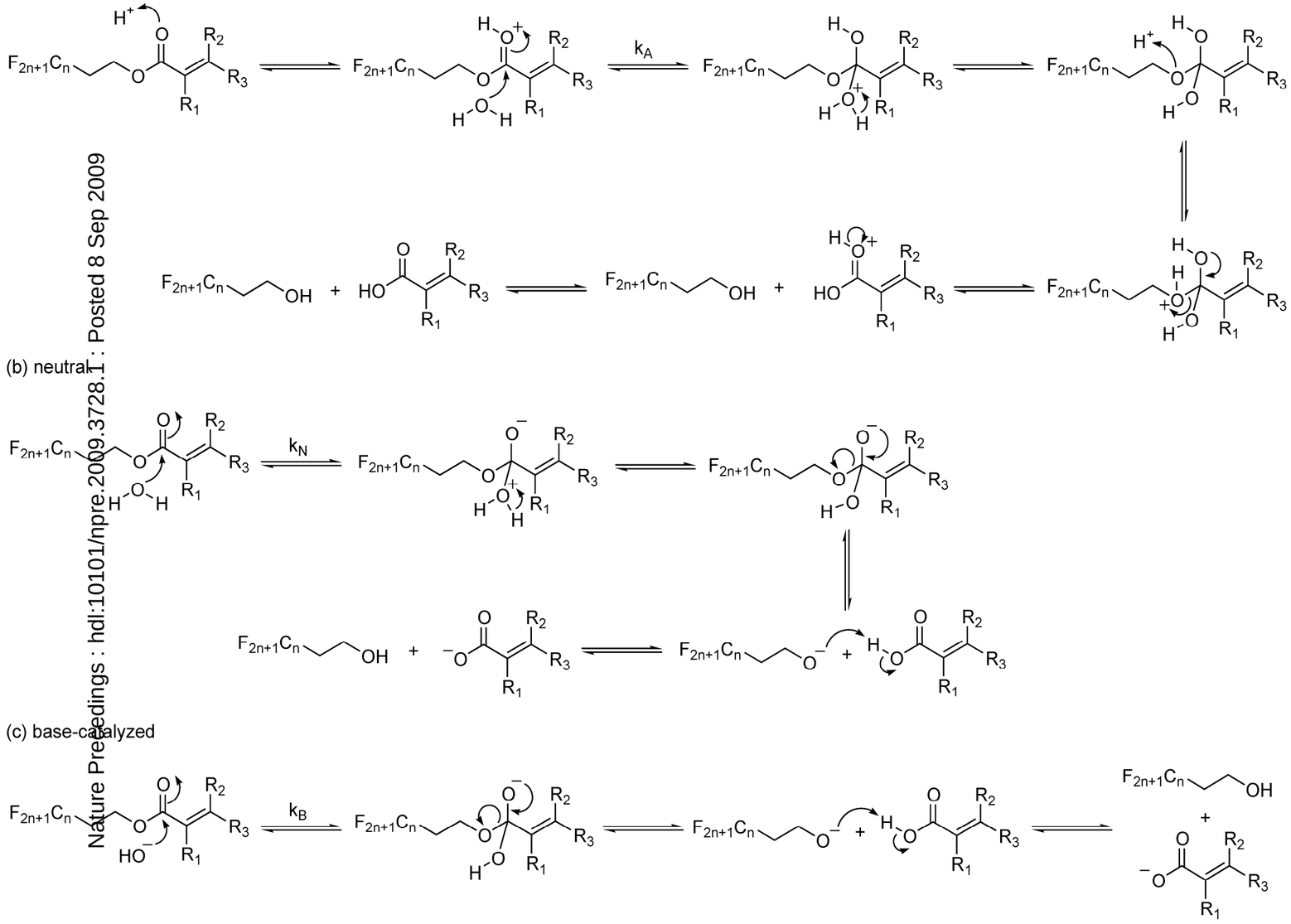


Fig. 2

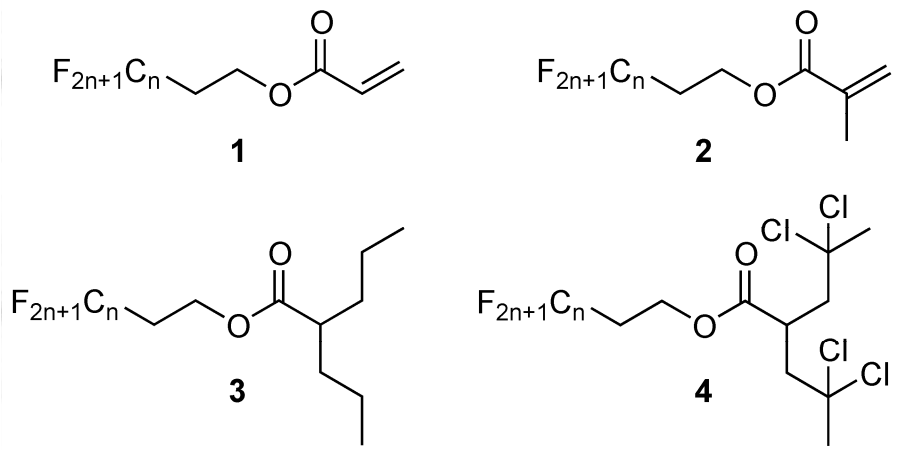


Fig. 3

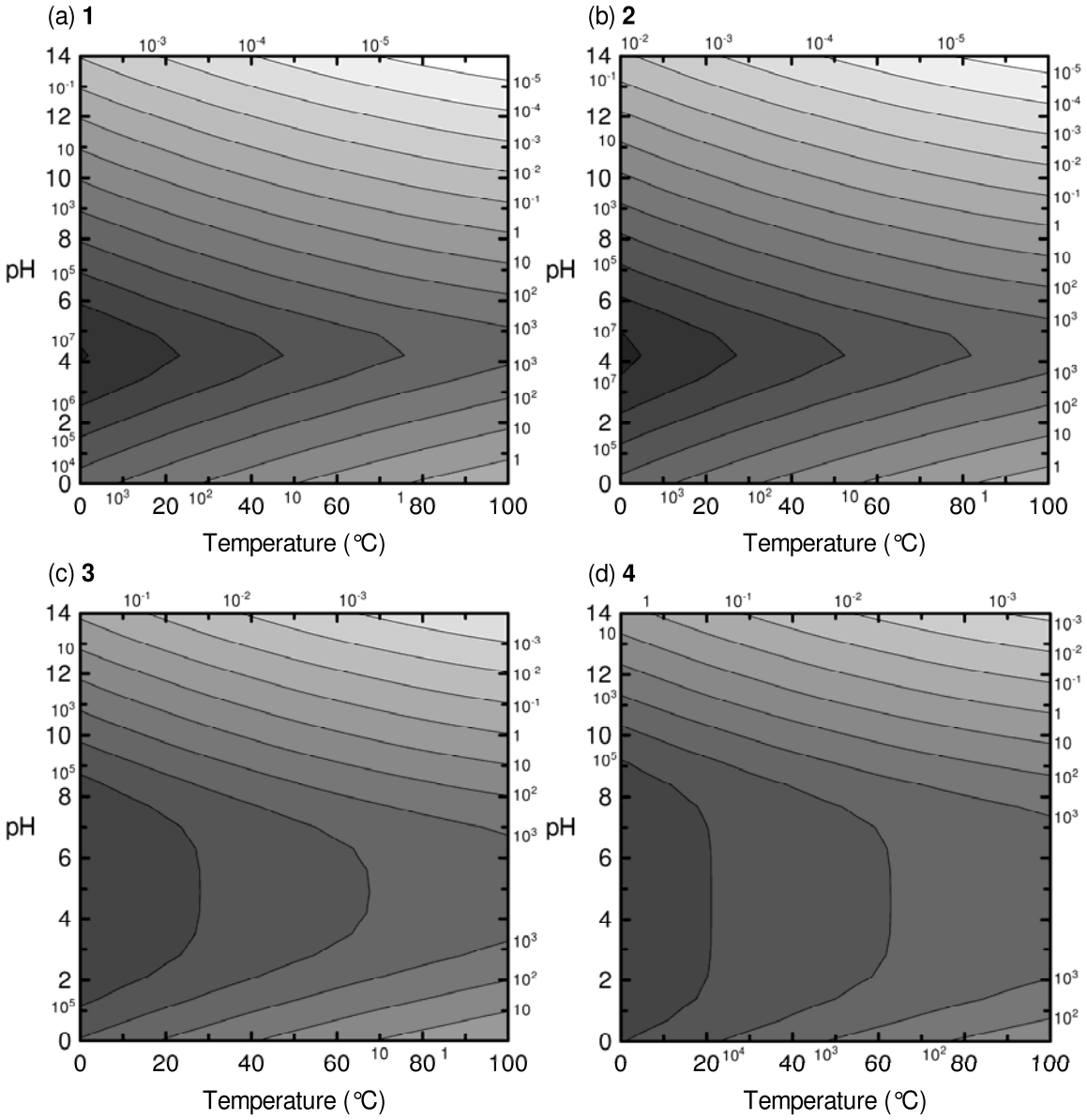


Fig. 4

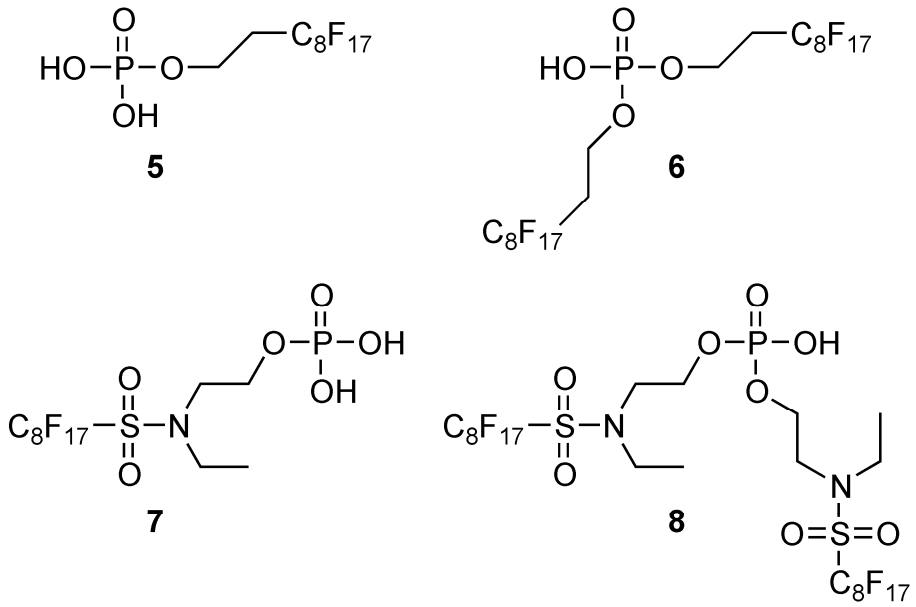


Fig. 5

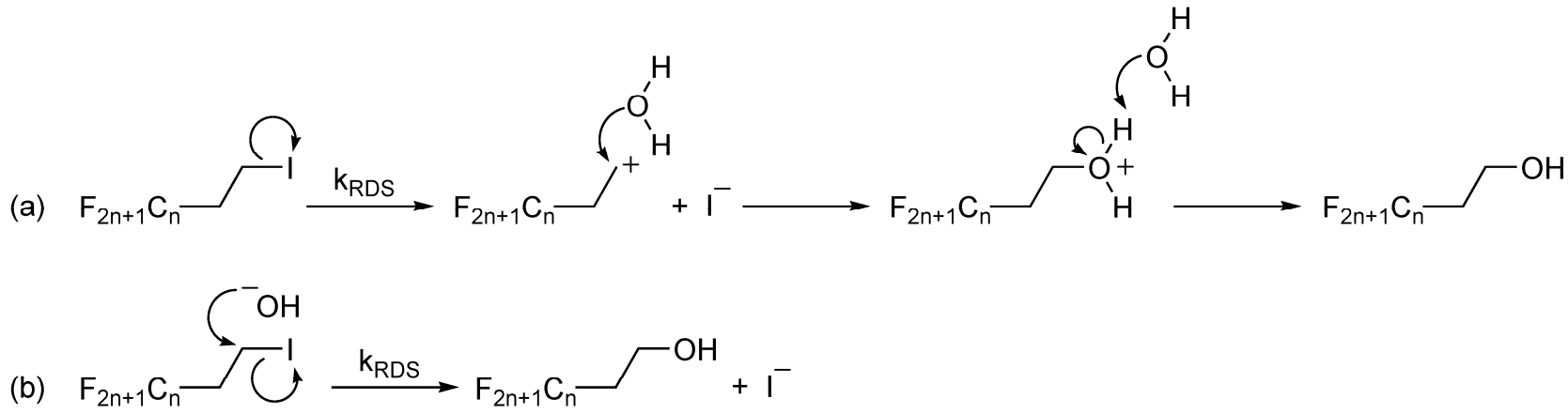


Fig. 6

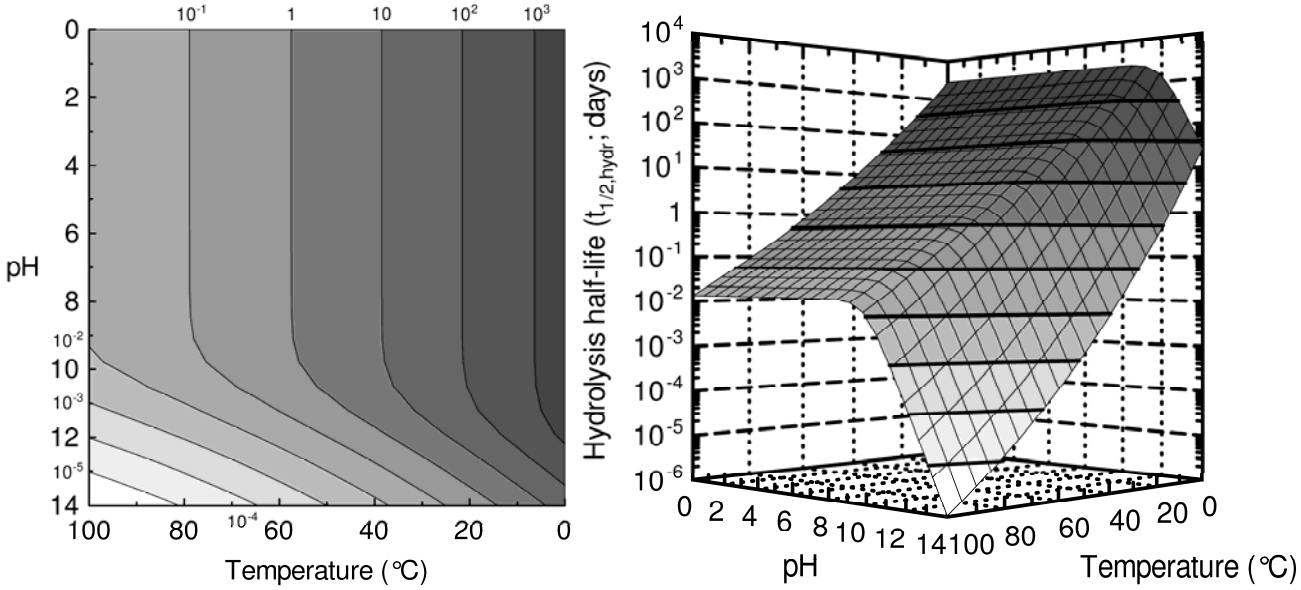


Fig. 7

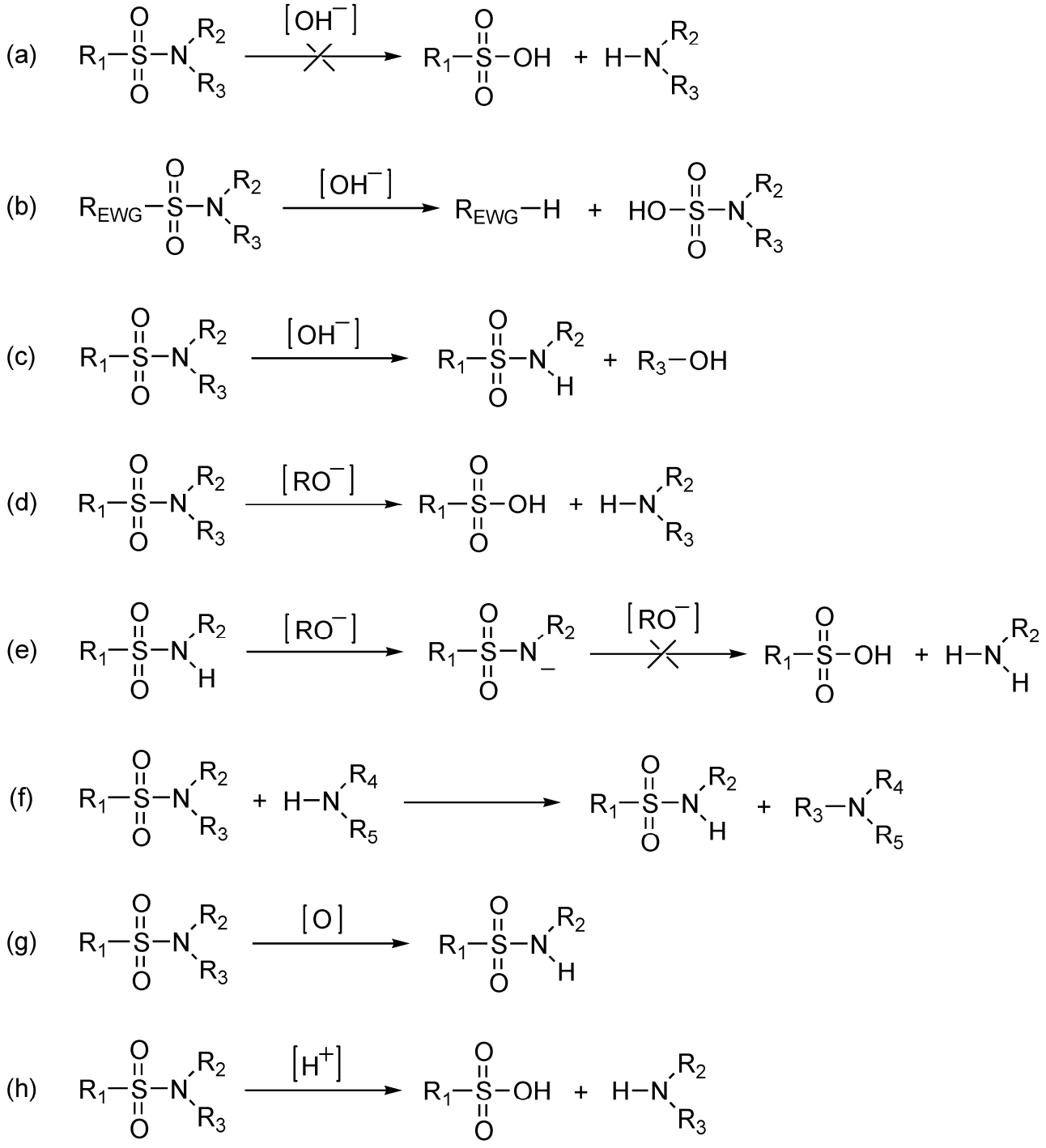


Fig. 8

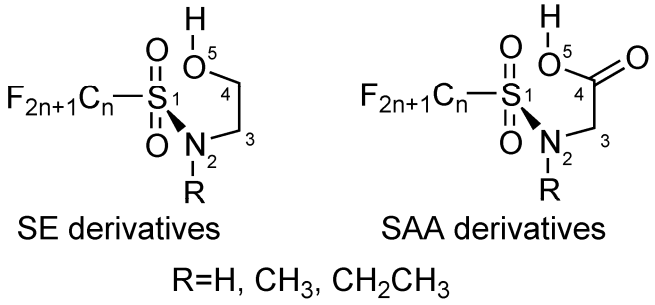


Fig. 9

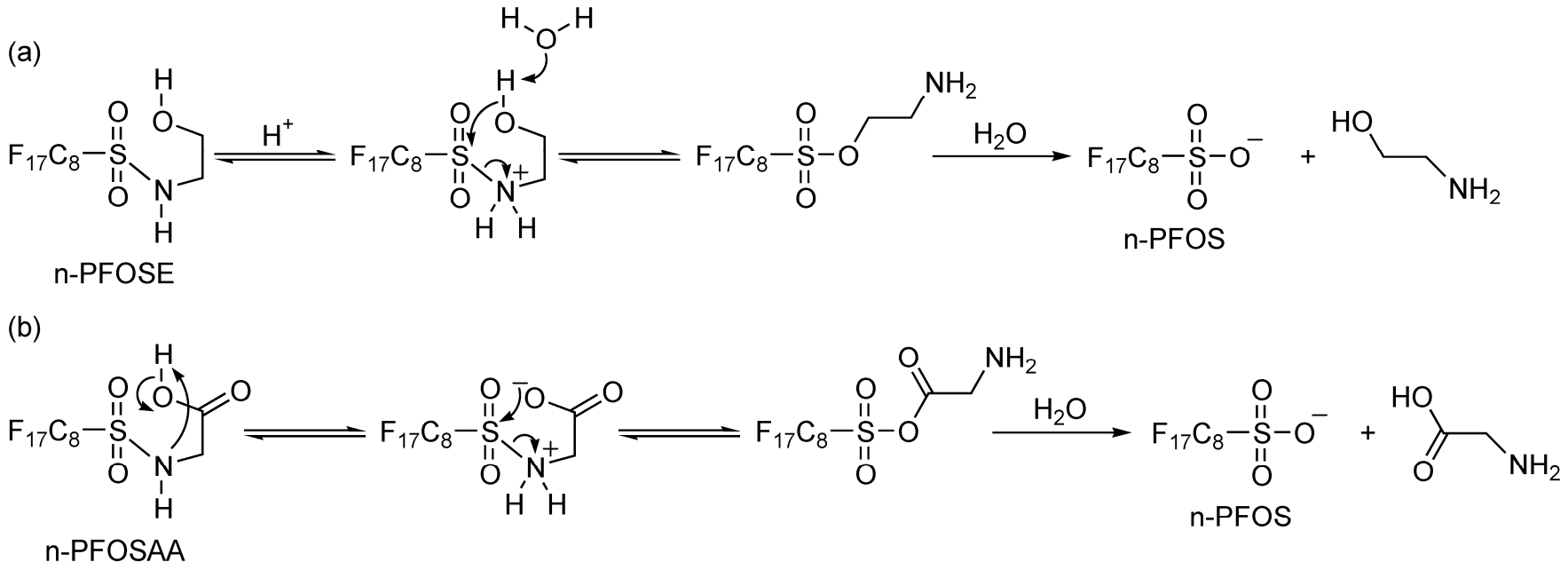
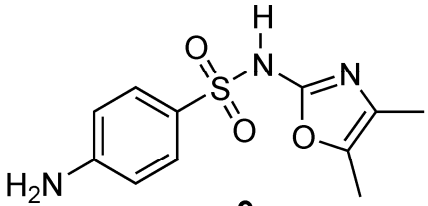


Fig. 10



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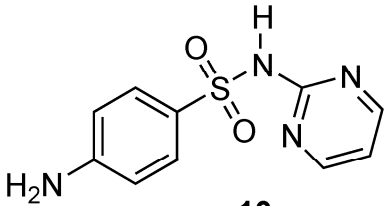

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Fig. 11

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