

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/52002784>

Investigation of the reactivity of hydrated electron toward perfluorinated carboxylates by laser flash photolysis

ARTICLE *in* CHEMICAL PHYSICS LETTERS · JANUARY 2007

Impact Factor: 1.9

CITATIONS

3

READS

31

1 AUTHOR:



Li Huang

Washington University in St. Louis

21 PUBLICATIONS 167 CITATIONS

SEE PROFILE

Investigation of the reactivity of hydrated electron toward perfluorinated carboxylates by laser flash photolysis

Li Huang, Wenbo Dong ^{*}, Huiqi Hou

Department of Environmental Science and Engineering, Institute of Environmental Science, Fudan University, Shanghai 200433, PR China

Received 5 October 2006; in final form 9 January 2007

Available online 17 January 2007

Abstract

Laser flash photolysis technique was employed to investigate the reactivity of hydrated electron (e_{aq}^-) toward a series of perfluorinated carboxylates, $C_nF_{2n+1}COO^-$ ($n = 1, 3, 7$), at 288 ± 1 K in aqueous phase. It was demonstrated that the length of $-C_nF_{2n+1}$ group exerted substantial influence on the rate constant. The second-order rate constants for e_{aq}^- with CF_3COO^- , $C_3F_7COO^-$, $C_7F_{15}COO^-$ were estimated to be $(1.9 \pm 0.2) \times 10^6 M^{-1} s^{-1}$ ($\mu = 0$), $(7.1 \pm 0.3) \times 10^6 M^{-1} s^{-1}$ ($\mu = 0$) and $(1.7 \pm 0.5) \times 10^7 M^{-1} s^{-1}$ ($\mu = 0.01$ M), respectively. © 2007 Elsevier B.V. All rights reserved.

1. Introduction

Owing to their distinguished characteristics such as low viscosity, low surface tension, high thermal and chemical stability and high light transparency, perfluorinated carboxylates ($C_nF_{2n+1}COO^-$, PFCAs) and their derivatives are widely used as emulsifying agents, surface treatment ingredients and water repellents [1]. Such compounds have recently received extensive attention since they are found globally distributed in all kinds of environmental matrixes [2,3]. PFCAs are bioaccumulative when the perfluoroalkyl chain exceeds six carbons [4]. As a result, high levels of long-chain PFCAs such as perfluorooctanoic acid have been detected in human and wildlife in urban areas as well as remote marine environments including polar regions [5,6]. What is worse is that PFCAs have been proved to exert toxic effects [7], such as accumulation of triglycerides in liver, uncoupling of mitochondrial oxidative phosphorylation, and reduction of thyroid hormone in circulation.

Perfluorinated carboxylates were ranked among the most recalcitrant organohalogen contaminants in view of their thermal, chemical and biological inertness. PFCAs

are stable to acids, bases, oxidants and reductants and are generally known to resist hydrolysis, photolysis, microbial degradation, and metabolism by vertebrates [1,8]. In spite of the studies devoted to chemical degradation of PFCAs, there are still no available kinetics data for the interaction of perfluorinated carboxylates with free radicals in aqueous solution. Our knowledge of the reactivity of PFCAs toward active species was limited to their reaction rate constants with OH in gas phase [9,10], which were estimated to be extremely slow. Environmental losses of such compounds through degradation are assumed to be negligible.

The toxicity and persistence of perfluoroalkyl carboxylates have highlighted the need for more research concerning their environmental fate and removal technique. It is well known that strong reductants are capable of completely dissociating perfluorinated compounds via fluoride elimination [11]. Hydrated electron (e_{aq}^-), a highly reactive and strongly reductive species, has been reported to readily decompose perfluoroaromatic compounds in aqueous solution [12]. Question then arose: what would happen if PFCAs encountered with hydrated electron? In this Letter, original laboratory study on the interaction between $C_nF_{2n+1}COO^-$ ($n = 1, 3, 7$) and hydrated electron by using laser flash photolysis technique was performed to improve our understanding of the reactivity of PFCAs and accordingly their environmental fate.

^{*} Corresponding author. Fax: +86 21 65643849.

E-mail addresses: lihuang0220@hotmail.com (L. Huang), wbdong@fudan.edu.cn (W. Dong), fdesi@fudan.edu.cn (H. Hou).

2. Materials and methods

2.1. Reagents

$K_4Fe(CN)_6$ (>99.5%), which was used as a radical source, was purchased from Guanghua Chemicals Co. (Shantou, PRC) and was used without further purification. Trifluoroacetic acid (99.0%, ABCR), heptafluorobutyric acid (99.0%, Aldrich) and perfluorooctanoic acid (98.0%, Lancaster) were used as received. The pH value of all solution was controlled at 10.0 ± 0.2 by the addition of sodium hydroxide (AR). When necessary, $NaClO_4$ (AR) was used to adjust the ionic strength of the solution. All the other reagents were of analytical grade available from Shanghai Chemical Reagent Co., Inc. Solutions were freshly prepared using triply distilled water. Unless specially stated, all samples were deoxygenated by 30 min bubbling of nitrogen (99.999%).

2.2. Photolysis procedure

A Nd:YAG laser (Quanta Ray LAB-150-10, radius of the laser beam cross section 0.4 cm, Spectra-Physics) operating at 266 nm with pulse durations of 8–10 ns was used for nanosecond laser flash photolysis. Transient species were monitored spectrophotometrically by focusing the emission from a 150 W Xenon arc lamp (XBO 150 W/CR-OFR, OSRAM) through the 1×1 cm quartz cell and into the entrance slit of a programmable $f/3.4$ grating monochromator. Before the flash, the optical signal was measured by a sample-and-hold circuit, and the change in absorption after the laser flash was detected by means of a differential amplifier (R928 photomultiplier). The electrical output from the photomultiplier was then transferred to a digitizing oscilloscope (Agilent 54820A, 2 GSa/s) connected to a computer. The timing of the experiment was controlled by a trigger generator. To avoid stray light and secondary photolysis of the sample by the analyzing light, suitable filters were employed.

Hydrated electron (e_{aq}^-) was produced by photolysis of $K_4Fe(CN)_6$ with laser energy of 3.0 mJ per pulse. Rate constants for the reactions of e_{aq}^- with PFCAs were determined by monitoring the decay of its absorption at 690 nm (see Section 3 for detailed description). All the experiments were carried out under a sample temperature of 288 ± 1 K. The reaction mixture was flowed through the reaction cell to refresh the solution between laser pulses.

3. Results and discussion

3.1. Production of hydrated electron by photolysis of $K_4Fe(CN)_6$ in aqueous solution

The absorption spectrum of the intermediates was obtained at 10 nm intervals between 350 nm and 850 nm upon the photolysis of 4.0×10^{-5} M $K_4Fe(CN)_6$ in nitrogen saturated water (Fig. 1, curve a). The broad optical

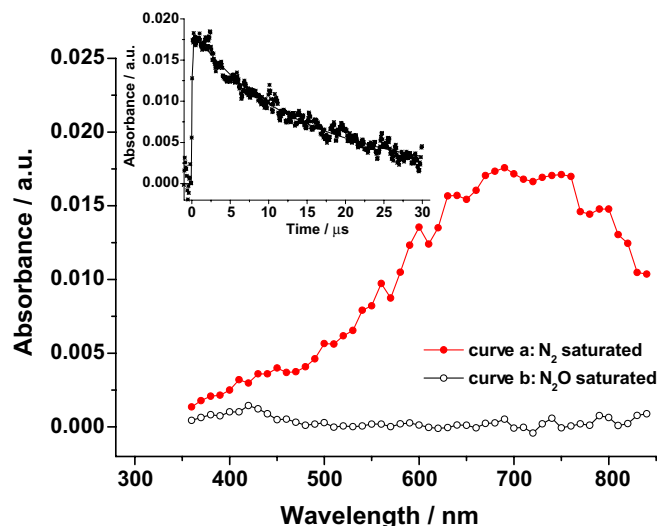
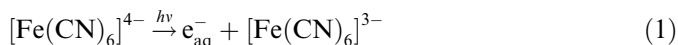
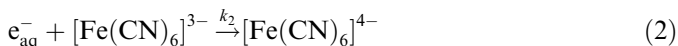


Fig. 1. Transient absorption spectrum recorded at 50 ns following the laser flash photolysis of 4.0×10^{-5} M $K_4Fe(CN)_6$ in N_2 saturated solution (●) as compared with that in N_2O saturated solution (○).

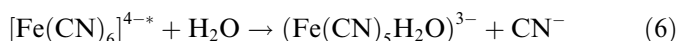
absorption with a peak at 690 nm was attributed to e_{aq}^- in respect that it was identical to the e_{aq}^- absorption spectrum acquired both theoretically [13] and experimentally [14]. The efficient scavenge of such absorption band by N_2O (Fig. 1, curve b) confirmed the attribution. Therefore, in excellent agreement with previous investigations [15,16], abundant hydrated electrons could be produced by photoexcitation of $[Fe(CN)_6]^{4-}$ in its CTTS band:



Inset of Fig. 1 illustrates the typical time profile of the absorption of e_{aq}^- at 690 nm. Hydrated electron decayed in the absence of added substrate due to the following three reactions:



The rate constant for the reaction between e_{aq}^- and H_2O , reported to be 1.0×10^3 s $^{-1}$ [17], was so slow that the loss of hydrated electron via this channel could be neglected. It should also be mentioned that pentacyanoaquo complex took place inevitably corresponding to the following photoexcitation process of $[Fe(CN)_6]^{4-}$, namely photoaquation process [18]:



With regard to its poor reactivity toward e_{aq}^- , the contribution of $(Fe(CN)_5H_2O)^{3-}$ to the decay of e_{aq}^- was negligible.

Therefore, two second-order reactions, reaction (2) and (3), were regarded as the main decay channel for e_{aq}^- . It

seemed pretty difficult to derive k_2 and k_3 . The situation, nevertheless, could be simplified considerably under controlled experimental conditions. We attempted to mix the solution of $K_4Fe(CN)_6$ with excess $K_3Fe(CN)_6$ to ensure that reaction (2) could be regarded as a pseudo-first-order one. Based on the published extinction coefficient of $20560\text{ M}^{-1}\text{ cm}^{-1}$ at 690 nm [16], the initial concentration of e_{aq}^- was calculated to be $1.0 \times 10^{-6}\text{ M}$. In this case, the addition of $1.0 \times 10^{-5}\text{ M}$ $K_3Fe(CN)_6$ is enough to hold the pseudo-first-order relation. The loss of e_{aq}^- turned to follow mixed first- and second-order kinetics expressed as the following equation:

$$A_t(e_{aq}^-) = \frac{\epsilon l k_2 [Fe(CN)_6]^{3-} A_0(e_{aq}^-) e^{-k_2 [Fe(CN)_6]^{3-} t}}{2k_3 A_0(e_{aq}^-) (1 - e^{-k_2 [Fe(CN)_6]^{3-} t}) + k_2 [Fe(CN)_6]^{3-} \epsilon l} \quad (7)$$

where l is the optical path length, ϵ is the molar extinction coefficient of e_{aq}^- , $A_0(e_{aq}^-)$ is the initial absorbance of e_{aq}^- , and $A_t(e_{aq}^-)$ is the transient absorbance of e_{aq}^- recorded at specific time point (t) after the laser pulse. Rate constant k_2 and k_3 could then be derived from the weighted least-squares fit of the plot of $A_t(e_{aq}^-)$ against t according to Eq. (7).

As concluded in earlier research, rate constant for reaction between two ions in aqueous phase is highly dependent on the ionic strength (μ) of the medium. The influence of ionic strength on k_2 and k_3 was examined systematically by carrying out experiments of varying ionic strength ranging from 0.003 up to 0.102 M by adding $NaClO_4$. Plots of $\log k_2$ and $\log k_3$ vs. $\mu^{1/2}/(1 + \mu^{1/2})$ were demonstrated in Fig. 2. The linear correlation between logarithm of rate constant and $\mu^{1/2}/(1 + \mu^{1/2})$ suggested the ionic strength dependence of k_2 agreed well with the Debye–Hückel theory prediction:

$$\log k_2 = \log k_2^{\mu=0} + 1.02 Z_a Z_b \frac{\mu^{1/2}}{1 + \mu^{1/2}} \quad (8)$$

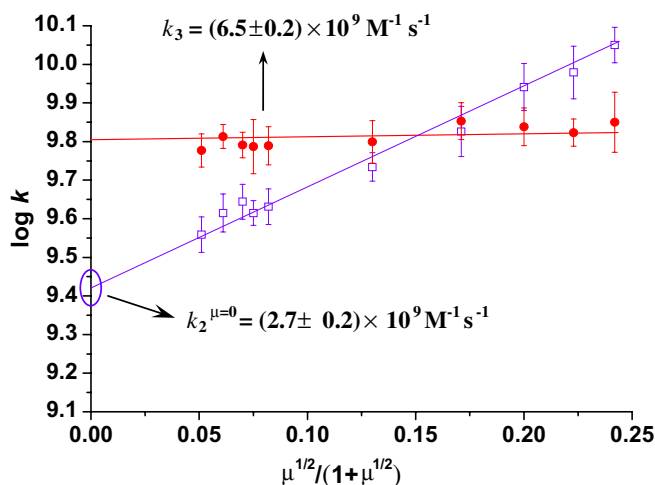


Fig. 2. Ionic strength dependence of the rate constant for the reaction of e_{aq}^- with $[Fe(CN)_6]^{3-}$ (the square dot) and the self-reaction of e_{aq}^- (the round dot).

where k_2 is the measured rate constant for reaction (2), $k_2^{\mu=0}$ is the rate constant at zero ionic strength, Z_a and Z_b are the charges of reacting ions. Thus the intercept of the line in Fig. 2 was equal to $\log k_2^{\mu=0}$. Our value of $k_2^{\mu=0} = (2.7 \pm 0.2) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ was comparable with those reported by Buxton [19], proving the validity and reliability of the approach used in this work. As for the self-reaction of e_{aq}^- , the observed rate constant deviated from the Debye–Hückel theory because diffusion was encumbered by the additional friction from the ionic atmosphere [20]. Within experimental uncertainties, there was no change in the measured rate constant over the ionic strength interval, and an average value of $k_3 = (6.5 \pm 0.2) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ was derived.

3.2. Rate constants for reaction of e_{aq}^- with $C_nF_{2n+1}COO^-$ ($n = 1, 3, 7$)

The decay of e_{aq}^- was observed to enhance gradually with increasing $[CF_3COONa]$ in the solution (as shown in Fig. 3). Obviously, such acceleration in decay rate arose from the additional consumption of e_{aq}^- by CF_3COO^- . In other words, the reaction between CF_3COO^- and e_{aq}^- must occur. On addition of excess CF_3COONa , totally two pseudo-first reactions and one second-order reaction accounted for the loss of e_{aq}^- in controlled experiments. Hydrated electron still decayed corresponding to mixed first- and second-order kinetics. Given that k_2 and k_3 were already obtained as a function of ionic strength, the rate constant for the reaction of e_{aq}^- with CF_3COO^- ($k_{e_{aq}-CF_3COO^-}$) could be derived similarly. The obtained $k_{e_{aq}-CF_3COO^-}$ varied with the initial concentration of CF_3COONa . This phenomenon was presumably related to the changes in ionic strength upon CF_3COONa concentration. Therefore, in the subsequent experiments, to determine $k_{e_{aq}-CF_3COO^-}$ at specific ionic strength, five sets of experiments were performed with different $[CF_3COONa]$ and constant ionic strength adjusted by $NaClO_4$. The

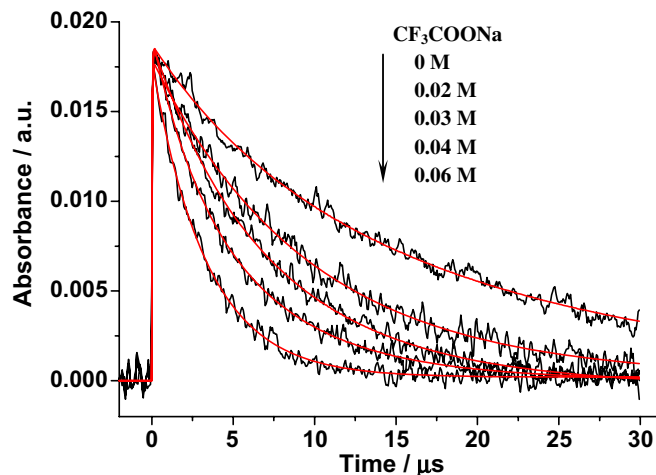


Fig. 3. Acceleration of the decay of e_{aq}^- by adding CF_3COONa measured at 690 nm .

$k_{e_{aq}^- - CF_3COO^-}$ derived at ionic strength of 0.010, 0.015, 0.035, 0.065, 0.10 M increased gradually. The linear relationship between $\log k_{e_{aq}^- - CF_3COO^-}$ and $\mu^{1/2}/(1 + \mu^{1/2})$ (see Fig. 4) supported our speculation that reaction between e_{aq}^- and CF_3COO^- is ionic strength dependent. Extrapolation of the line to zero ionic strength gave $k_{e_{aq}^- - CF_3COO^-}^{\mu=0}$ of $(1.9 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

To our knowledge, little research work was focused on the interaction of e_{aq}^- with perfluorinated carboxylates, resulting in only one value available for $k_{e_{aq}^- - CF_3COO^-}$ [21]. However, Anbar and Hart only provided the value of $k_{e_{aq}^- - CF_3COO^-} = (2.6 \pm 0.6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at ionic strength of 1.0 M through pulse radiolysis study. The discrepancy was fairly comprehensible since it might result from the different experimental conditions, such as ionic strength and room temperature.

In parallel, the rate constants for reactions of e_{aq}^- with $C_3F_7COO^-$ and $C_7F_{15}COO^-$ were obtained in the same

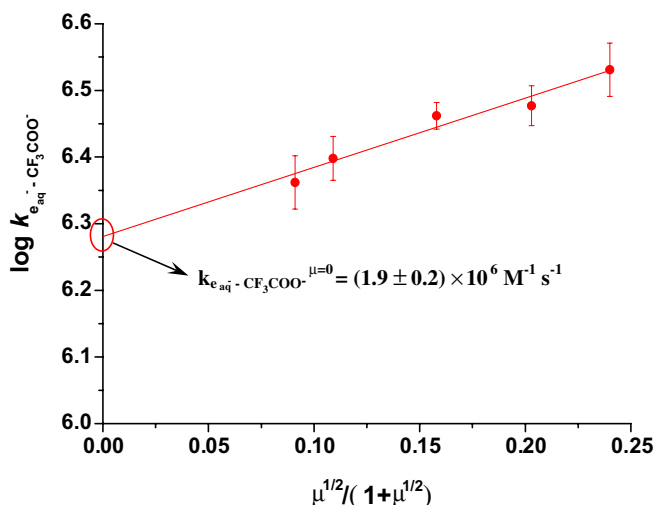


Fig. 4. Linear correlation of $\log k_{e_{aq}^- - CF_3COO^-}$ with $\mu^{1/2}/(1 + \mu^{1/2})$.

manner and summarized in Table 1 together with $k_{e_{aq}^- - CF_3COO^-}$. Similarly, ionic strength effect could not be ignored because the added reactants were salt and the ionic strength of the solution changed upon each addition. Both the measured rate constants and those corrected for ionic strength were included in Table 1. The rate constant appeared to increase with the length of perfluorinated chain, from $(2.3 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for CF_3COO^- to $(1.7 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for $C_7F_{15}COO^-$ at $\mu = 0.01 \text{ M}$.

It was well established that e_{aq}^- interacted with perfluoroaromatic compounds by a mechanism analogous to nucleophilic substitution. In these reactions, e_{aq}^- attacked the carbon atom in the aromatic ring followed by incorporation into the orbitals of the ring. In the case of perfluorinated carboxylates, all the C atoms, including the C atom in C–F bond and that in carboxylate, are saturated and therefore unable to provide orbital to accommodate the extra electron. Owing to the intensive repulsion, e_{aq}^- was unlikely to attack the O atom as well. Whereas, the fluorine atom was capable of withdrawing electron in view of its electron affinity up to 3.40 eV [22]. Hence, in contrast with perfluoroaromatic compounds, the fluorine atom, instead of the carbon atom, was the reaction center when e_{aq}^- approaching a perfluorinated carboxylate molecule. In consequence, longer perfluorinated chain brought about more attacking sites and a corresponding increment in reaction rate.

The addition ability of e_{aq}^- to perfluorinated carboxylates was expected to resemble that to other perhalogenated carboxylates. On the contrary, perfluorinated carboxylates exhibited lower reactivity toward e_{aq}^- as compared with other perhalogenated carboxylates. For instance, the rate constant of the reaction between CF_3COO^- and e_{aq}^- is three order of magnitude lower than that of CCl_3COO^- with e_{aq}^- [21]. The C–X (X represented halogen) bond energy then seemed to be another parameter dominating the reaction of e_{aq}^- with perhalogenated carboxylates. The reaction

Table 1

Comparison of rate constants for reactions of e_{aq}^- with perfluorinated carboxylates at $288 \pm 1 \text{ K}$ obtained in this work with previous work

Reactant	Present work			Previous work
	Ionic strength (M)	$k \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	$k^{\mu=0} \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	
CF_3COO^-	0.010	$(2.3 \pm 0.2) \times 10^6$	$(1.9 \pm 0.2) \times 10^6$	$(2.6 \pm 0.6) \times 10^6$ at ionic strength $\sim 1.0 \text{ M}$ by pulse radiolysis [21]
	0.015	$(2.5 \pm 0.2) \times 10^6$		
	0.035	$(2.9 \pm 0.1) \times 10^6$		
	0.065	$(3.0 \pm 0.2) \times 10^6$		
	0.10	$(3.4 \pm 0.3) \times 10^6$		
$C_3F_7COO^-$	0.010	$(8.8 \pm 0.2) \times 10^6$	$(7.1 \pm 0.3) \times 10^6$	NA ^b
	0.015	$(9.0 \pm 0.3) \times 10^6$		
	0.035	$(9.6 \pm 0.1) \times 10^6$		
	0.065	$(1.2 \pm 0.1) \times 10^7$		
	0.10	$(1.3 \pm 0.1) \times 10^7$		
$C_7F_{15}COO^-$ ^a	0.01	$(1.7 \pm 0.5) \times 10^7$	–	NA ^b

In this work, initial concentration of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ were fixed at $4.0 \times 10^{-5} \text{ M}$ and $1.0 \times 10^{-5} \text{ M}$, respectively.

^a Due to the low solubility of PFOA in water, the error of the obtained rate constant of the reaction between $C_7F_{15}COO^-$ and e_{aq}^- was relatively great. It's rather difficult to investigate the effect of ionic strength on this reaction. In consequence, we only reported the uncorrected rate constant for the reaction of $C_7F_{15}COO^-$ and e_{aq}^- obtained at ionic strength of 0.01 M.

^b NA, not available in the literature.

occurred only when the e_{aq}^- is attached to perfluorinated carboxylates efficiently leading to heterolytic cleavage of C–F bond.

4. Conclusions

Perfluorinated carboxylic acids were recognized as one family of wide-spread environmental contaminants. As far as their pK_a values were concerned, perfluorinated carboxylic acids present in natural water in the form of $C_nF_{2n+1}COO^-$ [23]. On account of their distinguished stability, clarifying the reactivity of perfluorinated carboxylates toward e_{aq}^- , the most attainable nucleophilic agent, was of environmental and chemical significance. The present work proved that the reaction of CF_3COO^- with e_{aq}^- occurs with a rate constant of $(1.9 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The longer the perfluorinated chain is, the higher the rate constant for the reaction of perfluoro carboxylates with e_{aq}^- is. Considering that a majority of hydrated electrons are generated in the course of radiation and non-thermal plasma, such technologies are believed to be capable of abating perfluorinated carboxylates.

The hydrated electron is reported to be produced upon the photolysis of humic and fulvic acids in natural waters [24,25]. To gain a clear picture of the fate of PFCAs in environmental aqueous phase, the reactivity of two strong one-electron oxidative radicals, SO_4^- and NO_3^- , toward PFCAs were also studied by laser flash photolysis. The rate constants for the reactions of PFCAs with SO_4^- and NO_3^- were determined to be no greater than $5.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, as compared with SO_4^- and NO_3^- , e_{aq}^- is reasonably regarded as a possible environmental sink for PFCAs.

Acknowledgement

This work is financially supported by the National Natural Science Foundation of China (NSFC 20377009).

References

- [1] E. Kissa, Surfactant Science Series, Marcel Dekker, New York, 2001.
- [2] J.P. Giesy, K. Kannan, Environ. Sci. Technol. 36 (2002) 146A.
- [3] R. Renner, Environ. Sci. Technol. 35 (2001) 154A.
- [4] J.W. Martin, S.A. Mabury, K.R. Solomon, D.C.G. Muir, Environ. Toxicol. Chem. 22 (2003) 196.
- [5] K. Kannan et al., Environ. Sci. Technol. 38 (2004) 4489.
- [6] J.W. Martin, M.M. Smithwick, P.F. Braune, P.F. Hoekstra, D.C.G. Muir, S.A. Mabury, Environ. Sci. Technol. 38 (2004) 373.
- [7] G.L. Kennedy Jr. et al., Crit. Rev. Toxicol. 34 (2004) 351.
- [8] D.A. Ellis, C.A. Moody, S.A. Mabury, in: A. Nielson (Ed.), Handbook of Environmental Chemistry, Springer Verlag, Heideberg, 2002.
- [9] S. Carr, J.J. Treacy, H.W. Sidebottom, R.K. Connell, C.E. Canosa-Mas, R.P. Wayne, J. Franklin, Chem. Phys. Lett. 227 (1994) 39.
- [10] M.D. Hurley, M.P. Sulbaek Andersen, T.J. Wallington, D.A. Ellis, J.W. Martin, S.A. Mabury, J. Phys. Chem. 108 (2004) 615.
- [11] R. Perry, in: R.E. Banks, D.W.A. Sharp, J.C. Tarlow (Eds.), Fluorine – The First Hundred Years, Elsevier, New York, 1986, p. 293.
- [12] L.C.T. Shoute, J.P. Mittal, J. Phys. Chem. 100 (1996) 14022.
- [13] H. Abramczyk, J. Kroh, J. Phys. Chem. 95 (1991) 6155.
- [14] E.J. Hart, J.W. Boag, J. Am. Chem. Soc. 84 (1962) 4090.
- [15] W.L. Waltz, A.W. Adamson, J. Phys. Chem. 73 (1969) 4250.
- [16] M.C. Sauer Jr., R.A. Crowell, I.A. Shkrob, J. Phys. Chem. 108 (2004) 5490.
- [17] H.A. Schwarz, J. Phys. Chem. 96 (1992) 8937.
- [18] M. Shirom, G. Stein, J. Chem. Phys. 55 (1971) 3379.
- [19] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513.
- [20] K.H. Schmidt, D.M. Bartels, Chem. Phys. 190 (1995) 145.
- [21] M. Anbar, E.J. Hart, J. Phys. Chem. 69 (1965) 271.
- [22] C. Blondel, P. Cacciani, C. Delsart, R. Trainham, Phys. Rev. A 40 (1989) 3698.
- [23] K. Prevedouros, I.T. Cousins, R.C. Buck, S.H. Korzeniowski, Environ. Sci. Technol. 40 (2006) 32.
- [24] R.G. Zepp, A.M. Braun, J. Hoigne, J.A. Leenheer, Environ. Sci. Technol. 21 (1987) 485.
- [25] T.E. Thomas-Smith, N.V. Blough, Environ. Sci. Technol. 35 (2001) 2721.