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Rate Constants for Some Reactions of Free Radicals with Haloacetates in Aqueous Solution

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Abstract

The kinetics of the acqueous-phase reactions of the free radicals $\cdot$OH, $\cdot$Cl$_2^-$, and SO$_4^-$ $\cdot$ with the halogenated acetates, CH$_2$FCOO$^-$, CHF$_2$COO$^-$, CF$_3$COO$^-$, and with CH$_2$ClCOO$^-$, CHCl$_2$COO$^-$, CCl$_3$COO$^-$ were investigated. Generally, the reactivity decreases with increasing halogen substitution and is in the order $k(\cdot OH) > k(SO_4^- \cdot) > k(\cdot Cl_2^-)$, but there is no general relation between the effect on reactivity of chlorine and fluorine substitution. © 1995 John Wiley & Sons, Inc.

Introduction

The substitution of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) for chlorofluorocarbons (CFCs) is taking place to reduce the depletion of the stratospheric ozone layer. Because of the presence of one of more hydrogen atoms, greater lability is imparted to these compounds which makes them susceptible to oxidation by hydroxyl radicals in the troposphere. Recently, a considerable amount of attention has been placed on the use of C$_2$ HFCs and HCFCs as possible CFC replacement compounds. Subsequent to their reaction with OH, a series of atmospheric reactions leads, often, to carbon—carbon bond scission and the formation of C$_1$ products which, upon dissolution in water, undergo mineralization [1]. For several of these compounds, however, the atmospheric reactions do not lead to carbon—carbon bond scission but to the formation of C$_2$ carbonyl halides. For example, the following mechanism takes place for CH$_2$FCF$_3$ (HFC-134a) [2]:

(1) $\qquad \cdot$OH + CH$_2$FCF$_3$ $\longrightarrow$ H$_2$O + $\cdot$CHFCF$_3$

(2) $\qquad \cdot$CHFCF$_3$ + O$_2$ $\longrightarrow$ CF$_3$CHFO$_2$ $\cdot$

(3) $\qquad$ CF$_3$CHFO$_2$ $\cdot$ + NO $\longrightarrow$ CF$_3$CHFO $\cdot$ + NO$_2$

(4) $\qquad$ CF$_3$CHFO $\cdot$ + O$_2$ $\longrightarrow$ CF$_3$CHFO + HO$_2$ $\cdot$

The carbonyl halide will hydrolyze in atmospheric droplets

(5) $\qquad$ CF$_3$CFO + H$_2$O $\longrightarrow$ HF + CF$_3$C(O)OH

to form, in this case, trifluoroacetic acid [3]. These halogenated acids have known toxic and phytotoxic properties and have been found in significant concentrations in conifer needles [4]. In order to understand the possible impact of future atmospheric production of these haloacids, information on possible formation and destruction mechanisms is needed. Presently there is very little known about the possible atmospheric reactions of these compounds, particularly for the highly unreactive

trifluoroacetic acid. Because of the high solubility of these acids, reactions which might take place within atmospheric water drops are of particular interest.
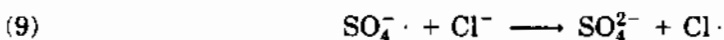
Organic acids dissolve in water to form anions which can transfer an electron to oxidizing free radicals, producing a radical which subsequently undergoes decarboxylation [5]

(6) $$CX_3COO^- + Ox \longrightarrow CX_3COO \cdot + Red$$

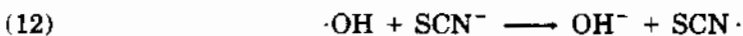(7) $$CX_3COO \cdot \longrightarrow \cdot CX_3 + CO_2$$
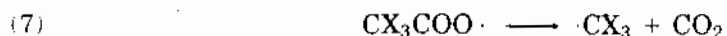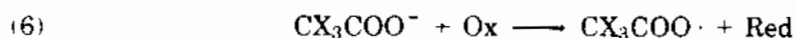
Although there have been many studies of the reactions of one-electron oxidants with acetate and carboxylate-containing organic compounds, there is essentially no information on the reactivity of the halogenated carboxylates [6,7]. We report here the results of a study of the reactions of some strong, one-electron oxidants with the halogenated acetates CH_2FCOO^- (MFA), CHF_2COO^- (DFA), CF_3COO^- (TFA), and CH_2ClCOO^- (MCA), $CHCl_2COO^-$ (DCA), CCl_3COO^- (TCA). We chose to investigate this set in order to establish clearly the behavior of the least reactive of them: the trifluoroacetate anion (TFA). The oxidants we have investigated are the free radicals $\cdot OH$, $\cdot Cl_2^-$, and $SO_4^- \cdot$, which are strong, one-electron oxidants with reduction potentials of 1.90, 2.09 [8], and 2.43 V [9], respectively. These are the radicals most likely to be able to react with haloacetates in atmospheric droplets. $\cdot OH$ can diffuse into droplets or can be formed by photolysis; $SO_4^- \cdot$ is an important intermediate in the free-radical oxidation of HSO_3^-; and $\cdot Cl_2^-$ will be the key reactive radical formed from these other radicals in chloride-containing droplets. Other atmospherically important radicals have significantly lower reduction potentials, e.g., $CO_3^- \cdot$ at 1.59 V [9], and are less likely to react with these acetates.

Experimental

Rate constants for the reactions of the free radicals $\cdot OH$, $\cdot Cl_2^-$, and $SO_4^- \cdot$ with haloacetates were measured by laser-flash photolysis. The basic apparatus and experimental technique have been described in detail previously [10,11]. The $SO_4^- \cdot$ radical was produced by the 248 nm excimer laser-flash photolysis of sodium persulfate solution and $Cl_2^- \cdot$ was produced by the reaction of $SO_4^- \cdot$ with Cl^-.

(8) $$S_2O_8^{2-} + h\nu \longrightarrow 2SO_4^- \cdot$$

(9) $$SO_4^- \cdot + Cl^- \longrightarrow SO_4^{2-} + Cl \cdot$$

(10) $$Cl \cdot + Cl^- \rightleftharpoons \cdot Cl_2^-$$

The reactions of $\cdot Cl_2^-$ and $SO_4^- \cdot$ were monitored by following the strong absorptions of the radicals at about 340 and 450 nm, respectively. OH radical reactions were studied by flash-photolyzing H_2O_2 in the presence of 0.1 mmol L^{-1} SCN^-:

(11) $$H_2O_2 + h\nu \longrightarrow 2 \cdot OH$$

(12) $$\cdot OH + SCN^- \longrightarrow OH^- + SCN \cdot$$

(13) $$SCN \cdot + SCN^- \longrightarrow (SCN)_2^- \cdot$$

Rate constants were then derived relative to the rate constant for the reaction of $\cdot OH + SCN^- k_{296} = 1.2 \times 10^{10}$ L mol^{-1} s^{-1} [12].

Decay or formation curves observed subsequent to the flash were averaged before undergoing least-squares analysis to obtain the first-order rate constants. First-order

rate constants were determined at four different substrate concentrations and second-order rate constants were derived from a weighted least-squares fit to a plot of the first-order rate constant against the substrate concentration.

Confirmation of the reactivity patterns and information on the products of some of these reactions were obtained by use of continuous photolytic and radiolytic methods. The reactions of $SO_4^- \cdot$ were investigated by photolyzing mixtures of $300-500 \ \mu mol \ L^{-1}$ haloacetate and 5 mmol L^{-1} peroxydisulfate with a 1000-W Xe arc lamp. The reactions of OH with the various haloacetates were investigated by using gamma radiolysis to produce OH. Aqueous solutions containing ca. $\sim 400 \ \mu mol \ L^{-1}$ haloacetate and saturated with N_2O were irradiated with gamma rays (dose rate $= 1.22 \ Gy \ s^{-1}$ or $4.10 \ Gy \ s^{-1}$). The irradiation energy is absorbed by water and results in the formation of hydroxyl radicals according to the reactions,

(14) $$H_2O \Longrightarrow \Longrightarrow \Longrightarrow e_{aq}^-, H^+, OH, H$$

(15) $$e_{aq}^- + N_2O + H^+ \longrightarrow N_2 + OH$$
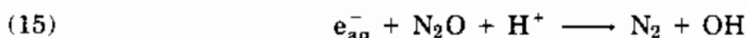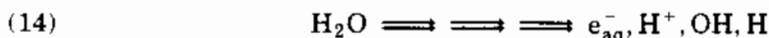
No scavenger was used to eliminate the small amount of H formed. In both the radiolysis and photolysis experiments, the amount of the haloacetate decomposed was determined by ion chromatography.

All the chemicals used were the purest grade available. Sodium salts of monochloroacetate (MCA), dichloroacetate (DCA), trichloroacetate (TCA), monofluoroacetate (MFA), and trifluoroacetate (TFA) were from Aldrich [13]. MFA, which contained 0.5% nigrosine dye, was purified by recrystallizing in methanol/acetonitrile. The trichloroacetate was found to contain (by anion chromatography described below) 2% dichloroacetate and 0.7% monochloroacetate, but was used as such. Difluoroacetate (DFA) was available (from Aldrich) only as the acid and was neutralized with NaOH before use. All the experiments were carried out in aqueous medium with water purified by a Millipore Milli-Q system. The pH of the solution (pH 4–5) was adjusted either with $HClO_4$ or NaOH and the ionic strength adjusted by addition of $NaClO_4$. Under these conditions, all of the halogenated carboxylic acids exist primarily as their anions.

Results

Second-order rate constants for the reactions of $SO_4^- \cdot$ and $Cl_2^- \cdot$ with the haloacetates were determined by measuring the first-order rate constants for the decay of $SO_4^- \cdot$ at 450 nm or of $Cl_2^- \cdot$ at 340 nm in the presence of various amounts of added substrate. Typically, the solution consisted of 1 mmol $L^{-1} \ S_2O_8^{2-}$, 50–100 mmol $L^{-1} \ Cl^-$ (for the $Cl_2^- \cdot$ experiments) or 20–50 mmol $L^{-1} \ NaClO_4$ (for the $SO_4^- \cdot$ experiments), and amounts of added substrate ranging from about 1 to 250 mmol L^{-1} [14].

Since, in most cases, the ionic strength would change upon each addition of the haloacetate, we have chosen to correct the measured rate constants by use of the equation

$$\log k_0 = \log k - 2z_a z_b [A\mu^{1/2}/(1 + \mu^{1/2})]$$

where k is the measured rate constant, k_0 is the rate constant at zero ionic strength, z is the species charge, μ is the ionic strength, and A is a collection of physical constants with the value 0.51 at room temperature. An example of a second-order plot with corrected and uncorrected first-order rate constants is given in Figure 1. In Table I, we list the derived second-order rate constants, corrected to zero ionic strength.
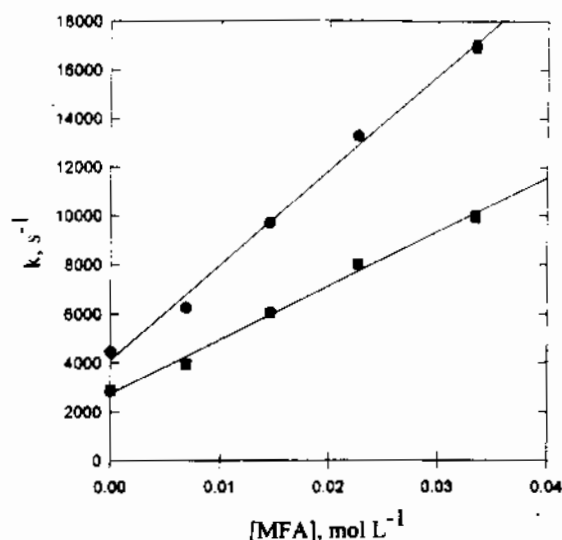
Figure 1. First-order rate constants for the reaction of $Cl_2^-\cdot$ with CH_2FCOO^- as a function of the acetate concentration. The upper line (circles) is for the data uncorrected for ionic strength; the lower line (squares) is for the data after correction for ionic strength.

Since the hydroxyl radical has a very weak optical absorption, rate constants for its reactions were measured relative to the rate constant for the reaction of OH with SCN^- by measuring the absorption due to $(SCN)_2^-\cdot$ at 480 nm. Solutions containing 5 mmol L^{-1} H_2O_2, 0.5 mmol L^{-1} KSCN, and various amounts of an added substrate were photolyzed at pH 6.2. As substrate was added, the absorption decreased. The relative rate constant was derived from the slope or a plot of Abs_0/Abs vs. [haloacetate]/[SCN^-] (Fig. 2). These rate constants are included in Table I. Since OH is uncharged, there was no need to correct the rate constants to zero ionic strength.

The rate constants for the reactions of the haloacetates with $SO_4^-\cdot$, $Cl_2^-\cdot$, and $\cdot OH$ reported in Table I are very low when compared with those typically found for these highly reactive radicals. Generally, the reactivity patterns are as expected, with the rate constants decreasing with increasing halogen substitution. For the reactions of $SO_4^-\cdot$ and $\cdot OH$ with the chlorinated acetates, this decrease is very small and, indeed, the rate constant for the reaction of $\cdot OH$ with DCA is greater than that for MCA. Since small amounts of reactive impurities can have a major impact on the measured rate of decay of the radicals, we have checked the relative reactivities of $SO_4^-\cdot$ with all of the haloacetates by use of steady-state photolysis and for the reactions of $\cdot OH$ with the chloroacetates by use of gamma radiolysis. In these studies, the rate of loss of the haloacetate is monitored, and small amounts of impurities have a much reduced effect.

In the photolysis experiments, a mixture of 0.3 to 0.5 mmol L^{-1} of the haloacetate and 5 mmol L^{-1} $S_2O_8^{2-}$ was illuminated through a quartz window by a 1000-W Xe arc lamp and the extent of reaction determined by periodically withdrawing samples for analysis by ion chromatography. The large peak due to persulfate caused some complications, but the extent of reaction could be monitored by following either the loss of the haloacetate or the formation of a product. In this way, the relative reactivities of the haloacetates was determined to be:

MCA > MFA > DCA > DFA > TCA > TFA.

TABLE I. Rate constants for some reactions of radicals with halogenated acids in water. Rate constants in units of L mol^{-1} s^{-1}.

	Acetate	MFA	DFA	TFA	MCA	DCA	TCA
NO$_3^-$[a]	2.3×10^6	2.2×10^6	2.1×10^5	3.9×10^3			
SO$_4^-$ ($\mu = 0$)	4.3×10^6[b]	$3.4 \pm 0.2 \times 10^6$	$8.7 \pm 0.1 \times 10^4$	$1.6 \pm 0.1 \times 10^4$	$4.5 \pm 0.2 \times 10^6$	$2.1 \pm 0.1 \times 10^6$	(2×10^6)
Cl$_2^-$ ($\mu = 0$)		$2.2 \pm 0.2 \times 10^5$	$< 10^4$	$< 10^4$	$6.5 \pm 0.1 \times 10^4$	$1.5 \pm 0.1 \times 10^3$	$\sim 4 \times 10^4$
OH	7.5×10^7[c]	1.2×10^8	1.1×10^7	$< 1 \times 10^6$	8.3×10^7	1.0×10^8	$(6 > 10^7)$

[a] See ref. [19].
[b] R. E. Huie and C. L. Clifton, *J. Phys. Chem.*, **94**, 8561 (1990).
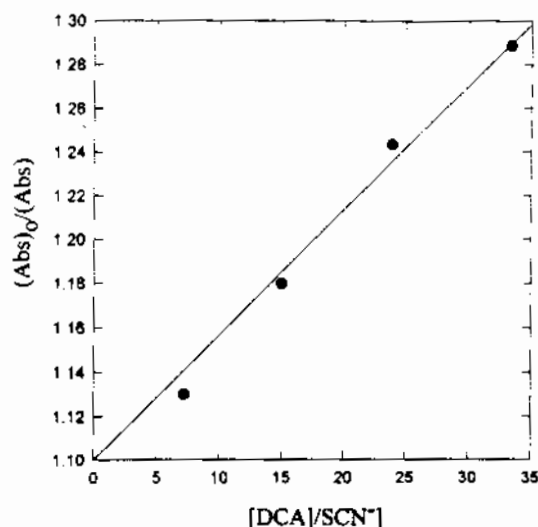[c] M. Chin and P. H. Wine, *Aquatic and Surface Photochemistry*, 85 (1994).

Figure 2. Competition-kinetic method for determining the rate constant for the reaction of ·OH with $CHCl_2COO^-$.

In the gamma-radiolysis experiments, a solution containing 0.3 mmol L^{-1} each of the chloroacetates and saturated with N_2O was irradiated at a dose rate of 4.1 Gy s^{-1}. Again, the reaction was monitored by withdrawing samples for analysis by ion chromatography (multiple columns in series were needed for a proper separation). The extent of reaction of each haloacetate is shown in Figure 3. Initially, DCA is removed more rapidly than MCA, in line with their relative reactivities toward ·OH; subsequently, MCA is removed more rapidly. This probably is due to competition by the product Cl^- for the ·OH, leading to the formation of Cl_2^-·, which reacts faster with

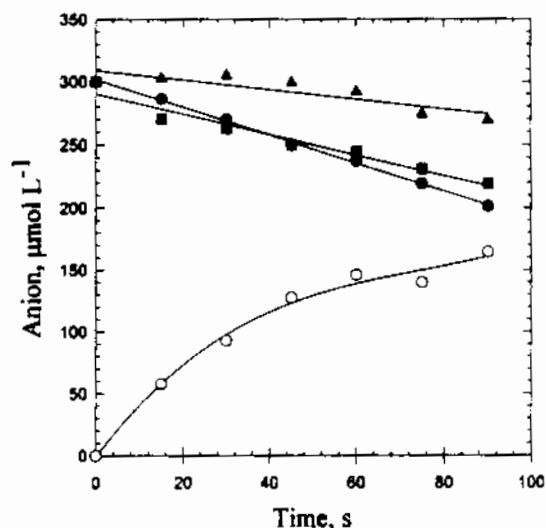
Figure 3. Gamma-radiolysis of an aqueous solution containing MCA (●), DCA (■), and TCA (▲). Dose rate = 4.1 Gy s^{-1} and pH = 6.0. Cl^- formed in the reactions is represented by (○).

MCA than DCA. TCA reacts very little in the initial period, but appears to be removed at long times. This may also reflect some loss of N_2O and subsequent competition of TCA for e_{aq}^-.

The initial rates of disappearance of MCA and DCA agree with their measured $\cdot OH$ rate constants. The relative rate of the TCA loss appears to be less than would be predicted from the rate constants in Table I. This suggests that reactive impurities make a substantial contribution to the measured OH rate constant for TCA and probably also for the reaction of $SO_4^- \cdot$ with TCA. For this reason, we consider the rate constants reported in Table I for the reactions of these radicals with TCA to be upper limits.

Discussion

There are few other data with which to compare the present results. Anbar et al. [15] found a value of 3×10^7 L mol^{-1} s^{-1} for the reaction of OH with MFA by a gamma-radiolysis technique, about four times less than our value. For the reaction of OH with MCA, Adams et al. [16] obtained 4.3×10^7 L mol^{-1} s^{-1} by pulse radiolysis and Yokohata et al. [17] obtained 4×10^8 L mol^{-1} s^{-1} by gamma radiolysis, as compared with our value of 8.3×10^7 L mol^{-1} s^{-1}. Wine et al. [18] have also measured rate constants for the reactions of $SO_4^- \cdot$ with the haloacetates by laser-flash photolysis. Our values for the rate constants for the fluoroacetates were all lower than those measured in that laboratory and our values for the chloroacetates were all higher. Finally, Exner et al. [19] have measured rate constants for the reactions of $NO_3 \cdot$ with the three fluoroacetates (Table I). This radical has about the same reduction potential as $SO_4^- \cdot$, but generally appears to react somewhat slower than that radical [20]. It is somewhat surprising, then, to see that DFA reacts faster with $NO_3 \cdot$ than $SO_4^- \cdot$. Also included in Table I are rate constants for the reactions of most of these radicals with the acetate ion.

For the reactions of $NO_3 \cdot$ and $SO_4^- \cdot$ with acetates, single halogenation makes little difference in the rate constant. Substitution of two fluorines leads to a substantial reduction in the rate constant, while two chlorines leads only to a small reduction in the rate constant for $SO_4^- \cdot$. For the reaction of $\cdot OH$ with acetate, substitution of a single halogen on the acetate leads to an increase in the rate constant; substitution of two chlorines continues this effect, but the substitution of two fluorines leads to a reduction in the rate constant. Substitution of three halogens reduces the rate constant considerably. These results for $\cdot OH$ probably indicate that hydrogen abstraction is probably the more important reaction pathway for this radical.

Acknowledgment

Bibliography

[1] E. C. Tuazon and R. A. Atkinson, *J. Atmos. Chem.*, **17**, 179 (1993).

[2] E. C. Tuazon and R. A. Atkinson, *J. Atmos. Chem.*, **16**, 301 (1993).

[3] E. O. Edney and D. J. Driscoll, *Water, Air, Soil Pollut.*, **66**, 97 (1993).

[4] H. Frank, H. Scholl, D. Renschen, B. Rether, A. Laouedj, and Y. Norokorpi, *Environ. Sci. & Pollut. Res.*, **1**, 1 (1993).

[5] V. Madhavan, H. Levanon, and P. Neta, *Radiat. Res.*, **76**, 15 (1978).

[6] P. Neta, R. E. Huie, and A. B. Ross, *J. Phys. Chem. Ref. Data*, **17**, 1027 (1988).

[7] G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Ref. Data*, **17**, 513 (1988).

[8] D. M. Stanbury, *Adv. Inorg. Chem.*, **33**, 69 (1989).

[9] R. E. Huie, C. L. Clifton, and P. Neta, *Radiat. Phys. Chem.*, **38**, 477 (1991).

[10] R. E. Huie, C. L. Clifton, and N. Alstein, *Radiat. Phys. Chem.*, **33**, 361 (1989).

[11] R. E. Huie and C. L. Clifton, *J. Phys. Chem.*, **94**, 8560 (1990).

[12] M. Chin and P. H. Wine, *J. Photochem. Photobiol. A: Chem.*, **69**, 17 (1992).

[13] The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

[14] The actual ionic strengths were, for the $SO_4^-\cdot$ reactions: $0.02-0.24$ (MFA), 0.5 (DFA), 0.5 (TFA), $0.02-0.25$ (MCA), $0.05-0.06$ (DCA), and $0.05-0.07$ (TCA), all in mol L^{-1}. For the $Cl_2^-\cdot$ reactions, the ionic strengths were $0.1-.03$ (MCA), $0.1-0.25$ (DCA), $0.1-0.36$ (TCA), $0.05-0.09$ (MFA), 0.5 (DFA), and 0.5 (TFA). The experiments with DFA, which was available only as the acid, involved neutralization with NaOH.

[15] M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc. Pt. B*, 742 (1966).

[16] G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, *Absolute Rate Constants for the Reaction of the Hydroxyl Radical with Organic Compounds*, in *Pulse Radiolysis*, M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Bisindole, Eds., Academic Press, New York, pp. 131–143, 1965.

[17] A. Yokohata, T. Ohmura, and S. A. Tsuda, *J. Phys. Chem.*, **73**, 4013 (1969).

[18] P. H. Wine, M. Nicovich, A. Nix, and D. LaGerda, private communication.

[19] M. Exner, H. Herrmann, J. Michel, and R. Zellner, *AFEAS Workshop Proceedings: Atmospheric Wet and Dry Deposition of Carbonyl and Haloacetyl Halides*, AFEAS, Washington, DC, p. 30, private communication.

[20] P. Neta and R. E. Huie, *J. Phys. Chem.*, **90**, 4644 (1986).