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Abstract

Rate coefficients for the reactions of hydroxyl radicals and chlorine atoms with methyl chlorodifluoroacetate and ethyl chlorodifluoroacetate have been determined at 298 K and atmospheric pressure. The decay of the organics was followed using a gas chromatograph with a flame ionization detector (GC-FID), and the rate constants were determined using a relative rate method with different references. Room temperature rate constants are found to be (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_1(\text{OH} + \text{CF}_2\text{ClC}(\text{O})\text{OCH}_3) = (1.1 \pm 0.3) \times 10^{-13}$, $k_2(\text{Cl} + \text{CF}_2\text{ClC}(\text{O})\text{OCH}_3) = (1.0 \pm 0.2) \times 10^{-13}$, $k_3(\text{OH} + \text{CF}_2\text{ClC}(\text{O})\text{OCH}_2\text{CH}_3) = (5.4 \pm 1.5) \times 10^{-13}$ and $k_4(\text{Cl} + \text{CF}_2\text{ClC}(\text{O})\text{OCH}_2\text{CH}_3) = (1.5 \pm 0.3) \times 10^{-12}$ with uncertainties representing $\pm 2\sigma$. This is the first kinetic study of the studied reactions under atmospheric pressure. Free-energy relationships are presented, and halogen substitution in the ester is discussed in terms of reactivity with OH radicals and Cl atoms. On the basis of our kinetic measurements, the tropospheric lifetimes of $\text{CF}_2\text{ClC}(\text{O})\text{OCH}_3$ and $\text{CF}_2\text{ClC}(\text{O})\text{OCH}_2\text{CH}_3$ are estimated to be around 53 and 11 days, respectively, primarily due to their reaction with hydroxyl radicals in the troposphere.

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1. Introduction

Chloroesters, which are important toxic environmental substances, are ubiquitous in the environment. They were found in atmospheric particulate matter [1], in the fog [2], and can be formed abiotically from humic material and soils in addition to their known biotic mode of formation [3]. Chlorinated fluoroesters (CFESs), like hydrofluorinated esters (FESs), could also be produced during the atmospheric oxidation of some hydrochlorofluoroethers (HCFEs) [4,5]. Consequently, it is necessary to understand the atmospheric chemistry of CFESs in order to evaluate the environmental acceptability of HCFEs. It has been suggested that in populous regions, atmospheric degradation of chlorinated solvents and CFC replacements are responsible for the presence of haloacetates in precipitation [6].

CFESs are likely dissolve in droplets and aerosols, hydrolyze, and undergo further oxidation in the liquid phase; its degradation may contribute to the environmental burden of chlorofluoroacetic acids and HF. These acids may be wet- or dry-deposited from the atmosphere to land surfaces, and hence possibly affect plant growth.

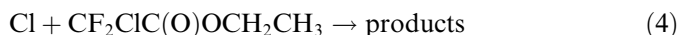
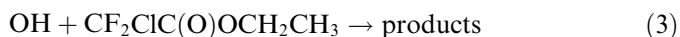
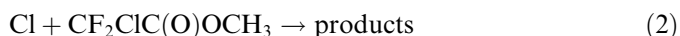
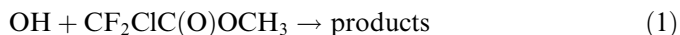
The atmospheric degradation of the saturated oxygenates is controlled mainly by chemical reaction with OH, contributing to tropospheric ozone production and the formation of other secondary photooxidants in polluted areas [7]. However, the reaction of chlorine atom with organic compounds is considered of potential relevance in the marine troposphere where significant chlorine atom concentration may be present [8–10]. Knowledge of the rate coefficients for the reactions with tropospheric oxidants like OH radicals and Cl atoms, as well as the degradation pathways are required to estimate the persistence, fate and harmful effects of chlorofluoroesters in the atmosphere.

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While there are many studies of OH radical and Cl atom reactions with a variety of oxygenated volatile organic compounds (OVOCs), only limited information is available for esters [7]. The database for haloesters is even scarcer [11], and there are virtually no chlorofluoroesters reactivity studies towards tropospheric oxidants like OH radicals or Cl atoms.

In this Letter, we report the rate coefficient data for the reactions of OH radicals and Cl atoms with methyl chlorodifluoroacetate ($\text{CF}_2\text{ClC}(\text{O})\text{OCH}_3$) and ethyl chlorodifluoroacetate ($\text{CF}_2\text{ClC}(\text{O})\text{OCH}_2\text{CH}_3$):



Experiments were conducted using the relative method with different reference compounds at room temperature and atmospheric pressure.

To the best of our knowledge, this work provides the first kinetic study for such reactions in atmospheric conditions. In addition, our Letter aims to better define the reactivity of the hydrochlorofluoroesters towards OH radicals and Cl atoms as an extension of previous work involving OH-initiated degradation of methacrylates and fluoroesters (FESs) [12,13]. In this sense, the results are discussed in terms of the halogen substituents effects on the reactivity of the esters studied and free-energy correlations are presented. Lifetimes of the hydrochlorofluoroesters studied in this work were calculated taking into account the experimental rate constants obtained.

2. Experimental

All experiments were performed in an 80-liter Tedlar or Teflon bag located in a wooden box with the internal walls covered with aluminum foil. Measured amounts of the organic reactants were flushed from calibrated bulbs into the bag through a stream of nitrogen or ultra pure air. The bag was then filled to its full capacity at atmospheric pressure with ultra pure air. Chlorine atoms were generated by photolysis at 360 nm of Cl_2 :



OH radicals were generated by UV irradiation at 254 nm of H_2O_2 :



Reaction mixtures consisting of a reference organic compound and the sample organic reactant, diluted in N_2 or pure air, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h. Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of zero grade N_2 or synthetic air, and the bag was then filled with the zero grade N_2 or synthetic air. Before each set of experiments, the bag was cleaned by filling it

with a mixture of O_2 and N_2 which was photolyzed for 15–25 min using 4 germicidal lamps (Philips 30 W) with a UV emission at 254 nm, to produce O_3 . After this procedure, the bag was cleaned again by repeated flushing with N_2 and checked before performing the experiments by gas chromatography that there were no observable impurities.

Periodically, gas samples were removed from the Tedlar bag using calibrated gas syringes. The organics were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak Q column (Alltech, 2.3 m) held from 140 to 200 °C for both esters.

In the presence of the oxidant X (Cl atom or OH radical), the CFES and the references decay through the following reactions:



Provided that the reference compound and the reactant are lost only by reactions (7) and (8), then it can be shown that:

$$\ln \left\{ \frac{[\text{CFES}]_0}{[\text{CFES}]_t} \right\} = \frac{k_7}{k_8} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (9)$$

where, $[\text{CFES}]_0$, $[\text{Reference}]_0$, $[\text{CFES}]_t$, and $[\text{Reference}]_t$ are the concentrations of the CFES and the reference compound at times $t = 0$ and t , respectively, and k_7 and k_8 are the rate constants of reactions (7) and (8), respectively.

The relative rate technique relies on the assumption that both the CFES and the reference organics are removed solely by reaction with the oxidant species X (Cl or OH). To verify this assumption, mixtures of chlorine or hydrogen peroxide and air with both organics were prepared and allowed to stand in the dark for two hours. In all cases, the reaction of the organic species with the precursor of X (Cl_2 or H_2O_2), in the absence of UV or visible light, was of negligible importance over the typical time periods used in this work. Additionally, to test for possible photolysis of the reactants used, mixtures of the CFESs in nitrogen or air, in the absence of molecular chlorine or hydrogen peroxide, were irradiated using the output of all the black or germicidal lamps surrounding the chamber for 30 min. No photolysis of any of the reactants was observed.

The initial concentrations used in the experiments were in the range of 176–228 ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) for the chlorofluoroacetates, and 191–261 ppm for chloromethane, ethane, propane, dichloromethane, 1,2-dichloroethane and acetone used as reference compounds. The concentration of Cl_2 ranged from 140 to 220 ppm in around 750 Torr of either N_2 or synthetic air.

3. Materials

The chemicals N_2 (AGA, 99.999%), methyl chlorodifluoroacetate (Aldrich, 99%), ethyl chlorodifluoroacetate

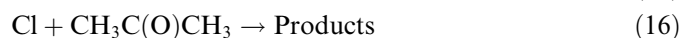
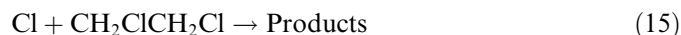
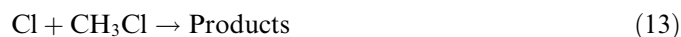
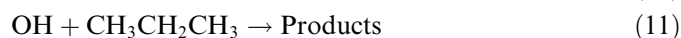
(Aldrich, 99%), chloromethane (Aldrich 99.5%), ethane (AGA, 99.99%), *n*-propane (Aldrich, 98%), dichloromethane (J.T. Baker, 99.5%), 1,2-dichloroethane (E.Merck, 99%), acetone (Ciccarelli, 99.5%) and H₂O₂ (Ciccarelli, 60% wt). CFES and reference compounds were degassed by repeated freeze-pump-thaw cycling. Chlorine, Cl₂, was prepared in our laboratory using the reaction between HCl and KMnO₄ and was purified by repeated trap to trap distillation until a sample of 99% purity was obtained, confirmed by IR and UV spectroscopy.

4. Results and discussion

By using this technique, the rate constants for the four reactions studied were obtained from Eq. (9). The data were fitted to a straight line by the linear least-squares procedure.

The losses of methyl chlorodifluoroacetate and ethyl chlorodifluoroacetate by OH radicals and Cl atoms are shown with different references in Figs. 1–4. For each organic reactant studied, several runs were performed for the rate constant determination; however, for the sake of clarity, only one example is presented in Figs. 1–4.

The following compounds were used as reference reactions to determine the rate coefficient of reactions (1)–(4):



where $k_{10} = (2.59 \pm 0.39) \times 10^{-13}$ [14], $k_{11} = (1.1 \pm 0.2) \times 10^{-12}$ [15], $k_{12} = (4.2 \pm 0.5) \times 10^{-14}$ [14], $k_{13} = (5.12 \pm 1.02) \times 10^{-13}$ [16], $k_{14} = (3.67 \pm 0.73) \times 10^{-13}$ [16],

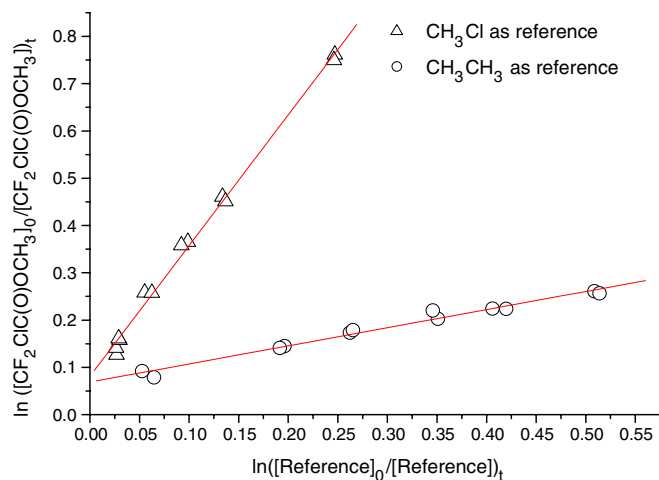


Fig. 1. Relative rate data for the OH reaction with methyl chlorodifluoroacetate using chloromethane and ethane as reference compounds at 298 K and atmospheric pressure of air.

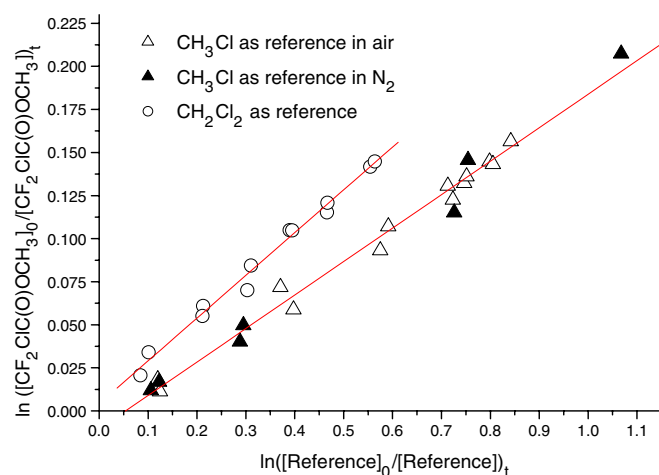


Fig. 2. Relative rate data for the Cl reaction with methyl chlorodifluoroacetate using chloromethane and dichloromethane as reference compounds at 298 K and atmospheric pressure of air or N₂.

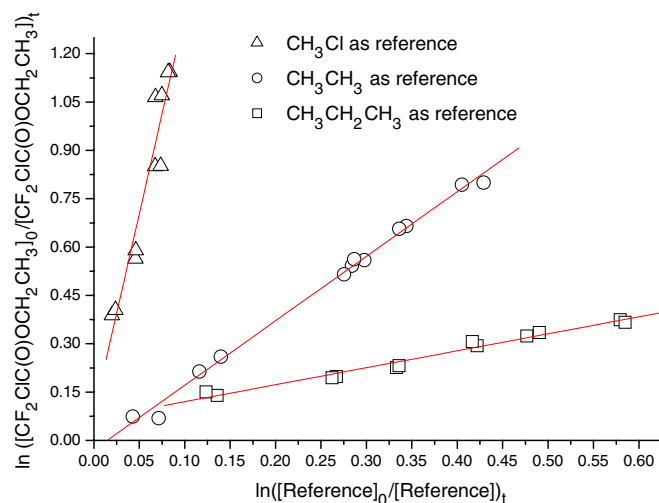


Fig. 3. Relative rate data for the OH reaction with ethyl chlorodifluoroacetate using chloromethane, ethane and propane as reference compounds at 298 K and atmospheric pressure of air.

$k_{15} = (1.3 \pm 0.2) \times 10^{-12}$ [17] and $k_{16} = (2.37 \pm 0.12) \times 10^{-12}$ [18]. All the k values are in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The data on relative rate constants $k_{\text{CFES}}/k_{\text{Reference}}$ and absolute rate constants k_{CFES} at room temperature (298 K) are presented in Table 1. The ratios were obtained from the average of several experiments using different initial concentrations of the reactants. It is gratifying to note the agreement between the experiments conducted with different reference compounds. The rate constants obtained by averaging the values from different experiments were the following:

$$k_1 = (1.1 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (1.0 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (5.4 \pm 1.5) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_4 = (1.5 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

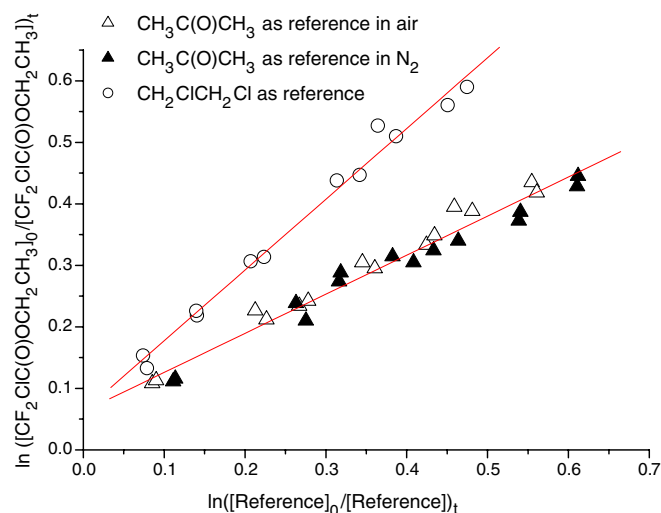


Fig. 4. Relative rate data for the Cl reaction with ethyl chlorodifluoroacetate using acetone and 1,2-dichloroethane as reference compounds at 298 K and atmospheric pressure of air or N₂.

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, to which we have considered also the corresponding error on the reference rate constants (10)–(16).

To the best of our knowledge, there are no other prior reported values of the rate constants for the reactions (1)–(4) of OH radicals and Cl atoms with methyl chlorodifluoroacetate and ethyl chlorodifluoroacetate. Thus, the present study is the first kinetic study of these reactions and therefore no direct comparison with the literature can be made.

Table 1

Reactant concentrations, slopes $k_{\text{CFES}}/k_{\text{ref}}$ and rate constants obtained for the reaction of methyl chlorodifluoroacetate and ethyl chlorodifluoroacetate with OH radicals and Cl atoms at (298 ± 2) K

CFES	[CFES] ₀ (ppm)	Reference	[Ref] ₀ (ppm)	Bath Gas	$k_{\text{CFES}}/k_{\text{reference}}$	k_{CFES} (cm ³ molecule ⁻¹ s ⁻¹)
CF ₂ ClC(O)OCH ₃ + OH	204	CH ₃ Cl	214	Air	2.78 ± 0.11	$(1.17 \pm 0.27) \times 10^{-13}$
	215	CH ₃ Cl	215	Air	2.77 ± 0.06	$(1.16 \pm 0.21) \times 10^{-13}$
	207	CH ₃ CH ₃	238	Air	0.40 ± 0.02	$(1.04 \pm 0.18) \times 10^{-13}$
	213	CH ₃ CH ₃	261	Air	0.38 ± 0.02	$(0.98 \pm 0.17) \times 10^{-13}$
		Average				$(1.1 \pm 0.3) \times 10^{-13}$
CF ₂ ClC(O)OCH ₃ + Cl	221	CH ₃ Cl	257	Air	0.20 ± 0.01	$(1.02 \pm 0.21) \times 10^{-13}$
	228	CH ₃ Cl	234	Air	0.19 ± 0.01	$(0.97 \pm 0.20) \times 10^{-13}$
	196	CH ₂ Cl ₂	194	Air	0.25 ± 0.01	$(0.92 \pm 0.19) \times 10^{-13}$
	205	CH ₂ Cl ₂	191	N ₂	0.30 ± 0.02	$(1.10 \pm 0.24) \times 10^{-13}$
		Average				$(1.0 \pm 0.2) \times 10^{-13}$
CF ₂ ClC(O)OCH ₂ CH ₃ + OH	206	CH ₃ Cl	193	Air	12.64 ± 0.17	$(5.31 \pm 1.53) \times 10^{-13}$
	225	CH ₃ Cl	213	Air	12.36 ± 0.13	$(5.19 \pm 1.29) \times 10^{-13}$
	186	CH ₃ CH ₃	188	Air	1.92 ± 0.06	$(4.97 \pm 1.05) \times 10^{-13}$
	214	CH ₃ CH ₃	211	Air	2.00 ± 0.05	$(5.18 \pm 1.04) \times 10^{-13}$
	213	CH ₃ CH ₂ CH ₃	192	Air	0.51 ± 0.02	$(5.61 \pm 1.13) \times 10^{-13}$
	188	CH ₃ CH ₂ CH ₃	208	Air	0.53 ± 0.02	$(5.83 \pm 1.18) \times 10^{-13}$
		Average				$(5.4 \pm 1.5) \times 10^{-13}$
CF ₂ ClC(O)OCH ₂ CH ₃ + Cl	204	CH ₃ COCH ₃	202	Air	0.62 ± 0.03	$(1.14 \pm 0.12) \times 10^{-12}$
	217	CH ₃ COCH ₃	199	N ₂	0.67 ± 0.02	$(1.59 \pm 0.11) \times 10^{-12}$
	217	CH ₂ ClCH ₂ Cl	220	Air	1.09 ± 0.02	$(1.42 \pm 0.25) \times 10^{-12}$
	176	CH ₂ ClCH ₂ Cl	198	Air	1.15 ± 0.04	$(1.50 \pm 0.29) \times 10^{-12}$
		Average				$(1.5 \pm 0.3) \times 10^{-12}$

Table 2 lists the rate coefficients of the reactions of OH radicals with both CFESs studied in this work and other fluoroesters, FESs, from previous work, and the corresponding fully hydrogenated esters obtained from the literature [19]. From this table, it is possible to note that an increase in the substitution of H atoms by F atoms in esters overcomes the activating effect of the ester function in reactions with the OH radical leading to a reduction of the rate constants. Table 2 shows that the higher the number of the hydrogen atoms in FES the greater the reaction rates with OH result: $k_{\text{CH}_3\text{COOCH}_2\text{CH}_3} > k_{\text{CH}_3\text{COOCH}_3} > k_{\text{CF}_2\text{HCOOCH}_3} > k_{\text{CF}_3\text{COOCH}_3}$ and $k_{\text{CF}_2\text{ClCOOCH}_2\text{CH}_3} > k_{\text{CF}_2\text{HCOOCH}_3} > k_{\text{CF}_2\text{ClCOOCH}_3}$. The reactivity of ethyl chlorofluoroacetate is around 5 times higher than that for methyl chlorofluoroacetate towards OH radicals. A similar tendency can be observed for the reactions of OH radicals with ethyl acetate and methyl acetate.

Table 2

Comparison of the rate constant values for the reaction of OH radicals with chlorofluoroacetates, hydrofluoroesters (HFEs) and fully hydrogenated esters at 298 K

Ester	$k_{\text{OH}}(298 \text{ K})$ (cm ³ molecule ⁻¹ s ⁻¹)
CF ₂ ClCOOCH ₃	1.1×10^{-13a}
CF ₂ ClCOOCH ₂ CH ₃	5.4×10^{-13a}
CF ₃ COOCH ₃	5.0×10^{-14b}
CF ₃ COOCH ₂ CH ₃	2.6×10^{-13b}
CF ₂ HCOOCH ₃	1.5×10^{-13b}
CH ₃ COOCH ₃	3.7×10^{-13b}
CH ₃ COOCH ₂ CH ₃	1.8×10^{-12b}

^a This work.

^b Ref. [14].

Table 3
Estimated tropospheric lifetimes of the chlorofluoroacetates studied in this work with OH radicals and Cl atoms

mechanism. Kutsuna et al. [22] have suggested that dissolution in clouds serves only a minor atmospheric sink for $\text{CF}_3\text{COOCH}_3$, although its dissolution in ocean water could be significant. The volatility of these compounds will render dry deposition and unlikely removal mechanism.

In conclusion, the atmospheric lifetime is determined by the OH-initiated oxidation for both chlorofluoroacetates studied, as observed in Table 3. These species survive long enough to become well dispersed from the source origin in which regional scale transport is likely. Urban emissions of these compounds are, therefore, unlikely to contribute to local ozone and photooxidant formation.

The relative short lifetimes of the CFESs studied by OH-initiated oxidation will hinder the entrance and transport of these esters to the stratosphere, making a minor or negligible contribution to the ozone depletion through ClOx catalytic cycles. Likewise, the ODPs of these compounds will be relatively smaller compared with other CFCs or HCFCs.

Finally, product studies on esters and fluorinated esters have shown that the oxidation of FESs leads mainly to the formation of the fluorinated acetic acid and the corresponding anhydrides, as well as CF_2O and its hydrolysis products, CO_2 and HF [7,20], which will be removed primarily by heterogeneous processes. Acids and anhydrides, especially those with lower molecular weight, are highly soluble compounds and may be rapidly incorporated into cloud droplets (where hydration of the anhydrides leads to acids) and rained out, contributing to the precipitation acidity.

Since the kinetics and the product distribution data are considerably scarce, further experiments should be done in order to elucidate the atmospheric degradation mechanism of these chlorofluorinated esters (CFESs) which contributes to evaluating the environmental burden of chlorinated and fluorinated acids, especially haloacetic acids and their derivatives, and to including more realistic kinetic and mechanistic information in atmospheric models.

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