# A Kinetic Study of the Reaction of Chlorine and Fluorine Atoms with $CF_3CHO$ at 295 ± 2 K

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## Abstract

Using a relative rate technique the reactions of chlorine and fluorine atoms with CF<sub>3</sub>CHO have been determined to proceed with rate constants of  $(1.8 \pm 0.4) \times 10^{-12}$  and  $(2.7 \pm 0.1) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. Experiments were performed at 295 ± 2 K and 700 torr total pressure of nitrogen. The results are discussed with respect to the design and interpretation of laboratory studies of the atmospheric chemistry of CFC replacements. © 1993 John Wiley & Sons, Inc.

## Introduction

Concerns regarding the environmental impact of chlorofluorocarbon (CFC) release into the atmosphere have led to an international effort to remove CFCs from industrial processes and consumer products. For example, the Ford Motor Company will not use any CFCs in its worldwide manufacturing processes beyond 1993. Hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) are two classes of potential CFC substitutes. In light of the future widespread use of HFCs and HCFCs, detailed information on the atmospheric chemistry, and hence environmental impact, of these compounds is needed.

In laboratory studies of the atmospheric chemistry of HFCs and HCFCs, chlorine or fluorine atom initiation provides a convenient surrogate for the OH radical initiation that occurs in the atmosphere. In the design and interpretation of such experiments it is desirable to have accurate kinetic data regarding the reactions of the halogen atoms with the HFC, or HCFC, of interest and the likely photooxidation products. With this information, significant secondary consumption of the primary oxidation products can be avoided, or corrected for. While recent studies in our laboratory [1,2] and elsewhere [3,4] have provided a substantial database for the kinetics of the reactions of Cl and F atoms with HFCs and HCFCs, there is little available information concerning the kinetics of the reactions of Cl and F atoms with likely photooxidation products.  $CF_3CHO$  is a likely oxidation product of CF<sub>3</sub>CH<sub>3</sub> (HFC-143) and CF<sub>3</sub>CH<sub>2</sub>Cl (HCFC-133). We have used a relative rate technique to measure the kinetics of the reaction of Cl and F atoms with CF<sub>3</sub>CHO. Experiments were performed at 295  $\pm$  2 K in the presence of 700 torr of N<sub>2</sub> diluent. Results are reported herein.

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#### Experimental

The apparatus and experimental techniques employed in this work have been described previously [5–7] and are only briefly discussed here. The apparatus consists of a Mattson Instruments Inc. Sirius 100 FT-IR spectrometer interfaced to a 140-liter, 2-meter long evacuable pyrex chamber (S/V = 0.14 cm<sup>-1</sup>). The pyrex chamber was surrounded by UV fluorescent lamps (GTE F40BLB) which were used to generate halogen atoms by the photolysis of molecular halogen.

(1) 
$$\operatorname{Cl}_2(\operatorname{or} F_2) + h\nu \longrightarrow 2\operatorname{Cl}(\operatorname{or} 2F)$$

White-type multiple reflection optics were mounted in the reaction chamber to provide a total path length of 26.6 m for the IR analysis beam. The spectrometer was operated at a resolution of  $0.25 \text{ cm}^{-1}$ .

Reaction mixtures consisting of  $CF_3CHO$ , a reference compound, and molecular halogen, were admitted to the reaction chamber in N<sub>2</sub> diluent. In the presence of atomic chlorine (or fluorine)  $CF_3CHO$  and the reference decay via reactions (2) and (3)

(2) 
$$Cl (or F) + CF_3CHO \longrightarrow products$$

$$(3) Cl + reference \longrightarrow products$$

Provided that  $CF_3CHO$  and the reference are lost solely by reactions (2) and (3) and that neither is reformed in any process, it can be shown that

$$\operatorname{Ln}\left\{\frac{[\operatorname{CF}_{3}\operatorname{CHO}]_{t}}{[\operatorname{CF}_{3}\operatorname{CHO}]_{t_{0}}}\right\} = \frac{k_{2}}{k_{3}} \operatorname{Ln}\left\{\frac{[\operatorname{reference}]_{t}}{[\operatorname{reference}]_{t_{0}}}\right\}$$

where  $[CF_3CHO]_{t_0}$  and  $[reference]_{t_0}$ , and  $[CF_3CHO]_t$  and  $[reference]_t$  are the concentrations of  $CF_3CHO$  and the reference compound at times  $t_0$  and t, respectively, and  $k_2$  and  $k_3$  are the rate constants of reactions (2) and (3), respectively.

The decay of CF<sub>3</sub>CHO and the reference were measured using their characteristic absorptions in the infrared over the following wavelength ranges (in cm<sup>-1</sup>); CF<sub>3</sub>CHO, 1000–1300; CH<sub>4</sub>, 1200–1400; CD<sub>4</sub>, 950–1050; CH<sub>3</sub>Cl, 700–800; and C<sub>2</sub>H<sub>5</sub>Cl, 900–1400. Initial concentrations of the gas mixtures were 5–8 mtorr of CF<sub>3</sub>CHO, 15–60 mtorr of the reference organic, and 107–207 mtorr of molecular halogen. CF<sub>3</sub>CHO was synthesized by the dropwise addition of trifluoroacetaldehyde methyl hemiacetal to a H<sub>2</sub>SO<sub>4</sub>/P<sub>2</sub>O<sub>5</sub> slurry and was kindly supplied by Joe Francisco of Wayne State University. IR analysis revealed no observable impurities in the CF<sub>3</sub>CHO sample. All other reagents were purchased from commercial vendors at purities of >99% and used without further purification. Experiments were performed at room temperature, 295 ± 2 K, and 700 torr total pressure.

#### Results

The relative rate technique relies on the assumption that both  $CF_3CHO$ and the reference compound are removed solely by reaction with halogen atoms. To verify this assumption, mixtures of the halogen (either chlorine or fluorine) with CF<sub>3</sub>CHO and each of the references used were prepared and allowed to stand in the dark. In all cases, the reaction of the organic species

allowed to stand in the dark. In all cases, the reaction of the organic species with molecular halogen, in the absence of ultraviolet light, was of negligible importance (< 2%) over the typical time periods used in this work. To test for possible photolysis, mixtures of CF<sub>3</sub>CHO and the reference compounds were prepared and irradiated for 2 min in the absence of added halogen. No photolysis (< 2%) of any compound was observed.

Figures 1 and 2 show plots of  $\ln([CF_3CHO]_{t_0}/[CF_3CHO]_t)$  vs.  $\ln([reference]_{t_0}/[reference]_t)$  for experiments involving Cl atoms and F atoms conducted in N<sub>2</sub> diluent. All plots are linear with intercepts at the origin suggesting the absence of complications due to secondary chemistry. For each reactant organic studied, at least two separate gas mixtures were prepared and irradiated to check the experimental reproducibility; in all cases indistinguishable results were obtained from successive experiments. Variation of the [molecular halogen]/[reference] concentration ratio by a factor of 2 had no observable effect on our results. Rate constant ratios, obtained from linear least squares analysis of the data shown in Figures 1 and 2, were  $k(Cl + CF_3CHO)/k_4 = 3.34 \pm 0.30$ ,  $k(Cl + CF_3CHO)/k_5 = 0.236 \pm 0.035$ ,  $k(F + CF_3CHO)/k_6 = 0.388 \pm 0.012$ , and  $k(F + CF_3CHO)/k_7 = 0.531 \pm 0.018$ . Quoted errors are 2 standard deviations.

$$(4) Cl + CH_3Cl \longrightarrow products$$

(5) 
$$Cl + C_2H_5Cl \longrightarrow products$$

(6) 
$$F + CH_4 \longrightarrow products$$

(7) 
$$\mathbf{F} + \mathbf{CD}_4 \longrightarrow \mathbf{products}$$

Literature values (units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) of  $k_4 = 4.9 \times 10^{-13}$  [8],  $k_5 = 8.0 \times 10^{-12}$  [9],  $k_6 = 6.8 \times 10^{-11}$  (average of data from refs. [10-14] see ref. [2] for more discussion), and  $k_7 = 5.0 \times 10^{-11}$  [15] can be used to place our measured rate constant ratios on an absolute basis. Hence, we derive values of  $k(Cl + CF_3CHO) = (1.64 \pm 0.15) \times 10^{-12}$  and  $(1.90 \pm 0.28) \times 10^{-12}$ , and  $k(F + CF_3CHO)$ , and  $= (2.64 \pm 0.08) \times 10^{-11}$ and  $(2.66 \pm 0.09) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The measured reactivities of Cl and F atoms towards  $CF_3CHO$  derived using two different references were consistent. This consistency suggests that only one reactive species in responsible for the loss of CF<sub>3</sub>CHO and the reference compound; namely the halogen atom. Also, the consistency of results obtained using different reference compounds suggests the absence of significant systematic errors associated with the values of the reference rate constants used. We choose to quote rate constants for the reactions of Cl and F atoms with  $CF_3CHO$  which are averages of the two determinations with error limits which encompass the extremes of the two determinations. Hence,  $k(Cl + CF_3CHO) = (1.8 \pm 0.4) \times 10^{-12}$  and  $k(F + CF_3CHO) =$  $(2.7 \pm 0.1) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Errors quoted thus far reflect statistical uncertainty. In addition, we estimate that there could potentially be an additional 20% systematic uncertainty associated with the values of the reference rate constants used.



Figure 1. Plot of the decay of  $CF_3CHO$  vs. those of  $CH_3Cl$  (•) and  $C_2H_5Cl$  ( $\blacktriangle$ ) in the presence of Cl atoms. Experiments were performed at 295 ± 2 K in 700 torr of  $N_2$  diluent.



Figure 2. Plot of the decay of CF<sub>3</sub>CHO vs. those of CH<sub>4</sub> ( $\bullet$ ) and CD<sub>4</sub> ( $\bullet$ ) in the presence of F atoms. Experiments were performed at 295  $\pm$  2 K in 700 torr of N<sub>2</sub> diluent.

CF<sub>3</sub>CHO is approximately 40 times less reactive than CH<sub>3</sub>CHO [16] towards Cl atom attack. This trend is consistent with the observation that Cl atom attack of HC(O)F [17] is more than 4 orders of magnitude slower than on HCHO [8]. These trends can be rationalized in simple terms by the destabilization of the carbon centered radical products by the inductive effects of the CF<sub>3</sub>- and F<sub>-</sub> groups. A similar trend is observed with F atom reactions. CH<sub>3</sub>CHO [18] is 5 times more reactive than CF<sub>3</sub>CHO, and HCHO [19] is 25 times more reactive than HC(O)F [20].

The motivation for the present study is to assess the feasibility of detecting CF<sub>3</sub>CHO product following Cl or F atom initiated oxidation of HFCs or HCFCs. The reactivity of CF<sub>3</sub>CHO towards Cl atoms measured in the present work is 2–4 orders of magnitude higher than the typical reactivities of HFCs and HCFCs [1,3]. For example, Cl atoms react with CF<sub>3</sub>CH<sub>3</sub> (HFC-143) and CF<sub>3</sub>CH<sub>2</sub>Cl (HCFC-133) with rate constants of  $2.5 \times 10^{-17}$  [21] and  $5.9 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [22]. These reactions are then factors of 72000 and 305 slower than reaction of Cl with CF<sub>3</sub>CHO. Consequentially, in experiments using Cl atom initiated oxidation of HFCs, or HCFCs, the detection of any CF<sub>3</sub>CHO product will be virtually impossible.

The reaction of F atoms with  $CF_3CHO$  is approximately a factor of 10 faster than reaction of F atoms with typical HFCs and HCFCs [2]. Therefore, to detect  $CF_3CHO$  as an oxidation product of HFCs and HCFCs, it is desirable to use F atom initiated oxidation.

# **Note Added in Press**

Scollard et al. [23] have recently used a relative rate technique to measure the ratio  $k(Cl + CF_3CHO)/k(Cl + CH_3COCH_3)$  and derive  $k(Cl + CH_3COCH_3)$  $CF_3CHO) = (2.7 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This result is 50% larger than measured in the present work. There are three possible explanations for this discrepancy. First, regeneration of CF<sub>3</sub>CHO or the reference compounds in either study. Second, the loss of  $CF_3CHO$  or the reference compounds in either study. Third, errors in the absolute values of the reference rate constants used. With regard to the first possibility, it is difficult to imagine any processes that would generate  $CF_3CHO$ , or the reference compounds ( $CH_3COCH_3$ ,  $CH_3Cl$ , and  $C_2H_5Cl$ ). With regard to the third possibility, the value of  $k(Cl + CH_3COCH_3)$ used by Scollard et al. [23] was taken from the study of Wallington et al. [7] in which the reactivity of  $CH_3COCH_3$  was measured relative to that of C<sub>2</sub>H<sub>5</sub>Cl. As part of the present work, additional experiments were performed to check the reactivity of Cl atoms towards  $CH_3COCH_3$ . A value of  $k(\text{Cl} + \text{CH}_3\text{COCH}_3)/k(\text{Cl} + \text{C}_2\text{H}_5\text{Cl}) = 0.27 \pm 0.02$  was derived, which is in excellent agreement with the published value of  $0.295 \pm 0.015$ [7]. With regard to the second possible explanation, it is of interest to note that CF<sub>3</sub>OH is a major product of the Cl atom initiated oxidation of CF<sub>3</sub>CHO [24,25]. CF<sub>3</sub>OH is formed from the reaction of CF<sub>3</sub>O radicals with  $CF_3CHO$ . In both relative rate investigations  $N_2$  was used as the diluent and so, in principal, there should be no formation of  $CF_3O_2$  and,

hence, CF<sub>3</sub>O radicals. However, the presence of trace amounts of O<sub>2</sub> is unavoidable in both systems (especially in the Teflon chamber system used by Scollard et al.). To investigate the possible role of CF<sub>3</sub>O radicals in the present work, additional experiments were performed in which the initial concentration ratios [CF<sub>3</sub>CHO]/[CH<sub>3</sub>Cl] and [CF<sub>3</sub>CHO]/[C<sub>2</sub>H<sub>5</sub>Cl] were varied over a factor of 25; there was no observable effect on the measured kinetics. Additionally, IR features of CF<sub>3</sub>OH were searched in our product spectra with no success. It seems reasonable to conclude that the present work is free from complications caused by the formation of CF<sub>3</sub>O radicals.

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