Atmospheric chemistry of \( \text{CF}_3\text{CF} = \text{CH}_2 \): Kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and O\(_3\)

O.J. Nielsen \(^{a,*}\), M.S. Javadi \(^{a}\), M.P. Sulbaek Andersen \(^{a}\), M.D. Hurley \(^{b}\), T.J. Wallington \(^{b,*}\), R. Singh \(^{c}\)

\(^{a}\) Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

\(^{b}\) Physical and Environmental Sciences Department, Ford Motor Company, Mail Drop SRL-3083, Dearborn, MI 48121, USA

\(^{c}\) Honeywell International Inc., 101 Columbia Road, Morristown, NJ 07962, USA

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Abstract

Long path length FTIR-smog chamber techniques were used to determine \( k(\text{Cl} + \text{CF}_3\text{CF} = \text{CH}_2) = (7.03 \pm 0.59) \times 10^{-11}\), \( k(\text{OH} + \text{CF}_3\text{CF} = \text{CH}_2) = (1.05 \pm 0.17) \times 10^{-12}\), and \( k(O_3 + \text{CF}_3\text{CF} = \text{CH}_2) = (2.77 \pm 0.21) \times 10^{-21}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1} \) in \( 700\text{ Torr of N}_2\), \( N_2/O_2\), or air diluent at \( 296\text{ K} \). \( \text{CF}_3\text{CF} = \text{CH}_2 \) has an atmospheric lifetime of approximately 11 days and a global warming potential (100 yr time horizon) of four. \( \text{CF}_3\text{CF} = \text{CH}_2 \) has a negligible global warming potential and will not make any significant contribution to radiative forcing of climate change.

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1. Introduction

Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere [1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. Unsaturated fluorinated hydrocarbons are a class of compounds which have been developed to replace CFCs and saturated hydrofluorocarbons in air conditioning units. Prior to their large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact, of these compounds is needed. To address this need the atmospheric chemistry of \( \text{CF}_3\text{CF} = \text{CH}_2 \) was investigated. Smog chamber/FTIR techniques were used to determine the following properties for this compound: (i) kinetics of its reaction with chlorine atoms, (ii) kinetics of its reaction with hydroxyl radicals, (iii) kinetics of its reaction with ozone and (iv) atmospheric implications. Results are reported herein.

2. Experimental

Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer [3]. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

\[
\text{Cl}_2 + hv \rightarrow \text{Cl} + \text{Cl}
\]

OH radicals were produced by photolysis of \( \text{CH}_3\text{ONO} \) in the presence of \( NO \) in air.

\[
\text{CH}_3\text{ONO} + hv \rightarrow \text{CH}_3\text{O} + \text{NO}
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO}
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]

In the relative rate experiments the following reactions take place.
Cl + Reactant → products (5)
Cl + Reference → products (6)
OH + Reactant → products (7)
OH + Reference → products (8)

It can be shown that

\[ \ln \left( \frac{[\text{Reactant}]_0}{[\text{Reactant}]_t} \right) = k_{\text{Reactant}} \ln \left( \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right) \]

where \([\text{Reactant}]_0\), \([\text{Reactant}]_t\), \([\text{Reference}]_0\), and \([\text{Reference}]_t\) are the concentrations of reactant and reference at times \(t_0\) and \(t\), and \(k_{\text{Reactant}}\) and \(k_{\text{Reference}}\) are the rate constants for the reactant and the reference. Plots of \(\ln([\text{Reactant}]_0/\text{[Reactant]})\) vs. \(\ln([\text{Reference}]_0/\text{[Reference]})\) should be linear, pass through the origin, and have a slope of \(k_{\text{Reactant}}/k_{\text{Reference}}\). The kinetics of the \(\text{O}_3\) reaction were studied using an absolute rate method in which the pseudo first-order loss of \(\text{CF}_3\text{CF}=\text{CH}_2\) was measured in the presence of excess \(\text{O}_3\).

\(\text{O}_3\) was produced from \(\text{O}_2\) via silent electrical discharge using a commercial \(\text{O}_3\) ozonizer. \(\text{CH}_3\text{ONO}\) was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of \(\text{NaNO}_2\) in methanol. Other reagents were obtained from commercial sources. Experiments were conducted in 700 Torr total pressure of \(\text{N}_2\), or \(\text{N}_2/\text{O}_2\) diluent. A linear least squares fit (unweighted, not forced through the origin) to the data in Fig. 1 gives \(k_{10}/k_{11} = 0.76 \pm 0.04\) and \(k_{10}/k_{12} = 1.38 \pm 0.06\).

Using \(k_{11} = (9.29 \pm 0.51) \times 10^{-11}\) [4] and \(k_{12} = (5.07 \pm 0.34) \times 10^{-11}\) [4] (700 Torr, 295 K) gives \(k_{10} = (7.06 \pm 0.54) \times 10^{-11}\) and \((7.00 \pm 0.56) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). The reaction of \(\text{Cl}\) atoms with propene proceeds via electrophilic addition to the \(>\text{C}<\) double bond. The presence of electron withdrawing fluorine substituents is expected to lead to decreased reactivity with \(\text{Cl}\) atoms. Consistent with expectations, the reactivity of \(\text{CF}_3\text{CF}=\text{CH}_2\) reported here lies between those of \(\text{CF}_3\text{CH}=\text{CH}_2\) and \(\text{CF}_3\text{CF}=\text{CF}_2\) reported previously.

3. Results and discussion

3.1. Kinetics of the Cl + CF\(_3\)CF=CH\(_2\) reaction

The rate of reaction (10) was measured relative to reactions (11) and (12):

\[ \text{Cl} + \text{CF}_3\text{CF}=\text{CH}_2 \rightarrow \text{products} \] (10)
\[ \text{Cl} + \text{C}_2\text{H}_4 \rightarrow \text{products} \] (11)
\[ \text{Cl} + \text{C}_2\text{H}_2 \rightarrow \text{products} \] (12)

Reaction mixtures consisted of 19.1–26.2 mTorr of \(\text{CF}_3\text{CF}=\text{CH}_2\), 104–133 mTorr \(\text{Cl}_2\), and either 4.33–30.2 mTorr \(\text{C}_2\text{H}_4\), or 2.35–8.5 mTorr \(\text{C}_2\text{H}_2\), in 700 Torr of air, or \(\text{N}_2\), diluent. The observed loss of \(\text{CF}_3\text{CF}=\text{CH}_2\) vs. those of the reference compounds is plotted in Fig. 1. As seen from Fig. 1, there was no discernable difference between the results obtained in \(\text{N}_2\), or air, diluent. A linear least squares fit (unweighted, not forced through the origin) to the data in Fig. 1 gives \(k_{10}/k_{11} = 0.76 \pm 0.04\) and \(k_{10}/k_{12} = 1.38 \pm 0.06\).

Using \(k_{11} = (9.29 \pm 0.51) \times 10^{-11}\) [4] and \(k_{12} = (5.07 \pm 0.34) \times 10^{-11}\) [4] (700 Torr, 295 K) gives \(k_{10} = (7.06 \pm 0.54) \times 10^{-11}\) and \((7.00 \pm 0.56) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). While there have been no previous studies of \(k_{10}\), we can compare our result with \(k(\text{Cl} + \text{CH}_3\text{CH}=\text{CH}_2) = 2.4 \times 10^{-10}\) [5], \(k(\text{Cl} + \text{CF}_3\text{CH}=\text{CH}_2) = (9.07 \pm 1.08) \times 10^{-11}\) [6], \(k(\text{Cl} + \text{C}_2\text{F}_5\text{CH}=\text{CH}_2) = (8.9 \pm 1.0) \times 10^{-11}\) [7], \(k(\text{Cl} + \text{C}_6\text{F}_{13}\text{CH}=\text{CH}_2) = (9.1 \pm 1.0) \times 10^{-11}\) [7], and \(k(\text{Cl} + \text{CF}_3\text{CF}=\text{CF}_2) = (2.7 \pm 0.3) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) [8]. The reaction of \(\text{Cl}\) atoms with propene proceeds via electrophilic addition to the \(>\text{C}<\) double bond. The presence of electron withdrawing fluorine substituents is expected to lead to decreased reactivity with \(\text{Cl}\) atoms. Consistent with expectations, the reactivity of \(\text{CF}_3\text{CF}=\text{CH}_2\) reported here lies between those of \(\text{CF}_3\text{CH}=\text{CH}_2\) and \(\text{CF}_3\text{CF}=\text{CF}_2\) reported previously.

3.2. Kinetics of the OH + CF\(_3\)CF=CH\(_2\) reaction

The rate of reaction (13) was measured relative to reactions (14) and (15):

\[ \text{OH} + \text{CF}_3\text{CF}=\text{CH}_2 \rightarrow \text{products} \] (13)
\[ \text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{products} \] (14)
\[ \text{OH} + \text{C}_2\text{H}_2 \rightarrow \text{products} \] (15)

Initial reaction mixtures consisted of 17.6–18.1 mTorr of \(\text{CF}_3\text{CF}=\text{CH}_2\), 110–200 mTorr \(\text{CH}_3\text{ONO}\), and 3.38 mTorr
C2H4 or 3.09 mTorr C2H2 in 700 Torr total pressure of air diluent. Fig. 2 shows the loss of CF3CF=CH2 plotted versus loss of the reference compounds. Linear least squares analysis gives \( k_{13}/k_{14} = 0.125 \pm 0.007 \) and \( k_{13}/k_{15} = 1.21 \pm 0.09 \).

Using \( k_{14} = (8.52 \pm 1.28) \times 10^{-12} \) \([9]\) (atmospheric pressure, 298 K) and \( k_{15} = (8.45 \pm 0.85) \times 10^{-13} \) \([10]\) gives \( k_{13} = (1.07 \pm 0.17) \times 10^{-12} \) and \( (1.02 \pm 0.13) \times 10^{-12} \) cm3 molecule\(^{-1}\) s\(^{-1}\). Indistinguishable values of \( k_{13} \) are obtained using the two different references. We choose to cite a final value which is the average of the individual determinations together with error limits which encompass the extremes of the determinations, hence \( k_{13} = (1.05 \pm 0.17) \times 10^{-12} \) cm3 molecule\(^{-1}\) s\(^{-1}\).

It is of interest to compare our result with the reactivity of propene and fluorinated propenes reported in the literature. The reaction of OH radicals with propene proceeds via electrophilic addition to the \( >C=\text{C}< \) double bond with a rate constant of \( 2.6 \times 10^{-11} \) cm3 molecule\(^{-1}\) s\(^{-1}\) in one atmosphere of air at 298 K \([9]\). Measurements of \( k(\text{OH} + \text{CF3CH}=\text{CH2}) \) by Orkin et al. \([11]\) and Sulbaek Andersen et al. \([6]\) are in good agreement, taking an average from the two studies gives \( k(\text{OH} + \text{CF3CH}=\text{CH2}) = 1.45 \times 10^{-12} \) cm3 molecule\(^{-1}\) s\(^{-1}\). McIlroy and Tully \([12]\), Dubey et al. \([13]\), Orkin et al. \([11]\), and Mashino et al. \([8]\) studied the reaction of OH radicals with CF3CF=CF2. The results at ambient temperature from the four studies were in good agreement; the average from the studies is \( k(\text{OH} + \text{CF3CH}=\text{CH2}) = 2.4 \times 10^{-12} \) cm3 molecule\(^{-1}\) s\(^{-1}\). In contrast to Cl atoms, the reactivity of OH radicals with CH3CH=CH2, CF3CH=CH2, CF3CF=CH2, and CF2CF=CF2 does not follow the trend expected assuming a simple electrophilic addition mechanism. Specifically, the reactivity of CF3CF=CF2 appears to be anomalously high. A computational study of the reaction of OH radicals with CF3CF=CF2 would be of interest to shed further light on the mechanism of these reactions.

### 3.3. Absolute Rate Study of \( k(\text{O}_3 + \text{CF}_3\text{CF}=\text{CH}_2) \)

The kinetics of reaction \( (16) \) were studied by observing the decay of CF3CF=CH2 when exposed to ozone in the reaction chamber. Reaction mixtures consisted of 14–28 mTorr CF3CF=CH2, 30–46 mTorr cyclohexane, and 180–1890 mTorr O3 in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of CF3CF=CH2 via reaction with OH radicals formed in reaction \( (16) \). Variation of the [cyclohexane] /[CF3CF=CH2] ratio over the range 1–3 had no discernable effect on the observed decay of CF3CF=CH2 suggesting that loss via reaction with OH radicals is not a significant complication. The loss of CF3CF=CH2 followed pseudo first-order kinetics in all experiments (see insert in Fig. 3).

Fig. 3 shows a plot of the pseudo first-order loss of CF3CF=CH2 vs. O3 concentration. The line through the data gives \( k_{16} = (2.77 \pm 0.21) \times 10^{-21} \) cm3 molecule\(^{-1}\) s\(^{-1}\).

\[
\text{CF}_3\text{CF}=\text{CH}_2 + \text{O}_3 \rightarrow \text{products} \\
\text{(16)}
\]

It is of interest to compare this result with the reported reactivity of ozone towards other fluoroalkenes and alkenes. The reported rate constants for reactions of O3 with propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and 1-decene are indistinguishable and are approximately \( 1.0 \times 10^{-17} \) cm3 molecule\(^{-1}\) s\(^{-1}\) \([9]\). The rate constants for reactions of O3 with CF3CF=CF2 and CF3CH=CH2 are \( (6.2 \pm 1.5) \times 10^{-22} \) \([14]\) and

![Graph](image_url)
The reactivity of fluorinated propenes towards ozone follows the trend expected (\(\text{CH}_2\text{CH}==\text{CH}_2 > \text{CF}_3\text{CH}==\text{CH}_2 > \text{CF}_2\text{CF}==\text{CH}_2 > \text{CF}_3\text{CF}==\text{CF}_2\)) for reaction proceeding via electrophilic addition of ozone to the \(\text{C}==\text{C}==\) double bond. In its reaction with \(\text{O}_3\), \(\text{CF}_3\text{CF}==\text{CH}_2\) is less reactive than its non-fluorinated counterpart by a factor of 3600. When compared to Cl atoms and OH radicals, \(\text{O}_3\) has the lowest reactivity and hence its rate of reaction with the compounds considered above is most sensitive to the presence of the electron withdrawing fluorine substituents. Finally, it is worth noting that while reactions of \(\text{O}_3\), Cl, and OH proceed via electrophilic addition to the \(\text{C}==\text{C}==\) double bond there are differences in mechanism with Cl adding across the double bond and Cl atoms and OH radicals adding to one of the carbon atoms.

4. Atmospheric lifetime and global warming potential

\(\text{CF}_3\text{CF}==\text{CH}_2\) will not undergo photolysis [11] and is not expected to be removed effectively by either wet or dry deposition. Cl atoms are not present in the atmosphere in sufficient quantity to impact the lifetime of \(\text{CF}_3\text{CF}==\text{CH}_2\). Reaction with OH and \(\text{O}_3\) are expected to be loss mechanisms for \(\text{CF}_3\text{CF}==\text{CH}_2\). The value of \(k(\text{OH} + \text{CF}_3\text{CF}==\text{CH}_2)\) measured in the present work can be used to provide an estimate of the atmospheric lifetime of \(\text{CF}_3\text{CF}==\text{CH}_2\). Using a global weighted-average OH concentration of \(1.0 \times 10^6\) molecules cm\(^{-3}\) [15] leads to an estimated lifetime of \(\text{CF}_3\text{CF}==\text{CH}_2\) with respect to reaction with OH radicals of 11 days. In a similar fashion our value of \(k(\text{O}_3 + \text{CF}_3\text{CF}==\text{CH}_2)\) can be combined with the global background \(\text{O}_3\) concentration of approximately 35 ppb [16] to provide an estimated lifetime with respect to reaction with ozone of 13 years. We conclude that the atmospheric lifetime of \(\text{CF}_3\text{CF}==\text{CH}_2\) is determined by its reaction with OH and is approximately 11 days. The approximate nature of this lifetime estimate should be stressed; the average daily concentration of OH radicals varies significantly with both location and season [17]. The quoted lifetime is a global average, the local lifetimes could be significantly shorter or longer.

The IR spectrum of \(\text{CF}_3\text{CF}==\text{CH}_2\) measured in the present work is shown in Fig. 4. \(\text{CF}_3\text{CF}==\text{CH}_2\) has an integrated IR absorption cross section (800–2000 cm\(^{-1}\)) of \((1.63 \pm 0.09) \times 10^{-16}\) cm molecule\(^{-1}\). The quoted uncertainty (±5%) is comprised of the following components: sample concentration (±2%), path length (±1.5%), residual baseline offset after subtraction of the background (±0.5%), and spectrometer accuracy (±1%) [18]. There are no literature IR data for \(\text{CF}_3\text{CF}==\text{CH}_2\) to compare with our result.

Using the method outlined by Pinnock et al. [18], the IR spectrum of \(\text{CF}_3\text{CF}==\text{CH}_2\) shown in Fig. 4, and the IR spectrum of \(\text{CFC-11}\) [19] we calculate instantaneous forcings for \(\text{CF}_3\text{CF}==\text{CH}_2\) and \(\text{CFC-11}\) of 0.22 and 0.26 W m\(^{-2}\) ppb\(^{-1}\), respectively. Values of the halocarbon global warming potential, HGWP [20], for \(\text{CF}_3\text{CF}==\text{CH}_2\) (relative to \(\text{CFC-11}\)) can then be estimated using the expression:

\[
\text{HGWP}_{\text{CF}_3\text{CF}==\text{CH}_2} = \left( \frac{\text{IF}_{\text{CF}_3\text{CF}==\text{CH}_2}}{\text{IF}_{\text{CFC-11}}} \right) \left( \frac{\tau_{\text{CF}_3\text{CF}==\text{CH}_2} \cdot M_{\text{CFC-11}}}{\tau_{\text{CFC-11}} \cdot M_{\text{CF}_3\text{CF}==\text{CH}_2}} \right) \left( 1 - \frac{1 - \exp(-t/\tau_{\text{CF}_3\text{CF}==\text{CH}_2})}{1 - \exp(-t/\tau_{\text{CFC-11}})} \right)
\]

where \(\text{IF}_{\text{CF}_3\text{CF}==\text{CH}_2}\), \(\tau_{\text{CF}_3\text{CF}==\text{CH}_2}\), \(M_{\text{CF}_3\text{CF}==\text{CH}_2}\), and \(\tau_{\text{CFC-11}}\) are the instantaneous forcings, molecular weights, and atmospheric lifetimes of \(\text{CF}_3\text{CF}==\text{CH}_2\) and \(\text{CFC-11}\), and \(t\) is the time horizon over which the forcing is integrated. Using \(\tau(\text{CF}_3\text{CF}==\text{CH}_2) = 11\) days and \(\tau_{\text{CFC-11}} = 45\) years [21] we estimate that the HGWP of \(\text{CF}_3\text{CF}==\text{CH}_2\) relative to \(\text{CFC-11}\) is \(1.9 \times 10^{-3}\) for a 20 yr horizon and \(7.6 \times 10^{-4}\) for a 100 yr time horizon, respectively. Relative to \(\text{CO}_2\), the GWP of \(\text{CFC-11}\) on 20 and 100 yr time horizons are 6300 and 4600 [21]. Hence, relative to \(\text{CO}_2\), the GWP of \(\text{CF}_3\text{CF}==\text{CH}_2\) is approximately 12 for a 20 yr horizon and 4 for a 100 yr time horizon, respectively. \(\text{CF}_3\text{CF}==\text{CH}_2\) has a negligible global warming potential and will not make any significant contribution to radiative forcing of climate change.

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References