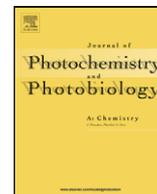




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Atmospheric chemistry of *trans*-CF₃CH=CHCl: Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O₃

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ABSTRACT

Long path length Fourier transform infrared (FTIR)–smog chamber techniques were used to study the kinetics of the gas-phase reactions of Cl atoms, OH radicals and O₃ with *trans*-3,3,3-trifluoro-1-chloropropene, *t*-CF₃CH=CHCl, in 700 Torr total pressure at 295 ± 2 K. Values of $k(\text{Cl} + t\text{-CF}_3\text{CH}=\text{CHCl}) = (5.22 \pm 0.72) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{OH} + t\text{-CF}_3\text{CH}=\text{CHCl}) = (4.40 \pm 0.38) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + t\text{-CF}_3\text{CH}=\text{CHCl}) = (1.46 \pm 0.12) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, were established (quoted uncertainties are 2σ; see *Experimental* section). The IR spectrum of *t*-CF₃CH=CHCl is reported. The atmospheric lifetime of *t*-CF₃CH=CHCl is determined by reaction with OH radicals and is approximately 26 days. The global warming potential of *t*-CF₃CH=CHCl is approximately 7 for a 100-year time horizon.

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1. Introduction

Recognition of the adverse environmental consequences of the release of chlorofluorocarbons (CFCs) into the atmosphere [1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. While safeguarding the ozone layer has been at the center of these efforts, concerns related to *global climate change* are becoming an increasingly important consideration in the choice of alternative compounds because of their significant atmospheric lifetime and radiative properties.

Saturated hydrofluorocarbons (HFCs), such as CH₂FCF₃ (HFC-134a), have become widely used CFC replacements. HFCs do not contain chlorine and therefore do not contribute to chlorine-based catalytic destruction of stratospheric ozone [3]. Unsaturated hydrochlorofluorocarbons are a class of compounds which has been developed as potential replacements for CFCs and saturated HFCs in air conditioning units. Prior to any 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 *t*-CF₃CH=CHCl was investigated. The kinetics of the gas-phase reaction of Cl atoms and ozone with *t*-CF₃CH=CHCl were determined at Ford Motor Company (Ford) and at University of Copenhagen (Copenhagen) using smog cham-

ber/Fourier transform infrared (FTIR) techniques. The IR spectrum of the title compound and the kinetics of its gas-phase reaction with OH radicals were measured at Ford. Results are reported herein.

2. Experimental

Detailed descriptions of the experimental procedures can be found elsewhere [4]. Therefore, only brief descriptions are given in the subsections below. Chlorine atoms were produced by photolysis of molecular chlorine:



OH radicals were produced by photolysis of CH₃ONO in the presence of NO in air:



In relative rate experiments the following reactions take place:



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It can be shown that

$$\ln \left(\frac{[\text{Reactant}]_{t_0}}{[\text{Reactant}]_t} \right) = \frac{k_{\text{Reactant}}}{k_{\text{Reference}}} \ln \left(\frac{[\text{Reference}]_{t_0}}{[\text{Reference}]_t} \right) \quad (1)$$

where $[\text{Reactant}]_{t_0}$, $[\text{Reactant}]_t$, $[\text{Reference}]_{t_0}$, and $[\text{Reference}]_t$ are the concentrations of reactant and reference at times t_0 and t , and k_{Reactant} and $k_{\text{Reference}}$ are the rate constants for the reactant and the reference. Plots of $\ln([\text{Reactant}]_{t_0}/[\text{Reactant}]_t)$ versus $\ln([\text{Reference}]_{t_0}/[\text{Reference}]_t)$ should be linear, pass through the origin, and have a slope of $k_{\text{Reactant}}/k_{\text{Reference}}$. The kinetics of the O_3 reaction were studied using an absolute rate method, in which the pseudo first order loss of Reactant was measured in the presence of excess O_3 . A linear plot of the pseudo-first-order rate constants versus the initial O_3 concentration gives a slope of k_9 :



In smog chamber experiments it is important to check for unwanted loss of reactants and products via photolysis, dark chemistry and heterogeneous reactions. Control experiments were performed at Ford and Copenhagen, in which mixtures of reactants (except Cl_2 or CH_3ONO) in air were subjected to UV irradiation for 15 min and reactant/product mixtures obtained after the UV irradiation were allowed to stand in the dark in the chamber for 30 min. There was no observable loss of reactants or reference compounds suggesting that photolysis, dark chemistry and heterogeneous reactions are not a significant complication in the present work.

Unless otherwise stated, quoted uncertainties are two standard deviations from the least squares regressions (forced through zero), together with our estimated uncertainties ($\pm 1\%$ of the initial concentration) associated with the IR spectral analysis of the relative reactant and reference concentrations.

2.1. FTIR-smog chamber system at Ford

Experiments were performed in a 140-l Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. CH_3ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of NaNO_2 in methanol. O_3 was produced from O_2 via silent electrical discharge using a commercial O_3 ozonizer. Samples of $t\text{-CF}_3\text{CH}=\text{CHCl}$ were supplied by Honeywell International Inc. at purities $>99.9\%$. All other reagents were obtained from commercial sources at purities $>99\%$.

Relative rate and absolute rate experimental methods were used as described above. Experiments were conducted in 700 Torr total pressure of air/ N_2 diluent at 295 ± 2 K. The loss of $t\text{-CF}_3\text{CH}=\text{CHCl}$ and reference compounds was monitored by FTIR spectroscopy using a calibrated analytical path length of 27.1 m and a spectral resolution of 0.25 cm^{-1} . A liquid nitrogen cooled midband MCT detector was used in this study. Infrared spectra were derived from 32 coadded interferograms. Reactant and reference compounds were monitored using absorption features over the following wavenumber ranges (cm^{-1}): C_2H_2 , 650–800; C_2H_4 , 900–1000; O_3 , 980–1070; $t\text{-CF}_3\text{CH}=\text{CHCl}$, 669, 847, 935, 1311, and 1648.

2.2. FTIR-smog chamber system at University of Copenhagen

The Copenhagen experiments were performed in a 100-l quartz reactor equipped with a Bruker IFS 66V FTIR spectrometer. The experimental setup was equipped with a temperature control system that kept the temperature steady at 293 ± 0.5 K. An InSb detector was chosen for this study. Chlorine atoms were produced by photolysis of Cl_2 according to reaction (1), using UVA

lamps (Osram Eversun L100/79) with the main emissions peak at 368 nm. Ozone was produced using a commercially available ozone generator from O_3 -Technology. The ozone was preconcentrated using a silica gel trap, reducing the amount of O_2 introduced into the chamber. Samples of $t\text{-CF}_3\text{CH}=\text{CHCl}$ were supplied by Honeywell International Inc. at purities $>99.9\%$. All other reagents were obtained from commercial sources at purities $>99\%$.

Relative rate and absolute rate experimental methods were used as described above. The Cl atom relative rate experiments were conducted in 700 Torr total pressure of N_2 diluent. Ozone kinetics experiments were conducted in 700 Torr total pressure of air diluent. The White-type optical system propagating the IR beam through the reaction chamber had a path length of 86 m. Spectra were obtained at a resolution of 0.115 cm^{-1} and were derived from 64 coadded interferograms. Reactant and reference compounds were monitored using absorption over the following wavenumber ranges (cm^{-1}): C_2H_2 , 3175–3375; C_2H_4 , 2940–3040; O_3 , 2950–3065; $t\text{-CF}_3\text{CH}=\text{CHCl}$, 3060–3130. FTIR spectra were analyzed using a linear least squares fitting procedure developed by Griffith [5]. Reference spectra of O_3 and HCl were taken from the HITRAN database [6], and used to improve the spectral fitting for the larger molecules. For the other components, reference spectra were recorded using the same conditions (700 Torr, 293 ± 0.5 K) employed in the kinetics experiments.

3. Results and discussion

3.1. Relative rate study of $k(\text{Cl} + t\text{-CF}_3\text{CH}=\text{CHCl})$ at Ford and Copenhagen

The kinetics of reaction (10) were measured relative to those of reactions (11) and (12):



Initial reaction mixtures employed at Ford consisted of 2.80–3.82 mTorr of $t\text{-CF}_3\text{CH}=\text{CHCl}$, 100–102 mTorr Cl_2 , and either 10.0–19.8 mTorr C_2H_4 , or 7.20–10.6 mTorr C_2H_2 , in 700 Torr of air diluent. Reaction mixtures employed at Copenhagen consisted of 5.6–47.8 mTorr of $t\text{-CF}_3\text{CH}=\text{CHCl}$, 100–200 mTorr Cl_2 , and either 4.1–7.1 mTorr of C_2H_4 or 3.1–5.0 mTorr of C_2H_2 , in 700 Torr of N_2 diluent. The observed loss of $t\text{-CF}_3\text{CH}=\text{CHCl}$ versus those of the reference compounds is plotted in Fig. 1. Linear least squares analysis of the data in Fig. 1 gives the results shown in Table 1. The measured rate constant ratios were placed on an absolute scale using $k_{11} = 9.29 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [7] and $k_{12} = 5.07 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [7]. The values for k_{10} obtained using different experimental setups at Ford Motor Company and University of Copenhagen were, within the experimental uncertainties, indistinguishable. We derive a final value for k_{10} , which is the average of the determinations with error limits which encompass the extremes of the determinations, of $k_{10} = (5.22 \pm 0.72) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

While there have been no previous studies of k_9 , we can compare our result with data for the reactions of chlorine atoms with propene and other halogen substituted propenes, presented in Table 2 [8–13]. The reaction of chlorine atoms with propene proceeds primarily via electrophilic addition to the >C=C< double bond. Substitution of the electron donating CH_3 group by the electron withdrawing CF_3 group would be expected to lower the reactivity of chlorine atoms towards the substituted propene. While the reactivities of $t\text{-CF}_3\text{CH}=\text{CHCl}$, $t\text{-CF}_3\text{CH}=\text{CHF}$, $E\text{-CF}_3\text{CF}=\text{CHF}$ and $Z\text{-CF}_3\text{CF}=\text{CHF}$, are all comparable and/or within the error limits of the

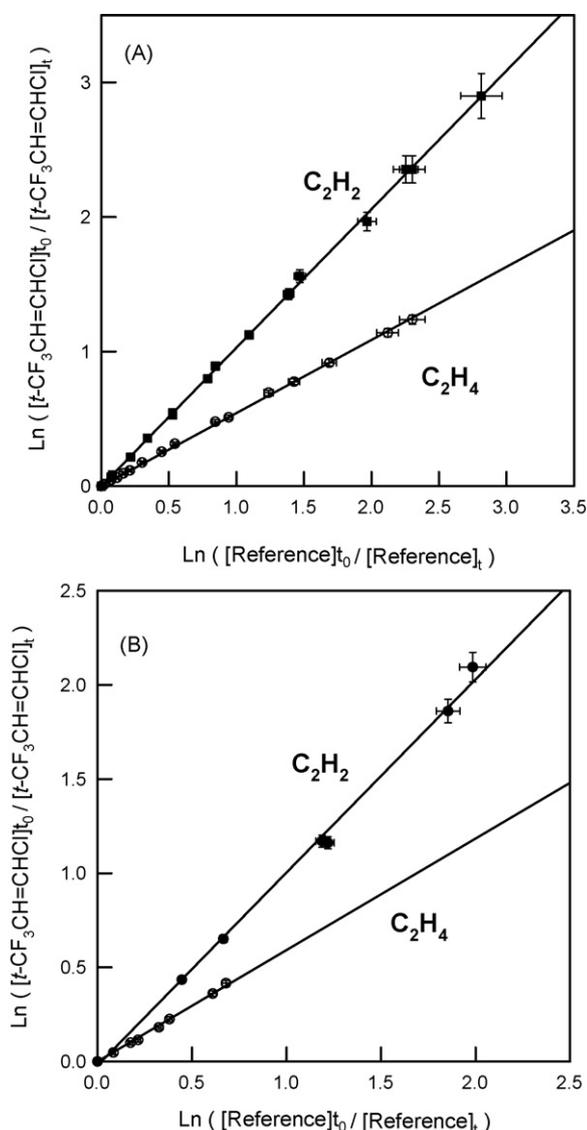


Fig. 1. Kinetic data for reactions of Cl atoms with $t\text{-CF}_3\text{CH}=\text{CHCl}$ measured at 295 ± 2 K in 700 Torr of air (Ford, A) and in 700 Torr of N_2 (Copenhagen, B). The error bars reflect uncertainty ($\pm 1\%$ of the initial concentration) in the determination of the reactant concentrations.

individual determinations, inspection of Table 2 reveals a general trend of decreased reactivity with increasing number and electron withdrawing strength of the halogen substituents.

3.2. Relative rate study of $k(\text{OH} + t\text{-CF}_3\text{CH}=\text{CHCl})$ at Ford

The kinetics of reaction (13) were measured relative to reactions (14) and (15):



Table 1
Results of the Cl atom relative rate experiments

Setup	Reference	$k_{\text{CF}_3\text{CH}=\text{CHCl}}/k_{\text{Reference}}$	$k_{\text{Reference}} (\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$k_{\text{Cl}+t\text{-CF}_3\text{CH}=\text{CHCl}} (\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
Ford (air)	C_2H_4	0.55 ± 0.04	9.29 [7]	(5.11 ± 0.37)
Ford (air)	C_2H_2	1.03 ± 0.06	5.07 [7]	(5.22 ± 0.30)
Copenhagen (N_2)	C_2H_4	0.59 ± 0.05	9.29 [7]	(5.48 ± 0.46)
Copenhagen (N_2)	C_2H_2	1.00 ± 0.09	5.07 [7]	(5.07 ± 0.46)

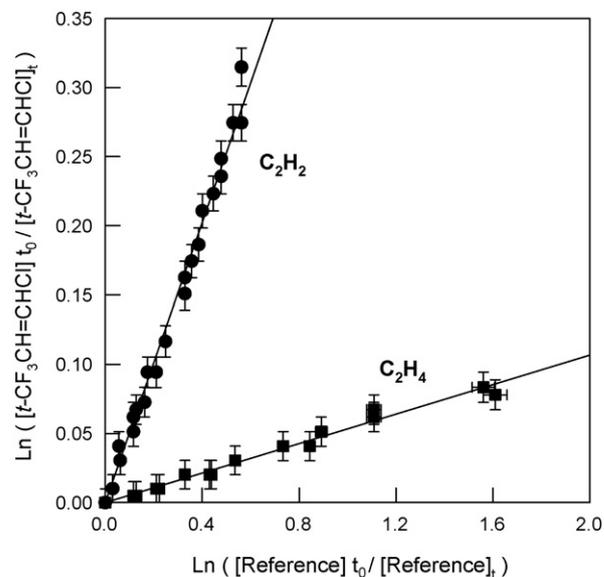


Fig. 2. Decay of $t\text{-CF}_3\text{CH}=\text{CHCl}$ vs. C_2H_2 (circles) and C_2H_4 (squares) in the presence of OH radicals in 700 Torr of air at 295 ± 2 K. The error bars reflect uncertainty ($\pm 1\%$ of the initial concentration) in the determination of the reactant concentrations.



Initial reaction mixtures consisted of 27.9–32.8 mTorr of $t\text{-CF}_3\text{CH}=\text{CHCl}$, 100–330 mTorr CH_3ONO , and 2.35–7.65 mTorr C_2H_4 or 1.47–2.74 mTorr C_2H_2 , and 0–25.4 mTorr NO. Fig. 2 shows the loss of $t\text{-CF}_3\text{CH}=\text{CHCl}$ plotted versus loss of the reference compounds. Linear least squares analysis gives $k_{13}/k_{14} = 0.053 \pm 0.003$ and $k_{13}/k_{15} = 0.506 \pm 0.031$. Using $k_{14} = 8.52 \times 10^{-12}$ [14] (atmospheric pressure, 298 K) and $k_{15} = 8.45 \times 10^{-13}$ [15] gives $k_{13} = (4.52 \pm 0.26) \times 10^{-13}$ and $(4.28 \pm 0.26) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Indistinguishable values of k_{13} were obtained using the two different references. The fact that consistent values of k_{13} were derived from experiments using different reference compounds suggests the absence of significant systematic errors in the present work. We choose to cite a final value which is the average of the individual determinations with error limits which encompass the extremes of the determinations, yielding $k_{13} = (4.40 \pm 0.38) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. No result has been reported for k_{13} previously.

Kinetic data for the reactions of hydroxyl radicals with propene and fluorinated propenes are presented in Table 2 [8–13,16–20]. Based on the structural similarity, one might expect the reactivity of $t\text{-CF}_3\text{CH}=\text{CHCl}$ towards OH radicals to be comparable to that of $t\text{-CF}_3\text{CH}=\text{CHF}$. Interestingly, the reactivity of $t\text{-CF}_3\text{CH}=\text{CHCl}$ is substantially lower (roughly a factor of 2). As with chlorine atoms, the reaction with hydroxyl radicals proceeds mainly via electrophilic addition to the >C=C< double bond [14]. Hence, the reactivity towards OH radicals is expected to decrease with the introduction of electron withdrawing substituents such as CF_3 -groups, chlorine and fluorine. Inspection of Table 2 reveals that the reactivity of OH radicals towards propene is greater than the fluorinated propenes and that there is a general trend toward lower

Table 2

Rate constants ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) for reactions of Cl, OH, and O_3 with $t\text{-CF}_3\text{CH}=\text{CHCl}$ and analogous halogenated propenes measured at $295 \pm 3 \text{ K}$ (where multiple determinations exist, the value given is the average of the determinations with error limits that encompass the extremes of the individual determinations)

Compound	k_{Cl}	k_{OH}	k_{O_3}
$\text{CF}_3\text{CF}=\text{CF}_2$	$(2.7 \pm 0.3) \times 10^{-11}$ [11]	$(2.3 \pm 0.7) \times 10^{-12}$ [11,16–19]	$(6.2 \pm 1.5) \times 10^{-22}$ [21]
$Z\text{-CF}_3\text{CF}=\text{CHF}$	$(4.36 \pm 0.48) \times 10^{-11}$ [12]	$(1.26 \pm 0.20) \times 10^{-12}$ [12,20]	$(1.45 \pm 0.15) \times 10^{-21}$ [12]
$E\text{-CF}_3\text{CF}=\text{CHF}$	$(5.00 \pm 0.56) \times 10^{-11}$ [12]	$(2.15 \pm 0.23) \times 10^{-12}$ [12]	$(1.98 \pm 0.15) \times 10^{-20}$ [12]
$t\text{-CF}_3\text{CH}=\text{CHF}$	$(4.64 \pm 0.59) \times 10^{-11}$ [13]	$(9.25 \pm 1.72) \times 10^{-13}$ [13]	$(2.81 \pm 0.21) \times 10^{-21}$ [13]
$t\text{-CF}_3\text{CH}=\text{CHCl}^a$	$(5.22 \pm 0.72) \times 10^{-11}$ ^a	$(4.40 \pm 0.38) \times 10^{-13}$ ^a	$(1.46 \pm 0.12) \times 10^{-21}$ ^a
$\text{CF}_3\text{CF}=\text{CH}_2$	$(7.03 \pm 0.59) \times 10^{-11}$ [10]	$(1.10 \pm 0.22) \times 10^{-12}$ [10,17,20]	$(2.77 \pm 0.21) \times 10^{-20}$ [10]
$\text{CF}_3\text{CH}=\text{CH}_2$	$(9.07 \pm 1.08) \times 10^{-11}$ [8]	$(1.45 \pm 0.33) \times 10^{-12}$ [8,17]	$(3.5 \pm 0.3) \times 10^{-19}$ [8]
$\text{CH}_3\text{CH}=\text{CH}_2$	$(2.7 \pm 0.7) \times 10^{-10}$ [9]	$(2.9 \pm 0.3) \times 10^{-11}$ [9]	$(1.0 \pm 0.1) \times 10^{-17}$ [9]

^a Determined in this work.

reactivity with increasing fluorination. However, in contrast to this general trend, perfluoropropene is significantly *more* reactive than the less fluorinated propenes. Furthermore, in contrast to a simple trend of decreasing reactivity with increasingly electron withdrawing substituents, as noted above, $\text{CF}_3\text{CH}=\text{CHF}$ is *more* reactive than $\text{CF}_3\text{CH}=\text{CHCl}$. It has recently been suggested that hydrogen bonding between OH and fluorine could lead to the observed enhancement of the reactivity of OH radicals towards the highly fluorinated propenes [13]. Computational work would be useful to investigate this suggestion.

3.3. Absolute rate study of $k(\text{O}_3 + t\text{-CF}_3\text{CH}=\text{CHCl})$ at Ford and Copenhagen

The kinetics of reaction (16) were studied by observing the decay of $t\text{-CF}_3\text{CH}=\text{CHCl}$ when exposed to O_3 in excess in the reaction chambers at Ford and Copenhagen:



An OH radical scavenger (cyclohexane) was added to the reaction mixtures to avoid potential problems associated with the loss of $t\text{-CF}_3\text{CH}=\text{CHCl}$ via reaction with OH radicals formed in reaction (16) [14]. Initial concentrations of reactants at Copenhagen were 6.9–14.2 mTorr $t\text{-CF}_3\text{CH}=\text{CHCl}$, 15.6–20.3 mTorr cyclohexane, and 3.42–4.36 Torr O_3 in 700 Torr of air diluent. Initial concentrations of reactants at Ford were 5.9–6.3 mTorr $t\text{-CF}_3\text{CH}=\text{CHCl}$, 14.0–30.6 mTorr cyclohexane, and 414–2070 mTorr O_3 in 700 Torr of air diluent. Variation of the [cyclohexane]/[$t\text{-CF}_3\text{CH}=\text{CHCl}$] ratio over the range 2.2–5.2 had no discernable effect on the observed decay of $t\text{-CF}_3\text{CH}=\text{CHCl}$ suggesting that loss via reaction with OH radicals is not a significant complication. The loss of $t\text{-CF}_3\text{CH}=\text{CHCl}$ followed pseudo first-order kinetics in all experiments (see insert in Fig. 3).

A plot of the pseudo first-order decay of $t\text{-CF}_3\text{CH}=\text{CHCl}$ versus O_3 concentration is shown in Fig. 3. A linear least squares fit to the data gives $k_{16} = (1.46 \pm 0.10) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We choose to cite a final value for k_{16} , with error limits which include two standard deviations from the least squares regression and a propagated 5% uncertainty in the O_3 calibration, of $k_{16} = (1.46 \pm 0.12) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The result is compared to the reactivity of O_3 towards propene and analogous fluorine substituted propenes in Table 2 [8–10,12,13,21]. In its reaction with O_3 , $t\text{-CF}_3\text{CH}=\text{CHF}$ is less reactive than its non-substituted counterpart by a factor of 6850. The reaction occurs by electrophilic addition to the $\text{C}=\text{C}$ double bond. When compared with Cl atoms and OH radicals, O_3 has the lowest reactivity and hence, is most sensitive to the presence of electron withdrawing constituents. The existing literature shows a broad trend of decreasing reactivity towards O_3 with increasing number and electron withdrawing strength of the halogen constituents.

However, there are exceptions to this broad trend as evident from inspection of the data in Table 2. The present work shows that $t\text{-CF}_3\text{CH}=\text{CHCl}$ has a remarkably low reactivity towards O_3 ; lower than the corresponding fluorinated compound $t\text{-CF}_3\text{CH}=\text{CHF}$, lower than $E\text{-CF}_3\text{CF}=\text{CHF}$, and comparable to $Z\text{-CF}_3\text{CF}=\text{CHF}$. It is clear that decreasing reactivity with increasingly electron withdrawing substituents is not entirely sufficient to explain the observed reactivity trend. Computational work would be of interest to investigate the factors involved in determining the trend of reactivity of the halopropenes towards ozone.

3.4. Infrared spectrum of $t\text{-CF}_3\text{CH}=\text{CHCl}$

The IR spectrum of $t\text{-CF}_3\text{CH}=\text{CHCl}$ measured in the present work in 700 Torr of air diluent at $295 \pm 2 \text{ K}$ is shown in Fig. 4. $t\text{-CF}_3\text{CH}=\text{CHCl}$ has IR features at 669, 847, 935, 1152, 1311 and 1648 cm^{-1} . The total (600–1800 cm^{-1}) integrated IR absorption cross-section of $t\text{-CF}_3\text{CH}=\text{CHCl}$ is $(1.74 \pm 0.20) \times 10^{-16} \text{ cm molecule}^{-1}$. Individual IR band absorption cross-sections are 6.22×10^{-18} (600–690 cm^{-1}), 2.15×10^{-17} (750–1030 cm^{-1}), 1.27×10^{-16} (1030–1350 cm^{-1}) and 1.78×10^{-17} (1600–1790 cm^{-1}). There are no literature IR data for $t\text{-CF}_3\text{CH}=\text{CHCl}$ to compare with our result.

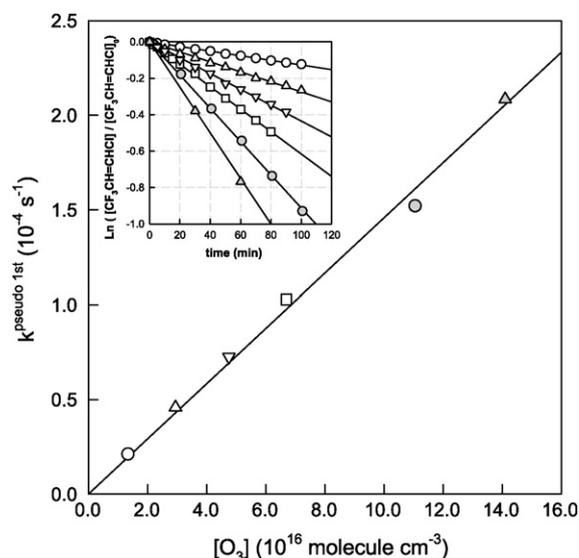


Fig. 3. Pseudo-first order loss of $t\text{-CF}_3\text{CH}=\text{CHCl}$ vs. O_3 concentration. Data obtained at Ford Motor Company and at University of Copenhagen are shown with open symbols and gray symbols, respectively. The insert shows the decay of $t\text{-CF}_3\text{CH}=\text{CHCl}$ when exposed to 414 mTorr (open circles), 911 mTorr (open upward triangles), 1.47 Torr (open downward triangles), 2.07 Torr (open squares), 3.42 Torr (gray circles) and 4.36 Torr (gray triangles) of O_3 in 700 Torr of air at $295 \pm 2 \text{ K}$.

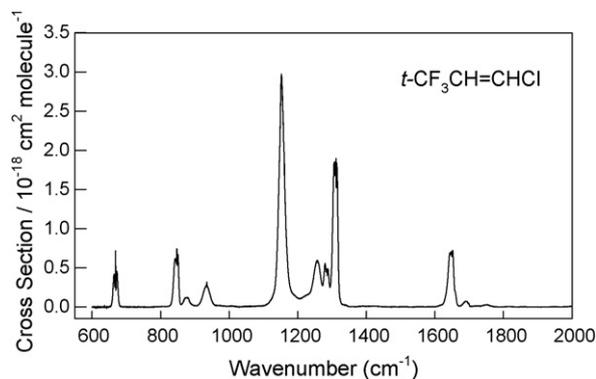


Fig. 4. IR spectrum of $t\text{-CF}_3\text{CH}=\text{CHCl}$ in 700 Torr of air, 295 ± 2 K (base e).

4. Implications for atmospheric chemistry

The present work improves our understanding of the atmospheric chemistry of $t\text{-CF}_3\text{CH}=\text{CHCl}$. Cl atoms and OH radicals react with $t\text{-CF}_3\text{CH}=\text{CHCl}$ with rate coefficients of $(5.22 \pm 0.72) \times 10^{-11}$ and $(4.40 \pm 0.38) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. O_3 reacts with $t\text{-CF}_3\text{CH}=\text{CHCl}$ with a rate constant of $(1.46 \pm 0.12) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. $t\text{-CF}_3\text{CH}=\text{CHCl}$ is not expected to undergo wet or dry deposition or photolysis [17] to an appreciable extent. Cl atoms are not present in the atmosphere in sufficient quantities to have a significant influence on the lifetime of $t\text{-CF}_3\text{CH}=\text{CHCl}$.

The value of $k(\text{OH} + t\text{-CF}_3\text{CH}=\text{CHCl})$ derived in the present work can be used to provide an estimate of the atmospheric lifetime of $t\text{-CF}_3\text{CH}=\text{CHCl}$. Using a global weighted-average OH concentration of $1.0 \times 10^6 \text{ molecules cm}^{-3}$ [22] leads to an estimated lifetime of $t\text{-CF}_3\text{CH}=\text{CHCl}$ with respect to reaction with OH radicals of 26 days. In a similar fashion our value for $k(\text{O}_3 + t\text{-CF}_3\text{CH}=\text{CHCl})$ derived above can be combined with the global background concentration of O_3 of approximately 35 ppb [23] to provide an estimate of the atmospheric lifetime of $t\text{-CF}_3\text{CH}=\text{CHCl}$ with respect to reaction with O_3 of 25 years. Hence we conclude that the atmospheric lifetime of $t\text{-CF}_3\text{CH}=\text{CHCl}$ is determined by reaction with OH radicals and is approximately 26 days. The approximate nature of this lifetime estimate should be stressed; the average daily concentration of OH radicals in the atmosphere varies significantly with both location and season [24]. The values above are estimates of global average lifetimes; local lifetimes could be different from those quoted above.

Using the method outlined by Pinnock et al. [25], the IR spectra of $\text{CF}_3\text{CH}=\text{CHCl}$ shown in Fig. 4 and the IR spectrum of CFC-11 [26] we calculate instantaneous forcings for $t\text{-CF}_3\text{CH}=\text{CHCl}$ and CFC-11 of 0.214 and $0.26 \text{ W m}^{-2} \text{ ppb}^{-1}$, respectively. Values of the halocarbon global warming potential, HGWP [27], for $t\text{-CF}_3\text{CH}=\text{CHCl}$ (relative to CFC-11) can then be estimated using the expression (II):

$$\text{HGWP}_{t\text{-CF}_3\text{CH}=\text{CHCl}} = \left(\frac{\text{IF}_{t\text{-CF}_3\text{CH}=\text{CHCl}}}{\text{IF}_{\text{CFC-11}}} \right) \left(\frac{\tau_{t\text{-CF}_3\text{CH}=\text{CHCl}} M_{\text{CFC-11}}}{\tau_{\text{CFC-11}} M_{t\text{-CF}_3\text{CH}=\text{CHCl}}} \right) \times \left(\frac{1 - \exp(-t/\tau_{t\text{-CF}_3\text{CH}=\text{CHCl}})}{1 - \exp(-t/\tau_{\text{CFC-11}})} \right) \quad (\text{II})$$

where $\text{IF}_{t\text{-CF}_3\text{CH}=\text{CHCl}}$, $\text{IF}_{\text{CFC-11}}$, $M_{t\text{-CF}_3\text{CH}=\text{CHCl}}$, $M_{\text{CFC-11}}$, $\tau_{t\text{-CF}_3\text{CH}=\text{CHCl}}$ and $\tau_{\text{CFC-11}}$ are the instantaneous forcings, molecular weights and atmospheric lifetimes of $t\text{-CF}_3\text{CH}=\text{CHCl}$ and CFC-11, and t is the time horizon over which the forcing is integrated. Using $\tau_{t\text{-CF}_3\text{CH}=\text{CHCl}} = 26$ days and $\tau_{\text{CFC-11}} = 45$ years [28] we estimate that the HGWP of $t\text{-CF}_3\text{CH}=\text{CHCl}$ relative to CFC-11 is 3.8×10^{-3} for a

20-year horizon and 1.5×10^{-3} for a 100-year time horizon, respectively. Relative to CO_2 , the GWP of CFC-11 on 20- and 100-year time horizons are 6730 and 4750, respectively [28]. Therefore, relative to CO_2 , the GWP of $t\text{-CF}_3\text{CH}=\text{CHCl}$ is approximately 26 for a 20-year horizon and 7 for a 100-year time horizon. $t\text{-CF}_3\text{CH}=\text{CHCl}$ has a negligible global warming potential and will not make a significant contribution to radiative forcing of climate change. It has been estimated that compounds with a tropospheric lifetime of 25 days, uniform landmass emissions, approximately the same mass as CFC-11 and containing one chlorine atom have an ozone depletion potential of approximately 0.003 [29]. The contribution of $t\text{-CF}_3\text{CH}=\text{CHCl}$ to stratospheric ozone depletion is expected to be negligible given its very short-atmospheric lifetime.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.05.013.

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