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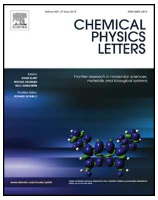

Atmospheric chemistry of *cis*-$CF_3CH=CHCl$ (HCFO-1233zd(Z)): Kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O_3

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ABSTRACT

FTIR smog chamber techniques were used to measure the rate coefficients $k(Cl + cis\text{-}CF_3CH{=}CHCl) = (6.26 \pm 0.84) \times 10^{-11}$, $k(OH + cis\text{-}CF_3CH{=}CHCl) = (8.45 \pm 1.52) \times 10^{-13}$, and $k(O_3 + cis\text{-}CF_3CH{=}CHCl) = (1.53 \pm 0.12) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}. The atmospheric lifetime of *cis*-$CF_3CH=CHCl$ is determined by reaction with OH radicals and is estimated to be 14 days. The infrared spectrum of *cis*-$CF_3CH=CHCl$ was recorded and the integrated absorption over the range 600–2000 cm^{-1} was measured to be $(1.48 \pm 0.07) \times 10^{-16}$ cm molecule^{-1}. Accounting for non-uniform horizontal and vertical mixing leads to a GWP_{100} value of essentially zero. Correction to account for unwanted Cl atom chemistry in our previous relative rate study of the kinetics of the reaction of OH with *trans*-$CF_3CH=CHCl$ gives $k(OH + trans\text{-}CF_3CH{=}CHCl) = (3.61 \pm 0.37) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

1. Introduction

Recognition of the environmental consequences of the release of chlorofluorocarbons (CFCs) and halons into the atmosphere [1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. While protection of the ozone layer has been the focus of these efforts, concerns related to global climate change are becoming an increasingly important consideration in the choice of alternative compounds.

Saturated hydrofluorocarbons (HFCs), such as CF_3CFH_2 (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]. Haloolefins are a new generation of CFC replacements which are being developed. Haloolefins have a greater reactivity than HFCs toward OH radicals and hence have shorter atmospheric lifetimes and smaller global warming potentials. *cis*-1-chloro-3,3,3-trifluoropropene (*cis*-$CF_3CH=CHCl$, HCFO-1233zd(Z)) is a haloolefin which has been developed for use in degreasing of mechanical parts and in dry cleaning. *cis*-$CF_3CH=CHCl$ contains a chlorine atom that potentially can participate in the destruction of the ozone layer. However, if the atmospheric lifetime of *cis*-$CF_3CH=CHCl$ is sufficiently low, the compound will not reach the stratosphere, and thus not participate in the catalytic destruction of the ozone layer. Prior to large-scale industrial use an assessment of the atmospheric chemistry and environmental impact of *cis*-$CF_3CH=CHCl$ is needed. To fulfill this need we have conducted an experimental investigation of the atmospheric chemistry of *cis*-$CF_3CH=CHCl$. Experiments were conducted in the smog chamber at Ford Motor Company (Ford), Michigan, USA, and in the photoreactor at the Copenhagen Center for Atmospheric Research (CCAR) at University of Copenhagen, Denmark. Fourier transform infrared (FTIR) smog chamber techniques were used to determine the kinetics of the gas-phase reactions of Cl atoms, OH radicals, and O_3 with *cis*-$CF_3CH=CHCl$. The IR spectrum of *cis*-$CF_3CH=CHCl$ was measured and the global warming potential (GWP) of *cis*-$CF_3CH=CHCl$ was calculated.

2. Experimental method

The experimental procedures are described in detail elsewhere [4] and only a brief summary is given here. Chlorine atoms were generated by photolysis of molecular chlorine:

$$Cl_2 + h\nu \rightarrow 2Cl \quad (1)$$

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Hydroxyl radicals (OH) were generated by UV irradiation of methyl nitrite (CH_3ONO) in air in the presence of nitric oxide:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{2}$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

The concentrations of reactants and products were monitored using in situ FTIR spectroscopy. Analysis of the spectra was carried out by a process of spectral stripping in which scaled reference spectra were subtracted from the sample spectrum. Reference spectra were acquired by expanding known volumes of reference compounds into the reaction chambers.

The relative rate method is a well-established technique for measuring the rate coefficients of chlorine atoms or OH radicals with organic compounds. Kinetic data were derived by monitoring the loss of *cis*-$CF_3CH{=}CHCl$ relative to one or more reference compounds. The decays of the reactant and reference are then plotted using the expression:

$$\mathrm{Ln}\left(\frac{[cis\text{-}CF_3CH{=}CHCl]_{t_0}}{[cis\text{-}CF_3CH{=}CHCl]_t}\right) = \frac{k_{\mathrm{Reactant}}}{k_{\mathrm{Reference}}}\mathrm{Ln}\left(\frac{[\mathrm{Reference}]_{t_0}}{[\mathrm{Reference}]_t}\right) \tag{I}$$

where $[cis\text{-}CF_3CH{=}CHCl]_{t_0}$, $[cis\text{-}CF_3CH{=}CHCl]_t$, $[\mathrm{Reference}]_{t_0}$ and $[\mathrm{Reference}]_t$ are the concentrations of *cis*-$CF_3CH{=}CHCl$ and the reference compound at times t_0 and t. The slope is then the ratio of the rate coefficient for reaction of either Cl atoms or OH radicals toward *cis*-$CF_3CH{=}CHCl$ and the corresponding reaction for the reference compound.

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 coefficients versus the initial O_3 concentration gives a slope of k_5.

$$O_3 + cis\text{-}CF_3CH{=}CHCl \rightarrow \mathrm{Products} \tag{5}$$

In smog chamber experiments unwanted loss of reactants, reference compounds, and products via photolysis and heterogeneous reactions need to be considered. To test for the presence of heterogeneous reactions, mixtures obtained after UV irradiation were allowed to stand in the dark in the chamber for 30 min. There was no observable (<2%) loss of reactants or products, suggesting that heterogeneous reactions are not a significant complication in the present experiments.

Potential systematic uncertainties inherent in the analysis of the IR spectra are typically ±1% of the initial reactant concentration. Unless otherwise stated, we choose to cite final values with error limits, which include two standard deviations from the least squares regression and 5% uncertainty in the reactant calibrations. *cis*-$CF_3CH{=}CHCl$ was supplied by Honeywell International Inc. with a purity of >99%. The sample was degassed in several freeze-pump-thaw cycles before use.

2.1. FTIR smog chamber system at ford

Experiments were performed in a 140 liter Pyrex reactor connected to a Mattson Sirus 100 FTIR spectrometer [5]. The reactor was surrounded by 22 fluorescent black lamps (GE F40BLB), which were used to photochemically initiate the experiments. Experiments were performed at 296 ± 1 K in 700 Torr of air or N_2 diluent. The IR spectra were derived from 32 co-added interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.6 m. Reactant and reference compounds were monitored using absorption features over the following wavenumber ranges: C_2H_2, 650–800 cm^{-1}; C_2H_4, 900–1000 cm^{-1}; *cis*-$CF_3CH{=}CHCl$, 850–890 cm^{-1}.

CH_3ONO was synthesized by drop-wise addition of concentrated H_2SO_4 to a saturated solution of $NaNO_2$ in methanol and was devoid of any detectable impurities using FTIR analysis. All other reagents were obtained from commercial sources at purities >99%.

2.2. FTIR photoreactor at University of Copenhagen

The CCAR photoreactor consists of a 101 liter quartz reactor connected to a Bruker IFS 66 v/s FTIR spectrometer [6]. Experiments were performed at 296 ± 1 K in 700 Torr of air diluent. The IR spectra were derived from 64 co-added interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length between 50.01 and 53.42 m. Reactant and reference compounds were monitored using absorption features over the following wavenumber ranges: C_2H_2, 650–800 cm^{-1}; C_2H_4, 900–1000 cm^{-1}; *cis*-$CF_3CH{=}CHCl$, 850–890 and 1610–1670 cm^{-1}; O_3, 2720–2785 cm^{-1}.

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. All other reagents were obtained from commercial sources at purities >99%.

3. Results and discussion

3.1. Relative rate study of Cl + cis-$CF_3CH{=}CHCl$

The rate of reaction (6) was measured relative to reactions (7) and (8):

$$Cl + cis\text{-}CF_3CH{=}CHCl \rightarrow \mathrm{Products} \tag{6}$$

$$Cl + C_2H_4 \rightarrow \mathrm{Products} \tag{7}$$

$$Cl + C_2H_2 \rightarrow \mathrm{Products} \tag{8}$$

The initial mixtures consisted of 4.41–15.8 mTorr *cis*-$CF_3CH{=}CHCl$, 58.8–106 mTorr Cl_2 and either 4.17–6.69 mTorr C_2H_4 or 4.41–4.85 mTorr C_2H_2 in a total pressure of 700 Torr air or N_2 diluent. The loss of *cis*-$CF_3CH{=}CHCl$ is plotted against the loss

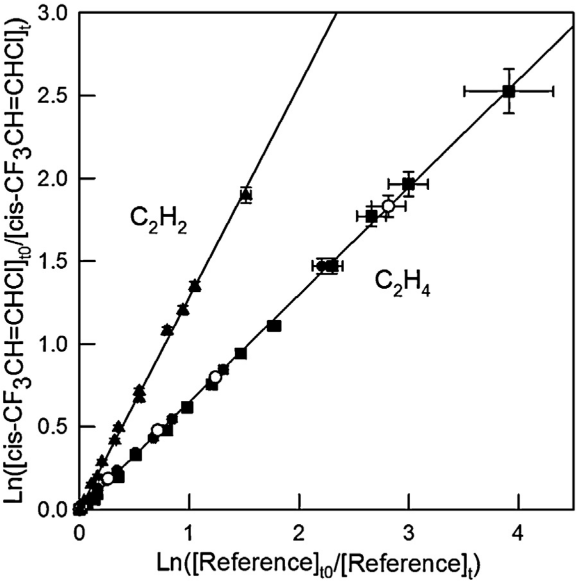

Figure 1. Loss of *cis*-$CF_3CH{=}CHCl$ relative to C_2H_4 (squares and circles) and C_2H_2 (triangles) in the presence of chlorine atoms in 700 Torr total pressure of air (solid symbols) or N_2 (open symbols), 296 ± 1 K. Experiments were performed at Ford (triangles and circles) and CCAR (squares). The error bars reflect the uncertainty in the determination of the reactant concentrations.

of the reference compound in Figure 1. Indistinguishable results were obtained from experiments performed in air and N_2 diluent.

Linear least squares analysis of the data in Figure 1 gives $k_6/k_7 = 0.65 \pm 0.04$ and $k_6/k_8 = 1.28 \pm 0.08$. Using $k_7 = (9.29 \pm 0.51) \times 10^{-11}$ and $k_8 = (5.07 \pm 0.34) \times 10^{-11}$ [7] gives $k_6 = (6.03 \pm 0.48) \times 10^{-11}$ and $(6.49 \pm 0.61) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. The fact that consistent values of k_6 were derived from experiments using different reference compounds suggests the absence of significant systematic errors in the present work. We choose to quote a final value for k_6 which is the average of the individual determinations together with uncertainties that encompass the extremes of the two individual determinations, hence, $k_6 = (6.26 \pm 0.84) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

This is the first study of the reaction of chlorine atoms with *cis*-$CF_3CH{=}CHCl$. We have previously studied the reactivity of chlorine atoms toward *trans*-$CF_3CH{=}CHCl$. The rate coefficient ratios measured for the *trans* isomer using C_2H_4 and C_2H_2 references were approximately 10% smaller [8] than those measured here showing that the *cis* isomer is slightly more reactive than the *trans* isomer toward chlorine atoms. This difference may be explained by steric hindrance.

3.2. Relative rate study of OH + cis-$CF_3CH{=}CHCl$

The kinetics of reaction (9) were measured relative to reactions (10) and (11):

$$OH + cis\text{-}CF_3CH{=}CHCl \rightarrow \text{Products} \tag{9}$$

$$OH + C_2H_4 \rightarrow \text{Products} \tag{10}$$

$$OH + C_2H_2 \rightarrow \text{Products} \tag{11}$$

Initial reaction mixtures consisted of 58.5–63.2 mTorr *cis*-$CF_3CH{=}CHCl$, 108–205.7 mTorr CH_3ONO, and 7.05–7.35 mTorr C_2H_4 or 4.26–7.35 mTorr C_2H_2, and 0–14.7 mTorr NO in a total pressure of 700 Torr air and N_2 diluent. Figure 2 shows the loss of *cis*-$CF_3CH{=}CHCl$ plotted as a function of the loss of the reference compound.

Linear least squares analysis of the data in Figure 2 gives $k_9/k_{10} = 0.129 \pm 0.016$ and $k_9/k_{11} = 1.01 \pm 0.07$. We have shown that Cl atoms are released during the OH initiated oxidation of $CF_3CH{=}CHCl$ [9]:

$$CF_3CHCH(OH)Cl + M \rightarrow Cl + CF_3CH{=}CH(OH) + M \tag{12}$$

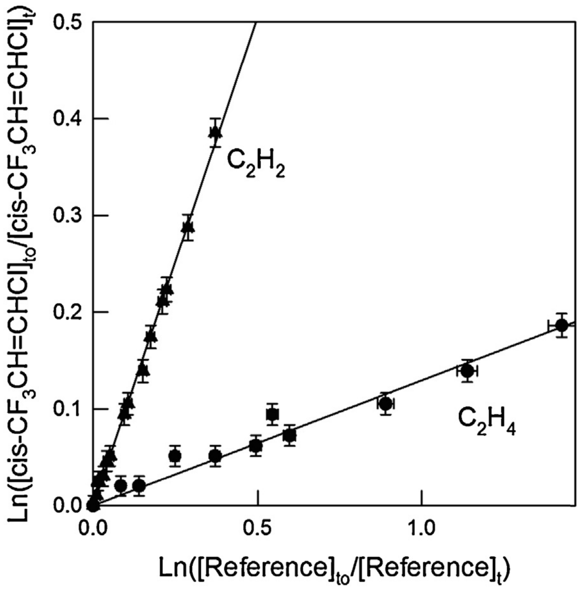

Figure 2. Loss of *cis*-$CF_3CH{=}CHCl$ relative to C_2H_4 (circles) and C_2H_2 (triangles) in the presence of OH radicals in 700 Torr total pressure of air and N_2, 296 ± 1 K. The error bars reflect the uncertainty in the determination of the reactant concentrations.

The Cl atoms will react with *cis*-$CF_3CH{=}CHCl$ and pose a challenge for the OH relative rate measurement of k_9. Ideally, to minimize such complications a competitor would be added to the reaction mixtures to scavenge the Cl atoms. Alkanes, such as C_2H_6, are often used as chlorine atom scavengers but are not suitable for use in the present experiments because their reactivity toward OH radicals is comparable to that of *cis*-$CF_3CH{=}CHCl$ and hence would scavenge both chlorine atoms and OH radicals. To account for additional loss of *cis*-$CF_3CH{=}CHCl$ in the OH relative rate experiments caused by Cl atoms the system was modeled numerically. A model was constructed which incorporated the concentrations of *cis*-$CF_3CH{=}CHCl$, C_2H_4, and C_2H_2 used in the experiments, values of k_6–k_8 and k_9–k_{11} given above, and a chlorine atom yield of 40% from OH radical initiated oxidation as found for *trans*-$CF_3CH{=}CHCl$ [9]. The value of k_9 in the model was iterated starting with an uncorrected value, computing a correction, and then using the corrected value in the model to reevaluate the correction. The correction was larger for the experiments using C_2H_4 as reference than for those using C_2H_2 as reference. This reflects the fact that there is an approximately 5-fold difference in the rate coefficient ratios k_6/k_7 and k_9/k_{10}, while there is only approximately 10% difference in the rate coefficient ratios k_6/k_8 and k_9/k_{11}. The corrections applied to the C_2H_4 data were approximately 20% while those to the C_2H_2 data were approximately 5%. Correcting for the impact of chlorine atoms and propagating an additional 5% uncertainty to account for uncertainties in the correction procedure gives $k_9/k_{10} = 0.103 \pm 0.014$ and $k_9/k_{11} = 0.960 \pm 0.082$.

Using $k_{10} = 8.52 \times 10^{-12}$ [10] and $k_{11} = 8.45 \times 10^{-13}$ [11] gives $k_9 = (8.78 \pm 1.19) \times 10^{-13}$ and $(8.11 \pm 0.69) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The fact that consistent values of k_9 were derived from experiments using different reference compounds suggests the absence of significant systematic errors in the present work. We choose to quote a final value for k_9, which is the average of the individual determinations with uncertainties that encompass the extremes of the individual determinations, hence, $k_9 = (8.45 \pm 1.52) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This result is consistent with the value of $(9.46 \pm 0.22) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} reported by Gierczak et al. [12].

3.3. Relative rate study of OH + trans-$CF_3CH{=}CHCl$

We have previously conducted a relative rate study of the kinetics of the reaction of OH radicals with *trans*-$CF_3CH{=}CHCl$ using C_2H_4 and C_2H_2 as references and reported rate coefficient ratios of $k_{13}/k_{10} = 0.053 \pm 0.003$ and $k_{13}/k_{11} = 0.506 \pm 0.031$ [8].

$$OH + trans\text{-}CF_3CH{=}CHCl \rightarrow \text{Products} \tag{13}$$

As discussed above, the formation of chlorine atoms is an unavoidable complication in relative rate studies of the reaction of OH radicals with $CF_3CH{=}CHCl$. To compute corrections to account for chlorine chemistry in the OH experiments a model was constructed which incorporated the concentrations of *trans*-$CF_3CH{=}CHCl$, C_2H_4, and C_2H_2 used in the previous experiments, values of k_6, k_7, k_8, k_{10}, k_{11}, and k_{13}, and a chlorine atom yield of 40% from OH radical initiated oxidation of *trans*-$CF_3CH{=}CHCl$. The corrections applied to the C_2H_4 data were approximately 20% while those for the C_2H_2 data were approximately 15%. Correcting for the impact of chlorine atoms and propagating an addition 5% uncertainty to account for uncertainties in the correction procedure gives $k_{13}/k_{10} = 0.042 \pm 0.004$ and $k_{13}/k_{11} = 0.430 \pm 0.034$. Using $k_{10} = 8.52 \times 10^{-12}$ [10] and $k_{11} = 8.45 \times 10^{-13}$ [11] gives $k_{13} = (3.58 \pm 0.34) \times 10^{-13}$ and

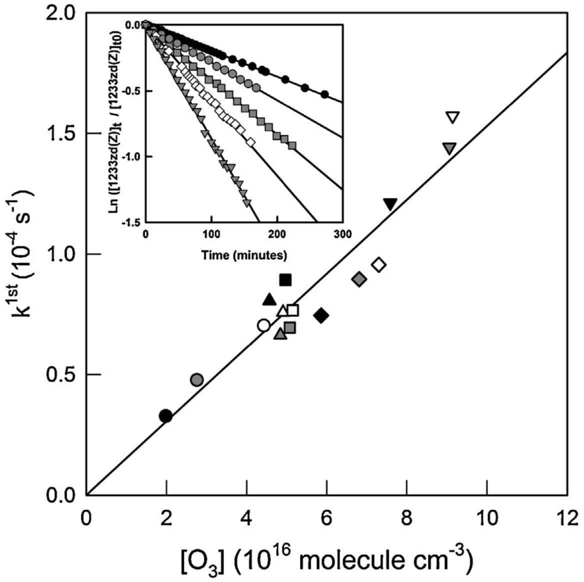

Figure 3. Pseudo-first order loss of *cis*-$CF_3CH=CHCl$ versus O_3 concentration. All data were obtained at CCAR. The inset shows the data obtained for 0.61, 0.85, 1.6, 2.3, and 2.80 Torr of O_3 in 700 Torr total pressure of air diluent, 295 ± 1 K.

$(3.63 \pm 0.29) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. We choose to quote a final value for k_{13}, which is the average of the individual determinations with uncertainties that encompass the extremes of the individual determinations, hence, $k_{13} = (3.61 \pm 0.37) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. This value is in agreement with the value of $(3.76 \pm 0.06) \times 10^{-13}$ (296 K) reported by Gierczak et al. [12] and the value of $(3.29 \pm 0.10) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (298 K) reported by Orkin et al. [13]. Interestingly, the *trans* isomer is approximately a factor of 2 less reactive than the *cis* isomer toward OH radicals. An investigation of the significant difference between the rate coefficients for the *trans* and the *cis* isomer could be performed with a computational study, but is beyond the scope of the present study.

3.4. Absolute rate of O_3 + *cis*-$CF_3CH=CHCl$

The kinetics of reaction (5) were studied by observing the decay of *cis*-$CF_3CH=CHCl$ when exposed to O_3 in the reaction chamber at CCAR:

$$O_3 + cis\text{-}CF_3CH=CHCl \rightarrow \text{Products} \qquad (5)$$

Cyclohexane was added to the reaction mixture as OH scavenger to avoid potential problems associated with the loss of *cis*-$CF_3CH=CHCl$ via reaction with OH radicals formed in reaction (5) [10]. Initial reaction mixtures consisted of 4.07–4.17 mTorr *cis*-$CF_3CH=CHCl$, 3.96–31.79 mTorr cyclohexane, and 0.61–2.82 Torr O_3 in a total pressure of 700 Torr air diluent. Variation in the [cyclohexane]/[*cis*-$CF_3CH=CHCl$] ratio over the range of 0.9–7.6 had no discernable effect on the observed decay of *cis*-$CF_3CH=CHCl$ suggesting that loss via reaction with OH radicals is not a significant complication.

The loss of *cis*-$CF_3CH=CHCl$ followed pseudo first-order kinetics in all experiments. The insert in Figure 3 shows the data obtained for 0.61, 0.85, 1.6, 2.3, and 2.80 Torr of O_3. A plot of the pseudo first-order decay of *cis*-$CF_3CH=CHCl$ versus O_3 concentration is shown in Figure 3. A linear least squares fit gives $k_5 = (1.53 \pm 0.09) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}. We choose to cite a final value for k_5 with error limits which include two standard deviations from the least squares regression and a propagated 5% uncertainty in the O_3 calibration, of $k_5 = (1.53 \pm 0.12) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}.

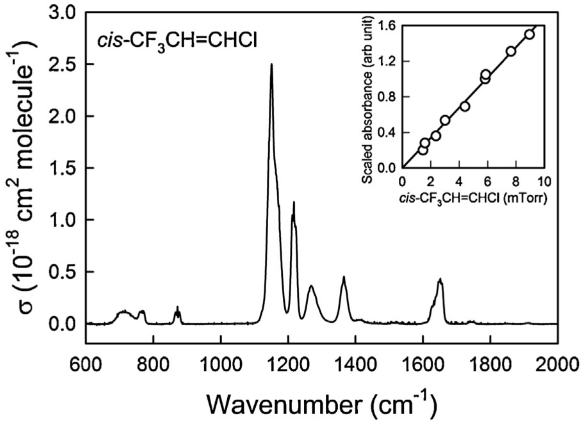

Figure 4. IR spectrum of *cis*-$CF_3CH=CHCl$ in 700 Torr of air at 295 K (Ford).

This is the first study of the reaction of O_3 with *cis*-$CF_3CH=CHCl$. We have previously reported a value of $(1.46 \pm 0.12) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1} for the *trans* isomer, *trans*-$CF_3CH=CHCl$ [8]. The reactivities of *cis*- and *trans*-$CF_3CH=CHCl$ toward O_3 are indistinguishable.

3.5. Infrared spectrum of *cis*-$CF_3CH=CHCl$

IR spectra were obtained by expanding known volumes of *cis*-$CF_3CH=CHCl$ into the chambers and recording spectra for different concentrations of *cis*-$CF_3CH=CHCl$. The IR spectra obtained at Ford and CCAR were in good agreement (within 5%). Below and in the following sections, we proceed using the spectrum obtained at Ford. Figure 4 shows the IR spectrum of *cis*-$CF_3CH=CHCl$ recorded in 700 Torr air diluent at 296 ± 1 K. As seen from the inset in Figure 4 the intensity of the absorption features increased linearly with the *cis*-$CF_3CH=CHCl$ concentration. The integrated absorption cross-section of *cis*-$CF_3CH=CHCl$ (600–2000 cm^{-1}) is $(1.48 \pm 0.07) \times 10^{-16}$ cm $molecule^{-1}$. Gierczak et al. [12] report a value of $(1.60 \pm 0.01) \times 10^{-16}$ cm $molecule^{-1}$ which is consistent with our measurement within the expected combined experimental uncertainties.

4. Implications for atmospheric chemistry

The present work improves our understanding of the atmospheric chemistry of *cis*-$CF_3CH=CHCl$. Cl atoms, OH radicals, and O_3 react with *cis*-$CF_3CH=CHCl$ with rate coefficients of $(6.26 \pm 0.84) \times 10^{-11}$, $(8.45 \pm 1.52) \times 10^{-13}$, and $(1.53 \pm 0.12) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. Organic compounds are removed from the atmosphere via photolysis, wet and dry deposition, and gas-phase reaction with OH radicals, O_3, and Cl atoms. *cis*-$CF_3CH=CHCl$ does not absorb at wavelengths greater than 200 nm and is volatile and hence will not be lost via photolysis or wet or dry deposition to any appreciable extent [14]. The value of k(OH + *cis*-$CF_3CH=CHCl$) derived in the present work can be used to provide an estimate of the atmospheric lifetime of *cis*-$CF_3CH=CHCl$. Using a global tropospheric 24 h average OH concentration of 1.0×10^6 molecule cm^{-3} [15] gives an estimated lifetime with respect to reaction with OH radicals of 14 days. The approximate nature of this lifetime should be stressed. The average daily concentration of OH radicals in the atmosphere varies significantly with location and season [16] and local atmospheric lifetimes of *cis*-$CF_3CH=CHCl$ will vary similarly.

Our value for k(O_3 + *cis*-$CF_3CH=CHCl$) can be combined with the global background concentration of O_3 of approximately 35 ppb

[17] to provide an estimate of the atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$ with respect to reaction with O_3 of 24 years, which is clearly of minor importance compared to the OH reaction pathway. Reaction with Cl atoms is a negligible fate for *cis*-$CF_3CH{=}CHCl$ as the atmospheric concentration of Cl atoms is generally low [17]. Assuming a global average Cl atom concentration of $10^3\,cm^{-3}$ we derive a lifetime with respect to Cl atom reaction of 6 months. We proceed on the assumption that the atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$ is dictated by reaction with OH radicals and is approximately 14 days.

The radiative efficiency for *cis*-$CF_3CH{=}CHCl$ calculated using the method of Pinnock et al. [18] and the IR spectrum in Figure 4 was $0.19\,W\,m^{-2}\,ppb^{-1}$. For short-lived compounds, such as *cis*-$CF_3CH{=}CHCl$, non-uniform horizontal and vertical mixing in the atmosphere need to be taken into account. Hodnebrog et al. [19] provide a correction factor of relative efficiencies for very short-lived compounds (Eq. (II)) that accounts for non-uniform horizontal and vertical mixing:

$$f(\tau) = \frac{a\tau^b}{1 + c\tau^d} \tag{II}$$

where τ is the lifetime of *cis*-$CF_3CH{=}CHCl$, a, b, c, and d are constants with values of 2.962, 0.9312, 2.994, and 0.9302, respectively. Using $\tau = 0.038$ years gives $f(\tau) = 0.122$. Hence we arrive at a final value of *cis*-$CF_3CH{=}CHCl$ of $0.0231\,W\,m^{-2}\,ppb^{-1}$.

Using Eq. (III) the global warming potential (GWP) can be calculated:

$$\mathrm{GWP}\left(x(t')\right) = \frac{\int_0^{t'} F_x \exp\left(-t/\tau_x\right) dt}{\int_0^{t'} F_{CO_2} R(t) dt} \tag{III}$$

where F_{CO_2} is the radiative efficiency of CO_2, $R(t)$ is the response function that describes the decay of an instantaneous pulse of CO_2, F_x is the radiative efficiency of *cis*-$CF_3CH{=}CHCl$, and τ_x is its atmospheric lifetime. The denominator in Eq. (III) is the absolute global warming potential (AGWP) for CO_2. Using the IPCC AR5 F_{CO_2} of $1.7517 \times 10^{-15}\,W\,m^{-2}\,kg^{-1}$ [20] with the time-integrated airborne CO_2 fractions evaluated by Joos et al. [21] for different time horizons, we arrive at AGWPs for CO_2 of 0.194, 0.715 and $2.512\,W\,m^{-2}\,ppb^{-1}$ for 20, 100, and 500 year time horizons, respectively.

Using the radiative efficiency of $0.0231\,W\,m^{-2}\,ppb^{-1}$ and atmospheric lifetime of 14 days, GWP values for *cis*-$CF_3CH{=}CHCl$ are estimated to 2, 0, and 0, for 20, 100, and 500 year horizons respectively. Gierczak et al. report a GWP_{100} value of approximately 3 [12] which is consistent with our result. *cis*-$CF_3CH{=}CHCl$ has a negligible GWP and will not make a significant contribution to radiative forcing of climate change. Patten and Wuebbles [22] conducted a modeling study and derived an ozone depleting potential (ODP) for *trans*-$CF_3CH{=}CHCl$ of 0.00034. The atmospheric lifetime of *cis*-$CF_3CH{=}CHCl$ is approximately half that of the *trans* isomer and hence the ODP for *cis*-$CF_3CH{=}CHCl$ will be even lower than for *trans*-$CF_3CH{=}CHCl$. We conclude that *cis*-$CF_3CH{=}CHCl$ will make negligible contributions to stratospheric ozone depletion and to radiative forcing of climate change.

Acknowledgements

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