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ARTICLE *in* CHEMICAL PHYSICS LETTERS · MAY 2007

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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

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Received 31 January 2007; in final form 6 March 2007

Available online 21 March 2007

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 $k(\text{O}_3 + \text{CF}_3\text{CF}=\text{CH}_2) = (2.77 \pm 0.21) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in 700 Torr of N_2 , N_2/O_2 , or air diluent at 296 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 reac-

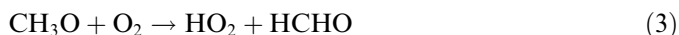
tion with ozone and (iv) atmospheric implications. Results are reported herein.

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.



OH radicals were produced by photolysis of CH_3ONO in the presence of NO in air.



In the relative rate experiments the following reactions take place.

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It can be shown that

$$\text{Ln}\left(\frac{[\text{Reactant}]_{t_0}}{[\text{Reactant}]_t}\right) = \frac{k_{\text{Reactant}}}{k_{\text{Reference}}} \text{Ln}\left(\frac{[\text{Reference}]_{t_0}}{[\text{Reference}]_t}\right) \quad (9)$$

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 $\text{Ln}([\text{Reactant}]_{t_0}/[\text{Reactant}]_t)$ vs. $\text{Ln}([\text{Reference}]_{t_0}/[\text{Reference}]_t)$ 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 $\text{CF}_3\text{CF}=\text{CH}_2$ was measured in the presence of excess O_3 .

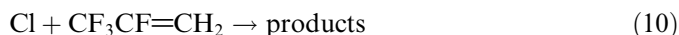
O_3 was produced from O_2 via silent electrical discharge using a commercial O_3 ozonizer. CH_3ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of NaNO_2 in methanol. Other reagents were obtained from commercial sources. Experiments were conducted in 700 Torr total pressure of N_2 , or N_2/O_2 diluent at 296 ± 1 K.

Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. To check for unwanted loss of reactants and reference compounds via heterogeneous reactions, reaction mixtures were left to stand in the chamber for 60 min. There was no observable ($<2\%$) loss of any of the reactants or products in the present work. Unless stated otherwise, quoted uncertainties are two standard deviations from least squares regressions.

3. Results and discussion

3.1. Kinetics of the $\text{Cl} + \text{CF}_3\text{CF}=\text{CH}_2$ reaction

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



Reaction mixtures consisted of 19.1–26.2 mTorr of $\text{CF}_3\text{CF}=\text{CH}_2$, 104–133 mTorr Cl_2 , and either 4.33–30.2 mTorr C_2H_4 , or 2.35–8.5 mTorr C_2H_2 , in 700 Torr of air, or 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 N_2 , or air, diluent. A linear least squares fit (unweighted, not forced through the origin)

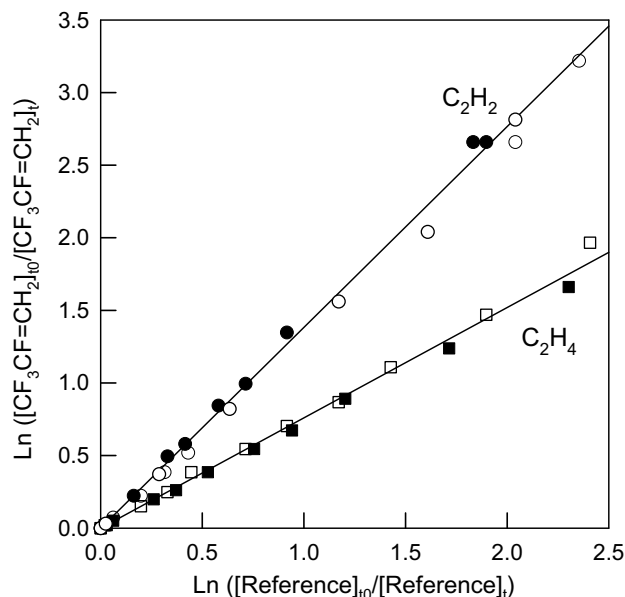


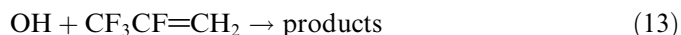
Fig. 1. Decay of $\text{CF}_3\text{CF}=\text{CH}_2$ vs. C_2H_4 and C_2H_2 in the presence of Cl atoms in 700 Torr of either air (open symbols) or N_2 (filled symbols) at 296 ± 2 K.

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 $(7.00 \pm 0.56) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 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 $k_{10} = (7.03 \pm 0.59) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 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], $k(\text{Cl} + \text{C}_4\text{F}_9\text{CH}=\text{CH}_2) = (8.9 \pm 1.0) \times 10^{-11}$ [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 $k(\text{Cl} + \text{CF}_3\text{CF}=\text{CF}_2) = (2.7 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [8]. The reaction of Cl atoms with propene proceeds via electrophilic addition to the $>\text{C}=\text{C}<$ double bond. The presence of electron withdrawing fluorine substituents is expected to lead to decreased reactivity with 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 $\text{OH} + \text{CF}_3\text{CF}=\text{CH}_2$ reaction

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



Initial reaction mixtures consisted of 17.6–18.1 mTorr of $\text{CF}_3\text{CF}=\text{CH}_2$, 110–200 mTorr CH_3ONO , and 3.38 mTorr

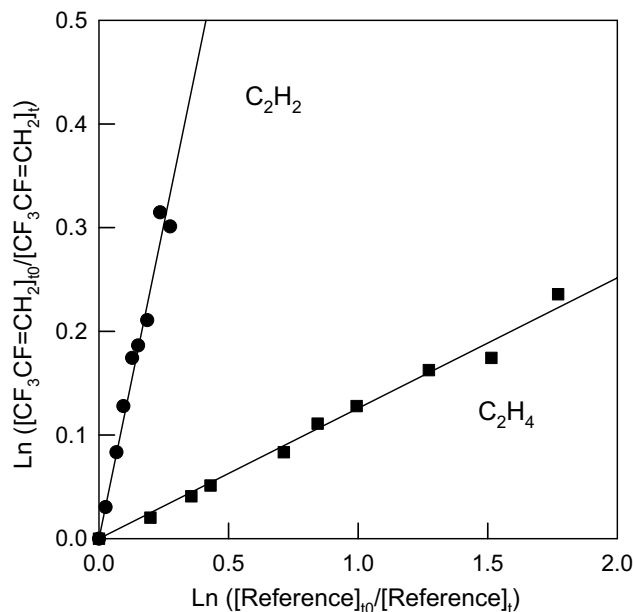


Fig. 2. Decay of $\text{CF}_3\text{CF}=\text{CH}_2$ vs. C_2H_4 and C_2H_2 in the presence of OH radicals in 700 Torr of air at 296 ± 2 K.

C_2H_4 or 3.09 mTorr C_2H_2 in 700 Torr total pressure of air diluent. Fig. 2 shows the loss of $\text{CF}_3\text{CF}=\text{CH}_2$ 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 $(1.02 \pm 0.13) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 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 $k_{13} = (1.05 \pm 0.17) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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 $>\text{C}=\text{C}<$ double bond with a rate constant of $2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in one atmosphere of air at 298 K [9]. Measurements of $k(\text{OH} + \text{CF}_3\text{CH}=\text{CH}_2)$ by Orkin et al. [11] and Sulbaek Andersen et al. [6] are in good agreement, taking an average from the two studies gives $k(\text{OH} + \text{CF}_3\text{CH}=\text{CH}_2) = 1.45 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. McIlroy and Tully [12], Dubey et al. [13], Orkin et al. [11], and Mashino et al. [8] studied the reaction of OH radicals with $\text{CF}_3\text{CF}=\text{CF}_2$. The results at ambient temperature from the four studies were in good agreement; the average from the studies is $k(\text{OH} + \text{CF}_3\text{CH}=\text{CH}_2) = 2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In contrast to Cl atoms, the reactivity of OH radicals with $\text{CH}_3\text{CH}=\text{CH}_2$, $\text{CF}_3\text{CH}=\text{CH}_2$, $\text{CF}_3\text{CF}=\text{CH}_2$, and $\text{CF}_3\text{CF}=\text{CF}_2$ does not follow the trend expected assuming a simple electrophilic addition mechanism. Specifically, the

reactivity of $\text{CF}_3\text{CF}=\text{CF}_2$ appears to be anomalously high. A computational study of the reaction of OH radicals with $\text{CF}_3\text{CF}=\text{CF}_2$ 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 $\text{CF}_3\text{CF}=\text{CH}_2$ when exposed to ozone in the reaction chamber. Reaction mixtures consisted of 14–28 mTorr $\text{CF}_3\text{CF}=\text{CH}_2$, 30–46 mTorr cyclohexane, and 180–1890 mTorr O_3 in 700 Torr of air diluent. Cyclohexane was added to avoid potential problems associated with the loss of $\text{CF}_3\text{CF}=\text{CH}_2$ via reaction with OH radicals formed in reaction (16). Variation of the [cyclohexane]/ $[\text{CF}_3\text{CF}=\text{CH}_2]$ ratio over the range 1–3 had no discernable effect on the observed decay of $\text{CF}_3\text{CF}=\text{CH}_2$ suggesting that loss via reaction with OH radicals is not a significant complication. The loss of $\text{CF}_3\text{CF}=\text{CH}_2$ 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 $\text{CF}_3\text{CF}=\text{CH}_2$ vs. O_3 concentration. The line through the data gives $k_{16} = (2.77 \pm 0.21) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. $\text{CF}_3\text{CF}=\text{CH}_2 + \text{O}_3 \rightarrow \text{products}$ (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 O_3 with propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and 1-decene are indistinguishable and are approximately $1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [9]. The rate constants for reactions of O_3 with $\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{CF}_3\text{CH}=\text{CH}_2$ are $(6.2 \pm 1.5) \times 10^{-22}$ [14] and

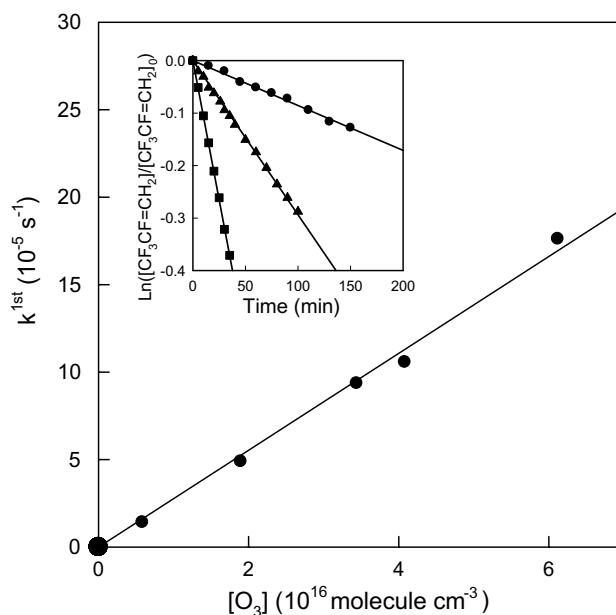


Fig. 3. Pseudo first-order loss of $\text{CF}_3\text{CF}=\text{CH}_2$ versus O_3 concentration. The insert shows typical decay plots for $\text{CF}_3\text{CF}=\text{CH}_2$ when exposed to 180 mTorr (circles), 585 mTorr (triangles), or 1890 mTorr (squares) of O_3 .

$(3.5 \pm 0.3) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [6], respectively. The reactivity of fluorinated propenes towards ozone follows the trend expected ($\text{CH}_3\text{CH}=\text{CH}_2 > \text{CF}_3\text{CH}=\text{CH}_2 > \text{CF}_3\text{CF}=\text{CH}_2 > \text{CF}_3\text{CF}=\text{CF}_2$) for reaction proceeding via electrophilic addition of ozone to the $>\text{C}=\text{C}<$ double bond. In its reaction with 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, 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 O_3 , Cl, and OH proceed via electrophilic addition to the $>\text{C}=\text{C}<$ double bond there are differences in mechanism with O_3 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 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 $1.0 \times 10^6 \text{ molecules cm}^{-3}$ [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 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 ($800\text{--}2000 \text{ cm}^{-1}$) of $(1.63 \pm 0.09) \times 10^{-16} \text{ cm molecule}^{-1}$. The quoted uncertainty ($\pm 5\%$) is comprised of the following components: sample concentration ($\pm 2\%$), path length ($\pm 1.5\%$), residual baseline offset after subtraction of the background ($\pm 0.5\%$), and spectrometer accuracy ($\pm 1\%$) [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 Pincock et al. [18], the IR spectrum of $\text{CF}_3\text{CF}=\text{CH}_2$ shown in Fig. 4, and the IR spectrum of CFC-11 [19] we calculate instantaneous forcings for $\text{CF}_3\text{CF}=\text{CH}_2$ and CFC-11 of 0.22 and $0.26 \text{ W m}^{-2} \text{ ppb}^{-1}$, respectively. Values of the halocarbon

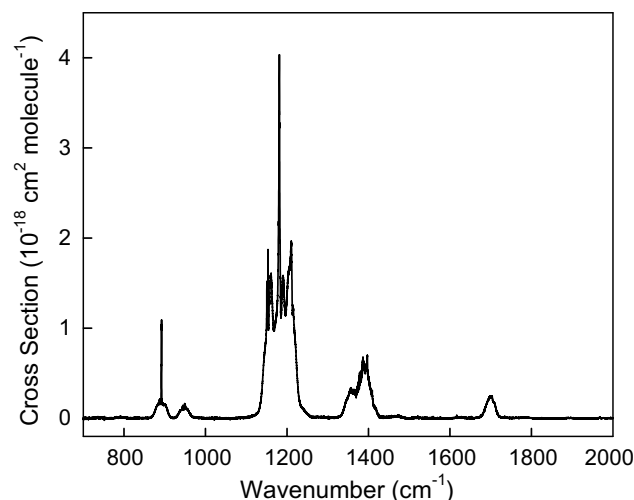


Fig. 4. IR spectrum of $\text{CF}_3\text{CF}=\text{CH}_2$.

global warming potential, HGWP [20], for $\text{CF}_3\text{CF}=\text{CH}_2$ (relative to CFC-11) can then be estimated using the expression:

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

where $\text{IF}_{\text{CF}_3\text{CF}=\text{CH}_2}$, $\text{IF}_{\text{CFC-11}}$, $M_{\text{CF}_3\text{CF}=\text{CH}_2}$, $M_{\text{CFC-11}}$, $\tau_{\text{CF}_3\text{CF}=\text{CH}_2}$, and $\tau_{\text{CFC-11}}$ are the instantaneous forcings, molecular weights, and atmospheric lifetimes of $\text{CF}_3\text{CF}=\text{CH}_2$ and 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 CFC-11 is 1.9×10^{-3} for a 20 yr horizon and 7.6×10^{-4} for a 100 yr time horizon, respectively. Relative to CO_2 , the GWP of CFC-11 on 20 and 100 yr time horizons are 6300 and 4600 [21]. Hence, relative to 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.

Acknowledgements

O.J.N., M.S.J., and M.P.S.A. acknowledge financial support from the Danish Natural Science Research Council for the Copenhagen Center for Atmospheric Research (CCAR). All statements, information, and data given herein are presented without guaranty, warranty, or responsibility of any kind, expressed or implied, for Honeywell International Inc.

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