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Atmospheric chemistry of hexafluorocyclobutene, octafluorocyclopentene, and hexafluoro-1,3-butadiene

(1)

T.J. Wallington *, M.D. Hurley

Systems Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, MI 48121-2053, USA

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1. Introduction

ABSTRACT

The relative rate method was used to measure $k(Cl + hexafluorocyclobutene) = (8.88 \pm 0.69) \times 10^{-13}$, $k(Cl + octafluorocyclopentene) = (1.02 \pm 0.11) \times 10^{-12}$, $k(Cl + hexafluoro-1,3-butadiene) = (7.28 \pm 0.99) \times 10^{-11}$, $k(OH + hexafluorocyclobutene) = (8.6 \pm 1.6) \times 10^{-14}$, $k(OH + octafluorocyclopentene) = (1.01 \pm 0.16) \times 10^{-13}$, and $k(OH + hexafluoro-1,3-butadiene) = (9.64 \pm 1.76) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ in 700 Torr N₂, or air, diluent at 295 K. The atmospheric lifetimes of hexafluorocyclobutene, octafluorocyclopentene, and hexafluoro-1,3-butadiene were estimated to be 135, 104, and 1.1 days, respectively. The 100 year time horizon global warming potentials for hexafluorocyclobutene and octafluorocyclopentene are 42 and 28.

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

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$
 (2)

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

$$HO_2 + NO \rightarrow OH + NO_2$$
 (4)

In the relative rate experiments the following reactions take place.

- $Cl + Reactant \rightarrow products$ (5)
- $Cl + Reference \rightarrow products$ (6)
- $OH + Reactant \rightarrow products$ (7)
- $OH + Reference \rightarrow products$ (8)

Assuming that the reactant and reference compounds are lost solely via reaction with Cl atoms or OH radicals and that neither the reactant, nor reference, are reformed in any processes, then it can be shown that

$$\operatorname{Ln}\left(\frac{[\operatorname{Reactant}]_{t_0}}{[\operatorname{Reactant}]_t}\right) = \frac{k_{\operatorname{Reactant}}}{k_{\operatorname{Reference}}}\operatorname{Ln}\left(\frac{[\operatorname{Reference}]_{t_0}}{[\operatorname{Reference}]_t}\right) \tag{I}$$

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 $\text{Ln}([\text{Reactant}]_{t_0}/[\text{Reactant}]_t)$ versus $\text{Ln}([\text{Reference}]_{t_0}/[\text{Reference}]_t)$ should be linear, pass through the origin, and have a slope of $k_{\text{Reactant}}/k_{\text{Reference}}$.

 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 air

are reported herein.

2. Experimental

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. Fluorinated alkenes are a class of compounds which have been developed to replace CFCs and satu-

rated hydrofluorocarbons [3]. Prior to their large-scale industrial

use an assessment of the atmospheric chemistry, and hence environmental impact, of these compounds is needed. To expand

and improve our knowledge of the atmospheric chemistry and

environmental impact of fluorinated alkenes the atmospheric

chemistry of hexafluorocyclobutene, octafluorocyclopentene, and

hexafluoro-1,3-butadiene were investigated. Smog chamber/FTIR techniques were used to provide information on the following

properties for these compounds: (i) kinetics of reactions with chlo-

rine atoms, (ii) kinetics of reactions with hydroxyl radicals, (iii)

atmospheric lifetimes, and (iv) global warming potentials. Results

Experiments were performed in a 140-l Pyrex reactor interfaced

to a Mattson Sirus 100 FTIR spectrometer [4]. The reactor was sur-

rounded by 22 fluorescent blacklamps (GE F15T8-BL) which were

used to photochemically initiate the experiments. Chlorine atoms





^{*} Corresponding author. E-mail address: twalling@ford.com (T.J. Wallington).

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diluent at 296 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, initial reaction mixtures were left to stand in the chamber for 60 min. There was no observable (<2%) loss of any of the reactants in such experiments. To check for loss via photolysis, reactants in 700 Torr of air were subjected to 5 min of UV irradiation using the output from 22 blacklamps. There was no discernable loss (<1%) of the reactants, indicating that photolysis is not a significant loss of the reactants in experiments using blacklamps. Unless stated otherwise, quoted uncertainties include two standard deviations from linear least squares regressions and uncertainties in the IR analysis of the reactant and reference (typically ±1% of the initial concentrations). The OH radical kinetic experiments were not performed with added NO and the possibility exists that NO₂ formed during the experiments could undergo photolysis leading to the formation of O₃ and NO₃ radicals. The IR spectra showed no evidence of O₃ or N₂O₅ formation indicating the absence of complications associated with the presence of O₃ or NO₃ radicals.

3. Results

3.1. Kinetics of the Cl + hexafluorocyclobutene reaction

The rate of reaction (9) was measured relative to reactions (10) and (11):

$Cl + hexafluorocyclobutene \rightarrow products$	(9)
$Cl + CH_3Cl \rightarrow products$	(10)

$$Cl + CH_3OCHO \rightarrow products$$
 (11)

Reaction mixtures consisted of 5.9–7.6 mTorr of hexafluorocyclobutene, 100 mTorr Cl₂, and either 26.5–29.4 mTorr CH₃Cl, or 3.1– 5.6 mTorr CH₃OCHO, in 700 Torr of N₂ diluent. The observed loss of hexafluorocyclobutene versus those of the reference compounds is plotted in Figure 1. Linear least squares analysis of the data in Fig-



Figure 1. Loss of hexafluorocyclobutene versus CH_3Cl (triangles) and CH_3OCHO (circles) following exposure to Cl atoms.

ure 1 gives $k_9/k_{10} = 1.82 \pm 0.10$ and $k_9/k_{11} = 0.68 \pm 0.05$. Using $k_{10} = 4.9 \times 10^{-13}$ [5] and $k_{11} = 1.3 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ [6] gives $k_9 = (8.92 \pm 0.49) \times 10^{-13}$ and $(8.84 \pm 0.65) \times 10^{-13}$ cm³ molecule⁻¹ 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 $k_9 = (8.88 \pm 0.69) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. While there have been no previous studies of k_9 , we can compare our result with $k(Cl + CF_3CF=CF_2) = (2.7 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ [7]. The reactivity of hexafluorocyclobutene with Cl atoms is significantly lower than with CF₃CF=CF₂, even though in both cases reaction of Cl atoms proceeds via electrophilic addition to the double bond.

3.2. Kinetics of the Cl + octafluorocyclopentene reaction

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

$$Cl + octafluorocyclopentene \rightarrow products$$
 (12)

 $Cl + CH_3Cl \rightarrow products$ (10)

 $Cl + CH_3OCHO \rightarrow products$ (11)

Reaction mixtures consisted of 2.9–6.2 mTorr of octafluorocyclopentene, 100 mTorr Cl₂, and either 6.0–7.3 mTorr CH₃Cl, or 1.6–3.1 mTorr CH₃OCHO, in 700 Torr of N₂ diluent. The observed loss of octafluorocyclopentene versus those of the reference compounds is plotted in Figure 2. Linear least squares analysis of the data in Figure 2 gives $k_{12}/k_{10} = 2.02 \pm 0.12$ and $k_{12}/k_{11} = 0.81 \pm 0.06$. Using $k_{10} = 4.9 \times 10^{-13}$ [5] and $k_{11} = 1.3 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ [6] gives $k_{12} = (9.90 \pm 0.59) \times 10^{-13}$ and $(1.05 \pm 0.08) \times 10^{-12}$ cm³ molecule⁻¹ 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 $k_{12} = (1.02 \pm 0.11) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. There have been no previous studies of k_{12} with which we can compare our result. As might be expected from the similarity of the molecular structure, the reactivity of chlorine atoms towards octafluorocyclopentene is very similar to that towards hexafluorocyclobutene (see Section 3.1).



Figure 2. Loss of octafluorocyclopentene versus CH₃Cl (triangles) and CH₃OCHO (circles) following exposure to Cl atoms.

3.3. Kinetics of the Cl + hexafluoro-1,3-butadiene reaction

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

$$Cl + hexafluoro-1, 3-butadiene reaction \rightarrow products$$
 (13)

$$Cl + C_2H_2 \rightarrow \text{products}$$
 (14)

$$Cl + C_2H_4 \rightarrow \text{products}$$
 (15)

Reaction mixtures consisted of 5.3–6.9 mTorr of hexafluoro-1,3butadiene reaction, 100 mTorr Cl₂, and either 1.6–2.3 mTorr C₂H₂, or 2.9–4.3 mTorr C₂H₄, in 700 Torr of N₂ diluent. The observed loss of hexafluoro-1,3-butadiene reaction versus those of the reference compounds is plotted in Figure 3. Linear least squares analysis of the data in Figure 3 gives $k_{13}/k_{14} = 1.32 \pm 0.11$ and $k_{13}/k_{15} = 0.70 \pm 0.05$. Using $k_{14} = 5.2 \times 10^{-11}$ [8] and $k_{15} = 1.1 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ [8] gives $k_{13} = (6.86 \pm 0.57) \times 10^{-11}$ and $(7.70 \pm 0.55) \times 10^{-11}$ cm³ molecule⁻¹ 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 $k_{13} = (7.28 \pm 0.99) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

While there have been no previous studies of k_{13} , we can compare our result to $k(Cl + CH_2=CHCH=CH_2) = 4.2 \times 10^{-10}$ [9] and $k(Cl + CF_3CF=CF_2) = (2.7 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The presence of electron withdrawing fluorine substituents results in decreased reactivity towards the electrophilic chlorine atoms. The reactivity of hexafluoro-1,3-butadiene and hexafluoropropene towards chlorine atoms scales approximately in proportion to the number of >C=C< double bonds. From the limited data available, it appears that chlorine atoms react with >C=C< double bonds in linear perfluoroalkenes with a rate constant of approximately 3×10^{-11} cm³ molecule⁻¹ s⁻¹. In contrast, chlorine atoms react with the >C=C< double bond in perfluorocyclobutene and perfluorocyclopentene with a rate constant of approximately 1×10^{-12} cm³ molecule⁻¹ s⁻¹.

3.4. Kinetics of the OH + hexafluorocyclobutene reaction

The rate of reaction (16) was measured relative to reaction (17):



Figure 3. Loss of hexafluoro-1,3-butadiene versus C_2H_2 (triangles) and C_2H_4 (circles) following exposure to Cl atoms.

$$OH + hexa fluorocyclobutene \rightarrow products$$
 (16)

$$OH + C_2H_2 \rightarrow products$$
 (17)

Initial reaction mixtures consisted of 7.35 mTorr of hexafluorocyclobutene, 100 mTorr CH₃ONO, and 1.9-3.7 mTorr C₂H₂ in 700 Torr total pressure of air diluent. Figure 4 shows the loss of hexafluorocyclobutene plotted versus the loss of C₂H₂. While photolysis of CH₃ONO is a convenient source of OH radicals in relative rate studies (we can not use other OH radical sources such as H₂O₂ or HNO₃ photolysis because our Pyrex chamber does not transmit at sufficiently short wavelength UV), CH₃ONO itself reacts with OH at a moderate rate (with a rate constant of approximately 3×10^{-13} cm³ molecule⁻¹ s⁻¹ [10]), scavenges OH radicals and makes loss of a less reactive compound small and difficult to measure. Such is the case here and the loss of hexafluorocyclobutene in these experiments is small, but discernable. Least squares analysis of the data in Figure 4 gives $k_{16}/k_{17} = 0.11 \pm 0.02$. Using $k_{17} = 7.8 \times 10^{-13}$ [8] gives $k_{16} = (8.6 \pm 1.6) \times 10^{-14}$ cm³ molecule⁻¹ s^{-1} .

While there have been no previous studies of k_{16} , we can compare our result with $k(OH + CF_3CF=CF_2) = (2.4 \pm 0.3) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ [7]. The reactivity of hexafluorocyclobutene with OH radicals is significantly less than with CF₃CF=CF₂, even though in both cases reaction of OH radicals proceeds via electrophilic addition to the double bond.

3.5. Kinetics of the OH + octafluorocyclopentene reaction

The rate of reaction (18) was measured relative to reaction (17):.

$$OH + octafluorocyclopentene \rightarrow products$$
 (18)

$$OH + C_2H_2 \rightarrow products$$
 (17)

Initial reaction mixtures consisted of 7.2 mTorr of octafluorocyclopentene, 51-100 mTorr CH₃ONO, and 1.5 mTorr C₂H₂ in 700 Torr total pressure of air diluent. Figure 4 shows the loss of octafluorocyclopentene plotted versus loss of C₂H₂. As with hexafluorocyclobutene, the loss of octafluorocyclopentene in these



Figure 4. Loss of hexafluorocyclobutene (circles) and octafluorocyclopentene (triangles) versus C_2H_2 following exposure to OH radicals. The data for octafluorocyclopentene have been displaced vertically by 0.02 units for clarity.

experiments is small, but discernable. Least squares analysis of the data in Figure 4 gives $k_{18}/k_{17} = 0.13 \pm 0.02$. Using $k_{17} = 7.8 \times 10^{-13}$ [8] gives $k_{18} = (1.01 \pm 0.16) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. There have been no previous studies of k_{18} to compare with our result. As might be expected from the similarity of the molecular structure, the reactivity of OH radicals towards octafluorocyclopentene is similar to that towards hexafluorocyclobutene (see Section 3.4).

3.6. Kinetics of the OH + hexafluoro-1,3-butadiene reaction

The rate of reaction (19) was measured relative to reactions (17) and (20):

 $OH + hexafluoro-1, 3-butadiene \rightarrow products$ (19)

$$OH + C_2H_2 \rightarrow products$$
 (17)

$$OH + C_2H_4 \rightarrow products$$
 (20)

Initial reaction mixtures consisted of 6.2–7.3 mTorr of hexa-fluoro-1,3-butadiene, 100 mTorr CH₃ONO, and either 1.5–1.8 mTorr C₂H₂ or 2.6–4.4 mTorr C₂H₄ in 700 Torr total pressure of air diluent. Figure 5 shows the loss of hexafluorocyclobutene plotted versus the loss of the reference compounds. Linear least squares analysis of the data in Figure 5 gives $k_{19}/k_{17} = 14.0 \pm 1.0$ and $k_{19}/k_{20} = 1.06 \pm 0.08$. Using $k_{17} = 7.8 \times 10^{-13}$ [8] and $k_{20} = 7.9 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ [8] gives $k_{19} = (1.09 \pm 0.08) \times 10^{-11}$ and $(8.37 \pm 0.63) \times 10^{-12}$ cm³ molecule⁻¹ 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 $k_{19} = (9.64 \pm 1.76) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

Acerboni et al. [11] conducted a relative rate study of reaction (19) and reported $k_{19} = (1.1 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value of k_{19} was obtained from experiments conducted using three different reference compounds (ethene, propene, and cyclohexane) and is in good agreement with that measured here. However, the rate constant ratio $k_{19}/k_{20} = 1.3394 \pm 0.0253$ measured by Acerboni et al. [11] is approximately 25% higher than the ratio $k_{19}/k_{20} = 1.06 \pm 0.08$ measured here and hence for reasons which are unclear there is small, but discernable, difference between our results and those of Acerboni et al. [11].



Figure 5. Loss of hexafluoro-1,3-butadiene versus C_2H_2 (triangles) and C_2H_4 (circles) following exposure to OH radicals.

While there have been no previous studies of k_{19} , we can compare our result with $k(OH + CH_2=CHCH=CH_2) = 6.78 \times 10^{-11}$ [12] and $k(OH + CF_3CF=CF_2) = (2.4 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [12]. Comparing k_{19} with $k(OH + CH_2=CHCH=CH_2)$ we see that the presence of electron withdrawing fluorine substituents results in decreased reactivity with OH radicals. This behavior is expected considering the electrophilic nature of OH radicals. Unlike the situation for the chlorine atom reactions discussed in Section 3.3, there is no simple relationship between the number of >C=C< double bonds and the reactivity of OH radicals towards linear perfluoroalkenes with k_{19} being approximately a factor of four times larger than $k(OH + CF_3CF=CF_2)$.

3.7. Atmospheric lifetimes and global warming potentials

As with other perfluoroalkenes [7], the atmospheric lifetimes of the compounds investigated in the present work will be dictated by the rates of their reactions with OH radicals. Rate constants were measured in the present work at 295 K. However, the appropriate temperature to use for atmospheric lifetime calculations is 272 K [13]. Taking the behavior of the reaction of OH radicals with perfluoropropene as a guide [14], we expect the rate constants for reactions of OH radicals with the title perfluoroalkenes to increase by approximately 10% between 295 and 272 K. Proceeding on this assumption and using a global average OH radical concentration of 10^{6} cm⁻³ [15] gives atmospheric lifetimes of 135, 104 and 1.1 days for hexafluorocyclobutene, octafluorocyclopentene, and hexafluoro-1,3-butadiene, respectively. The approximate nature of these lifetime estimates should be stressed; the average daily concentration of OH radicals in the atmosphere varies significantly with both location and season [16]. The values above are estimates of the global average lifetime; local lifetimes could be significantly different.

The halocarbon global warming potentials relative to CFC-11 (HGWP) for the title perfluoroalkenes (PFA) can be estimated using the expression [17]:

$$\text{HGWP}_{\text{PFA}} = \left(\frac{\text{RE}_{\text{PFA}}}{\text{RE}_{\text{CFC-11}}}\right) \left(\frac{\tau_{\text{PFA}} M_{\text{CFC-11}}}{\tau_{\text{CFC-11}} M_{\text{PFA}}}\right) \left(\frac{1 - \exp(-t/\tau_{\text{PFA}})}{1 - \exp(-t/\tau_{\text{CFC-11}})}\right)$$

where RE_{PFA}, RE_{CFC-11}, M_{PFA}, M_{CFC-11}, τ_{PFA} , and τ_{CFC-11} are the radiative efficiencies, molecular weights, and atmospheric lifetimes of the perfluoroalkenes and CFC-11, and *t* is the time horizon over which the forcing is integrated. Given its very short (1.1 day) atmospheric lifetime, hexafluoro-1,3-butadiene will not make any significant contribution to radiative forcing of climate change and estimation of a global warming potential for this molecule is not meaningful. Using the lifetimes estimated above; τ (CFC-11) = 45 years [18]; RE = 0.28 and 0.32 W m⁻² ppb⁻¹ for hexafluorocyclobutene and octafluorocyclopentene, respectively [19]; and RE_{CFC-11} = 0.25 W m⁻² ppb⁻¹ [18] gives 100 year time horizon HGWPs of 8.7 × 10⁻³ and 5.9 × 10⁻³ for hexafluorocyclobutene and octafluorocyclopentene. Scaling these values using the GWP value of CFC-11 of 4750 [18] gives GWPs of 42 and 28 for hexafluorocyclobutene and octafluorocyclopentene.

4. Discussion

Kinetic data are reported for reactions of chlorine atoms and OH radicals with hexafluorocyclobutene, octafluorocyclopentene, and hexafluoro-1,3-butadiene. With the exception of the reaction of OH radicals with hexafluoro-1,3-butadiene, the present work is the first study of these reactions. For reactions with both chlorine atoms and OH radicals the order of reactivity is hexafluorocyclobutene \approx octafluorocyclopentene < CF₃CF=CF₂ < CF₂=CF-CF=CF₂. There is no evidence for a dependence of reaction rate on ring

strain. Chlorine atoms and OH radicals are electrophilic and the reactions proceed via addition at the >C=C< double bonds. The fact that hexafluorocyclobutene and octafluorocyclopentene react more slowly than CF₃CF=CF₂ presumably reflects lower electron density around the double bond. Computational studies would be of interest to provide more insight into the factors influencing the kinetics of the reactions of chlorine atoms and OH radicals with fluorinated alkenes. As with all other fluorinated alkenes studied to date [20,21], the compounds investigated here have short, or modest, atmospheric lifetimes and hence will not contribute significantly to radiative forcing of climate change (depending on usage).

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