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CHF₂OCHF₂ (HFE-134): IR Spectrum and Kinetics and Products of the Chlorine-Atom-Initiated Oxidation

Mads P. Sulbaek Andersen,^{*,†} Michael D. Hurley,[‡] Vibeke F. Andersen,[§] Ole J. Nielsen,[§] and Timothy J. Wallington^{*}

Department of Chemistry, 572 Rowland Hall, University of California Irvine, Irvine, California 92697-2025, System Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, Michigan 48121-2053, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

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Smog chamber/FTIR techniques were used to measure $k(\text{Cl} + \text{CHF}_2\text{OCHF}_2) = (5.7 \pm 1.5) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in 700 Torr of N₂/O₂ diluent at $296 \pm 1 \text{ K}$. This result is 100 times lower than the previous literature value. The chlorine-atom-initiated atmospheric oxidation of CHF₂OCHF₂ gives COF₂ in a molar yield of $(185 \pm 22) \%$. The IR spectrum was recorded, and a radiative efficiency of $0.44 \text{ W m}^{-2} \text{ ppb}^{-1}$ was determined. The results are discussed with respect to the atmospheric chemistry and environmental impact of CHF₂OCHF₂.

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 CFCs with environmentally acceptable alternatives. Hydrofluoroethers (HFEs), perfluoropolyethers (PFPEs), and hydrofluoropolyethers (HFPEs) have found use as replacements for CFCs as heat transfer and refrigeration working fluids. Bis-difluoromethyl ether, CHF₂OCHF₂, (HFE-134) does not contain chlorine and therefore does not contribute to chlorine-based catalytic destruction of stratospheric ozone.

The atmospheric lifetime of CHF₂OCHF₂ is determined by its reaction with OH radicals. The kinetics of reaction 1 are well established, $k_1 = 2.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,³ and the atmospheric lifetime of CHF₂OCHF₂ has been estimated to be 26 years.⁴



When combined with a radiative efficiency of $0.45 \text{ W m}^{-2} \text{ ppb}^{-1}$ (recommended by the IPCC) this lifetime leads to an estimate of 6320 for global warming potential of CHF₂OCHF₂ on a 100 year time horizon.⁴

CHF₂OCHF₂ and CHF₂OCF₂OCHF₂ react with OH radicals at comparable rates.^{3,5} Given the similar chemical environment of the C–H bonds, it is expected that the reactivity of these molecules toward OH radicals is similar. Surprisingly, the literature data indicate that with respect to reaction with chlorine atoms, CHF₂OCHF₂ is ~1000 times more reactive than CHF₂OCF₂OCHF₂.^{5,6} It is difficult to understand why CHF₂OCHF₂ and CHF₂OCF₂OCHF₂ react with chlorine atoms at such different rates. It appears that either there are differences

in the mechanisms of the OH and chlorine atom reactions or there are errors in the kinetic data.

Only one study of the reactivity of Cl atoms toward CHF₂OCHF₂ exists in the literature. Using the very low-pressure reactor technique, Kambanis et al.⁷ reported $k_3 = 1.03 \times 10^{-12} \exp(-867/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which yields $k_3 = 5.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. To improve our understanding of the atmospheric chemistry of HFEs and, in particular, the chlorine radical kinetics for CHF₂OCHF₂, we used smog chamber/FTIR techniques to investigate the kinetics and products of the chlorine-atom-initiated oxidation of CHF₂OCHF₂. The IR spectrum of CHF₂OCHF₂ was also reassessed.

2. Experimental Methods

Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer.⁸ The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to initiate the experiments photochemically. The loss of CHF₂OCHF₂ and the formation of 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 27.4 m.

Cl atoms were generated by the photolysis of molecular chlorine in air diluent



CHF₂OCHF₂ was obtained from Matrix Scientific with a stated purity of >97%. The sample of CHF₂OCHF₂ was subjected to freeze–pump–thaw cycling prior to use. All experiments were performed at $296 \pm 1 \text{ K}$ in 700 Torr total pressure of N₂/air diluent. The decay of the reactants and references was measured using their characteristic absorptions in the infrared over the following frequency ranges (in cm^{−1}): CHF₂OCHF₂, 991–1025 and 1350–1435; COF₂, 773–775; CF₂ClCH₃, 850–950; and CF₃CF₂H, 710–730.

* Corresponding authors. (M.P.S.A.) E-mail: mads@sulbaek.dk. Tel/Fax: (949) 824-2905. (T.J.W.) E-mail: twalling@ford.com. Tel: (313) 390-5574. Fax: (313) 323-1129.

[†] University of California.

[‡] Ford Motor Company.

[§] University of Copenhagen.

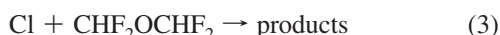
The relative rate method is a well-established technique for measuring the reactivity of Cl atoms with organic compounds. Kinetic data are derived by monitoring the loss of the compound of interest relative to one or more reference compounds. Provided that the $\text{CHF}_2\text{OCHF}_2$ and the reference are lost only by reaction with chlorine atoms and neither $\text{CHF}_2\text{OCHF}_2$ nor the reference compounds are reformed in any process, then it can be shown that

$$\ln\left(\frac{[\text{CHF}_2\text{OCHF}_2]_{t_0}}{[\text{CHF}_2\text{OCHF}_2]_t}\right) = \frac{k_{\text{CHF}_2\text{OCHF}_2}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right)$$

where $[\text{CHF}_2\text{OCHF}_2]_{t_0}$, $[\text{CHF}_2\text{OCHF}_2]_t$, $[\text{reference}]_{t_0}$, and $[\text{reference}]_t$ are the concentrations of the $\text{CHF}_2\text{OCHF}_2$ and the reference compound at times t_0 and t , and $k_{\text{CHF}_2\text{OCHF}_2}$ and $k_{\text{reference}}$ are the rate constants for reactions of $\text{CHF}_2\text{OCHF}_2$ and the reference with chlorine atoms. Plots of $\ln([\text{CHF}_2\text{OCHF}_2]_{t_0}/[\text{CHF}_2\text{OCHF}_2]_t)$ versus $\ln([\text{reference}]_{t_0}/[\text{reference}]_t)$ should be linear, pass through the origin, and have a slope of $k_{\text{CHF}_2\text{OCHF}_2}/k_{\text{reference}}$. 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. The quoted uncertainty ($\pm 5\%$) in the reported IR cross sections is composed of: sample concentration ($\pm 2\%$), path length ($\pm 1.5\%$), residual baseline offset after subtraction of the background ($\pm 0.5\%$), and spectrometer accuracy ($\pm 1\%$).⁹

3. Results and Discussion

3.1. Measurement of $k(\text{Cl} + \text{CHF}_2\text{OCHF}_2)$. Relative rate methods were used to investigate the kinetics of reaction 3. The techniques are described in detail elsewhere.¹⁰ The rate of reaction 3 was measured relative to reactions 4 and 5



Reaction mixtures consisted of 7.5–13.5 mTorr $\text{CHF}_2\text{OCHF}_2$, 498–525 mTorr Cl_2 , and 8.2–13.7 mTorr of either $\text{CF}_3\text{CF}_2\text{H}$ or $\text{CH}_3\text{CF}_2\text{Cl}$ in 700 Torr of air or N_2 diluent. The observed loss of $\text{CHF}_2\text{OCHF}_2$ versus those of reference compounds is shown in Figure 1. Linear least-squares analysis of the data in Figure 1 gives $k_3/k_4 = 2.24 \pm 0.09$ and $k_3/k_5 = 1.46 \pm 0.05$. Using literature values of $k_4 = (2.5 \pm 0.6) \times 10^{-16} \text{ s}^{-1}$ and $k_5 = (3.90 \pm 0.52) \times 10^{-16} \text{ s}^{-1}$ gives $k_2 = (5.6 \pm 1.4) \times 10^{-16}$ and $(5.7 \pm 0.8) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Indistinguishable values of k_3 were obtained using the two different references and two different diluent gases. The fact that consistent values of k_3 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 that is the average of the individual determinations together with error limits that encompass the extremes of the determinations, and hence $k_3 = (5.7 \pm 1.5) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In contrast, Kambanis et al.⁷ reported $k_3 = 5.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$

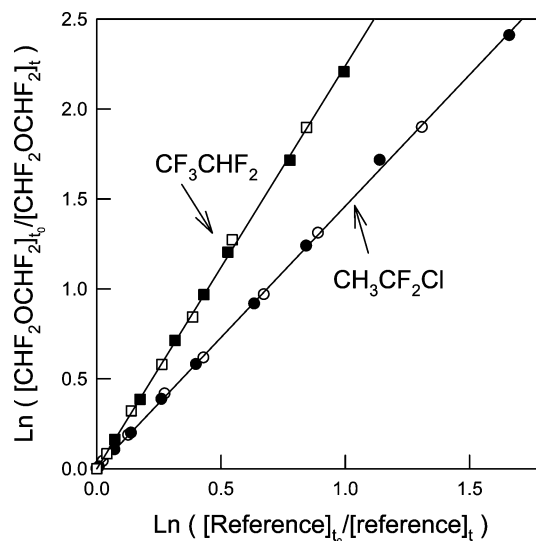


Figure 1. Decay of $\text{CHF}_2\text{OCHF}_2$ versus $\text{CF}_3\text{CF}_2\text{H}$ (squares) and $\text{CH}_3\text{CF}_2\text{Cl}$ (circles) in the presence of Cl atoms in 700 Torr total pressure of air (open symbols) or N_2 (solid symbols).

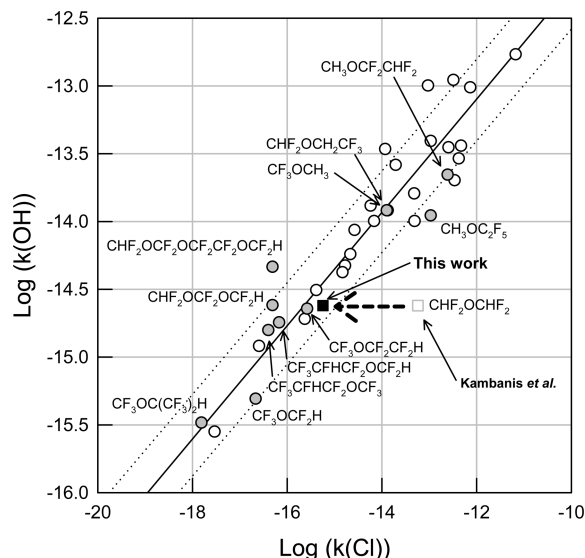


Figure 2. $\text{Log}(k(\text{OH}))$ versus $\text{Log}(k(\text{Cl}))$ for saturated HFCs (gray circles), HFCs and HCFCs (open circles), and $\text{CHF}_2\text{OCHF}_2$ (squares with k_2 values taken from either the present work (filled) or from Kambanis et al. (open)).

s^{-1} at 298 K; this is a factor of 100 greater than that measured in the present work.

We can compare the reactivity of Cl atoms and OH radicals toward $\text{CHF}_2\text{OCHF}_2$ to expectations based on the correlation of the rates of abstraction of hydrogen atoms from hydrofluorocarbons and hydrofluorochlorocarbons, reported by Sulbaek Andersen et al.¹² The open circles in Figure 2 are the data used by Sulbaek Andersen et al.¹² to derive the relationship $\log(k(\text{OH})) = (0.412 \pm 0.049) \times \log(k(\text{Cl})) - (8.16 \pm 0.72)$, which is shown as the solid line. The dotted lines show variation from the solid line by a factor of 2. It can be seen from Figure 2 that the reactivity of most saturated hydrofluorocarbons and hydrofluorochlorocarbons toward OH radicals can be predicted to within a factor of 2 from their reactivity toward chlorine atoms. The gray circles in Figure 2 show literature data for HFCs (adapted from ref 13). Despite

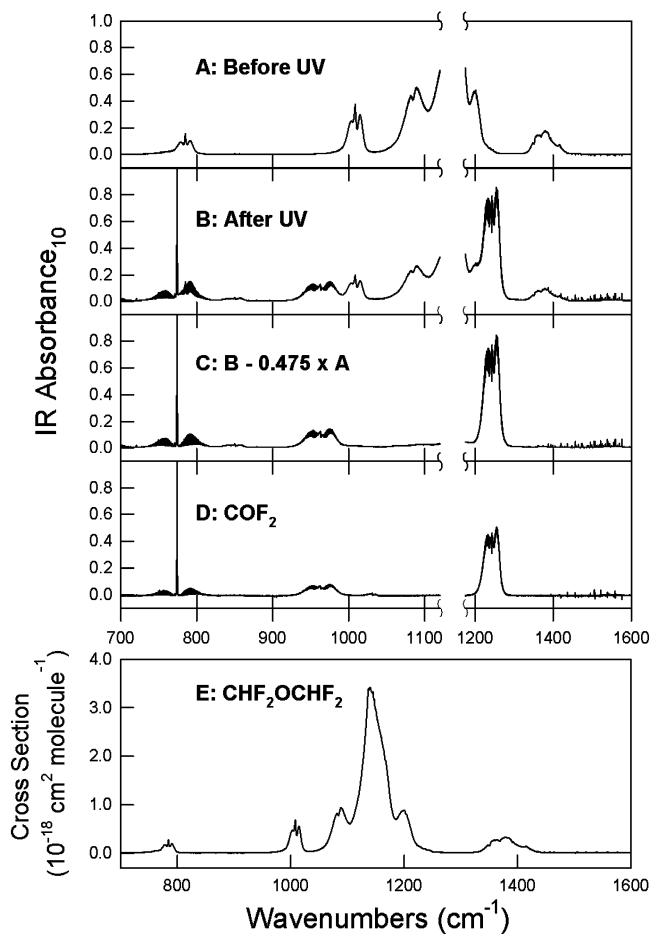


Figure 3. IR spectra of a mixture of 14.4 mTorr CHF₂OCHF₂ and 510 mTorr Cl₂ in 700 Torr air diluent (A) before and (B) after 15 min of UV irradiation. Subtraction of features attributed to CHF₂OCHF₂ from panel B gives the product spectra shown in panel C. A reference spectrum of COF₂ is shown in panel D. Panel E shows the calibrated IR spectrum for CHF₂OCHF₂.

the scatter in the data, it appears that the trend of reactivity of HFEs toward OH radicals and Cl atoms is broadly similar to that for HFCs and HCFCs. It can be seen from Figure 2, that our measured value of k_3 is consistent with that expected on the basis of the well-established value of k_1 ³ and the correlation between k_{Cl} and k_{OH} evident in Figure 2.

The reason for the large discrepancy between our result and that from Kambanis et al.⁷ is unclear. However, it is worth noting that there are also substantial discrepancies between the rate constants reported by Kambanis et al.⁷ for reactions of chlorine atoms with CF₃CH₂OCHF₂ and CF₃CH₂OCH₂CF₃ and the results from subsequent studies by other workers.^{14–20} The simplest explanation for the discrepancies is the presence of significant systematic errors in the work by Kambanis et al.⁷

3.2. Cl Atom-Initiated Oxidation of CHF₂OCHF₂. The atmospheric degradation mechanism was studied using the UV irradiation of CHF₂OCHF₂/Cl₂/air mixtures. Reaction mixtures consisted of 14.4–30.0 mTorr CHF₂OCHF₂ and 507–510 Torr Cl₂ in 700 Torr of air diluent. Figure 3 shows IR spectra obtained before (panel A) and after (panel B) subjecting a mixture containing 14.4 mTorr CHF₂OCHF₂ and 0.51 Torr Cl₂ in 700 Torr of air to UV irradiation for 15 min. Subtraction of the IR features attributed to CHF₂OCHF₂ from panel B gives the product spectrum in panel C. Comparison of the product features

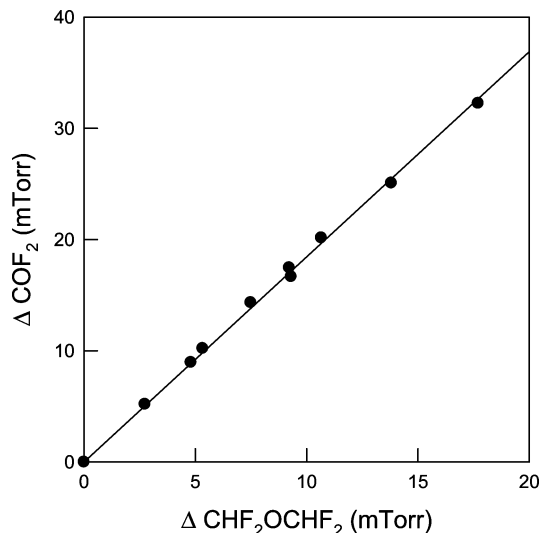


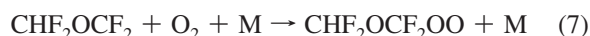
Figure 4. Formation of COF₂ versus loss of CHF₂OCHF₂ following UV irradiation of CHF₂OCHF₂/Cl₂ mixtures in 700 Torr of air diluent.

in panel C with the reference spectrum in panel D shows the formation of COF₂.

It is well known that C–F bonds are unreactive toward Cl atoms (and OH radicals), and the reaction of Cl atoms with CHF₂OCHF₂ occurs via hydrogen abstraction



The alkyl radicals formed in reaction 6 will add O₂ to give peroxy radicals, which will undergo self-reaction to produce the corresponding alkoxy radicals



The alkoxy radicals are expected to decompose via the elimination of COF₂ and formation of an alkoxy radical, which subsequently reacts with O₂ to form a second molecule of COF₂

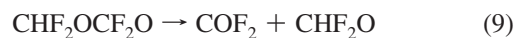


Figure 4 shows a plot of the observed formation of COF₂ versus the loss of CHF₂OCHF₂. As seen from Figure 4, the formation of COF₂ scaled linearly with the CHF₂OCHF₂ loss over the range studied (up to 74% consumption). The linearity of the formation of COF₂ shown in Figure 4 suggests the absence of significant loss of COF₂ via secondary reactions in the chamber. The line through the data in Figure 4 gives a molar yield of COF₂ of (185 ± 22) %. Quoted uncertainties include two standard deviations from the regression analysis and 5% uncertainties in the calibration of the COF₂ and CHF₂OCHF₂ spectra. Within the experimental uncertainties, the observed

TABLE 1: Integrated Band Intensities of CHF₂OCHF₂

range (cm ⁻¹)	integrated absorption cross sections, 10 ⁻¹⁶ cm ² molecule ⁻¹ cm ⁻¹				
	this work	Orkin et al. ²⁸	Heathfield et al. ²⁷	Garland et al. ²⁹	Myhre et al. ³⁰
700–1500	2.57 ± 0.13				
741–803	0.0568 ± 0.0029	0.0531 ± 0.0008	0.0390 ± 0.005		
770–1430	2.52 ± 0.13	2.54 ^b		2.53 ^{a,b}	
965–1443	2.46 ± 0.12	2.490 ± 0.003	2.52 ± 0.04		
25–3250					2.5 ± 0.3

^a Recalculated by ref 27. ^b No stated error limits.

formation of COF₂ accounts for the entire loss of the CHF₂OCHF₂. Given the absence of any other product features, we conclude that COF₂ accounts for the entire loss of the CHF₂OCHF₂. The products from the Cl-initiated oxidation of CHF₂OCHF₂ have previously been studied by Good et al.,²¹ who reported COF₂ as the only observed product in a yield of 200 ± 12%. Our results are consistent with those of Good et al.²¹

4. Atmospheric Implications

The atmospheric oxidation of CHF₂OCHF₂ gives carbonyl fluoride, COF₂, as the major product. COF₂ is removed from the troposphere via contact with water surfaces and hydrolysis to HF and CO₂ in rain/aerosol/cloud/seawater with a lifetime of approximately 5–10 days.²² It is germane to note that the self-reaction of CHF₂OCF₂O₂ radicals, reaction 8, will not be of atmospheric significance. In the atmosphere, the fate of the fluorinated peroxy radicals will be reaction with NO, NO₂, HO₂, or CH₃O₂ radicals.^{6,22,23} The importance of these reactions is determined by the relative abundances of NO, NO₂, HO₂, and CH₃O₂. Reaction with NO gives the corresponding alkoxy radical and NO₂ as major products with a fluorinated organic nitrate as a minor product. Reaction with NO₂ gives a thermally unstable peroxyxynitrate whose fate is decomposition to reform NO₂ and the peroxy radical.^{24,25} Reaction with HO₂ radicals gives a hydroperoxide, which will be returned back to the fluorinated peroxy radical pool via reaction with OH radicals or photolysis.²⁶ Reaction with CH₃O₂ radicals is expected to proceed via two channels, leading to the formation of either a fluorinated alkoxy and a CH₃O radical or a fluorinated alcohol and formaldehyde. The atmospheric fate of the fluorinated alcohol is expected to be heterogeneous elimination of HF, followed by hydrolysis of the resulting acid fluoride to give a carboxylic acid; for example, from CHF₂OCHF₂, one might expect formation of CHF₂OC(O)OH.

As part of the present work, the IR spectrum of CHF₂OCHF₂ was measured in 700 Torr of air diluent at 296 ± 1 K. Results are shown in Figure 3 (panel E), and integrated band intensities are reported in Table 1 together with results from previous studies. The total (700–1500 cm⁻¹) integrated absorption cross-section for CHF₂OCHF₂ is (2.57 ± 0.13) × 10⁻¹⁶ cm² molecule⁻¹ cm⁻¹, which is in good agreement with the literature data. Using the method outlined by Pinnock et al.⁹ and the IR spectrum (700–1500 cm⁻¹) of CHF₂OCHF₂ shown in Figure 3 (panel D), we calculate a radiative efficiency for CHF₂OCHF₂ of 0.44 ± 0.02 W m⁻² ppb⁻¹. This value is indistinguishable from that used in the latest IPCC report, 0.45 W m⁻² ppb⁻¹,⁴ which was based on the IR spectra reported by Heathfield et al.²⁷ and Orkin et al.²⁸

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