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Abstract

Smog chamber/FTIR techniques were used to measure $k(\text{Cl} + \text{C}_2\text{F}_5\text{CHO}) = (1.96 \pm 0.28) \times 10^{-12}$ and $k(\text{OH} + \text{C}_2\text{F}_5\text{CHO}) = (5.26 \pm 0.80) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in 700 Torr of N_2 or air at $296 \pm 2 \text{ K}$. The Cl initiated oxidation of $\text{C}_2\text{F}_5\text{CHO}$ in the presence of NO in air diluent gave COF_2 , CF_3ONO_2 , and $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ in molar yields of $180 \pm 19\%$, $6.1 \pm 0.6\%$, and $1.0 \pm 0.3\%$, respectively. The IR spectrum for $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ is reported. Results are discussed with respect to the potential for the atmospheric degradation of fluorinated aldehydes, $\text{C}_n\text{F}_{2n+1}\text{CHO}$, to contribute to the observed environmental burden of fluorinated carboxylic acids, $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{OH}$.

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1. Introduction

Concerns regarding the environmental impact of chlorofluorocarbon (CFC) release into the atmosphere have led to the replacement of CFCs in industrial processes and consumer products. Hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) are two classes of compounds which have gained widespread use as CFC substitutes. Polyfluorinated alcohols are currently used in a variety of industrial products (paints, coatings, polymers, adhesives, waxes, polishes, electronic materials, and caulks [1]). Perfluorinated

aldehydes are formed during the atmospheric oxidation of HFCs, HCFCs, and fluorinated alcohols [2,3]. For example, $\text{C}_2\text{F}_5\text{CHO}$ has been identified as the primary oxidation product of pentafluoropropanol ($\text{C}_2\text{F}_5\text{CH}_2\text{OH}$) [4] and is a likely oxidation product of $\text{C}_2\text{F}_5\text{CH}_3$ (HFC-245cb) and $\text{C}_2\text{F}_5\text{CH}_2\text{Cl}$ (HCFC-235ca) [2].

Long-chain perfluoroalkyl carboxylic acids (PFCAs, $\text{C}_n\text{F}_{2n+1}\text{COOH}$, where $x = 6\text{--}12$) have recently been observed in fish [5,6] and mammals [7] in a variety of locations around the world. PFCAs are not generally used directly in consumer or industrial materials, other than in aqueous film forming foams or as polymerization aids in fluoropolymer manufacture [8]. Thermolysis of fluoropolymers produces PFCAs, however the

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magnitude of this source appears insufficient to account for the observed global environmental burden of these compounds [9]. The PFCAs observed in the environment are presumably the degradation products of precursor chemicals. However, the identity of the precursors and mechanism by which they are converted into PFCAs are unknown at the present time.

Perfluorinated aldehydes of the general formula $C_nF_{2n+1}CHO$ have a molecular formula which is similar to that of perfluoroalkyl carboxylic acids. Atmospheric oxidation of perfluorinated aldehydes offers a potential route to the formation of PFCAs. Unfortunately, there is little information available in the literature concerning the atmospheric chemistry and degradation mechanism of perfluorinated aldehydes. At the present time it is not possible to assess the contribution, if any, of the atmospheric oxidation of perfluorinated aldehydes to the observed budget of PFCAs. To improve our understanding of the atmospheric chemistry, and hence environmental impact, of fluorinated organics in general and specifically the ability of perfluorinated aldehydes to contribute to the observed burden of PFCAs we have conducted a study of the oxidation mechanism of C_2F_5CHO . Chemical intuition, combined with our recent experience with long-chain fluorinated alcohols [10] and acids [11] suggests that C_2F_5CHO will serve as a useful model with which to understand the degradation mechanism of longer chain perfluoroaldehydes.

We have used smog chamber FTIR techniques to study the kinetics of reactions of Cl atoms and OH radicals with C_2F_5CHO , oxidation products of Cl initiated oxidation of C_2F_5CHO , and IR spectrum of $C_2F_5C(O)O_2NO_2$. Results are reported herein and discussed with respect to the atmospheric chemistry and environmental impact of fluorinated organic compounds.

2. Experimental

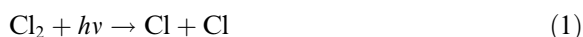
2.1. Synthesis of C_2F_5CHO

Perfluoropropionaldehyde, C_2F_5CHO , was synthesized by the drop wise addition of 10 g of

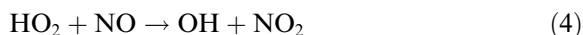
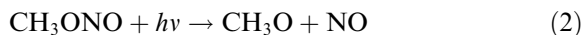
perfluoropropionaldehyde hydrate ($C_2F_5CH(OH)_2$) into a heated flask ($\approx 60^\circ C$) containing 25 g P_2O_5 . The mixture was heated while a slow ($\approx 20\text{ cm}^3\text{ min}^{-1}$) flow of nitrogen gas was passed across the top of the hydrate/aldehyde solution and then through a liquid nitrogen trap. C_2F_5CHO was collected in the trap. IR analysis revealed the presence of a small amount of C_2H_4 impurity in the crude sample of C_2F_5CHO collected in the trap. This is presumably attributable to ethyl hemiacetal impurities in the hydrate sample, which upon dehydration with P_2O_5 yields the aldehyde and ethene. By freezing the sample at liquid nitrogen temperature, pumping on the sample and then discarding the first fraction that evaporates as the sample was allowed to warm to room temperature we were able to remove all traces of C_2H_4 impurity.

2.2. Kinetic and mechanistic experiments

The apparatus and experimental techniques used in this work have been described elsewhere [12,13]. Experiments were performed in a 140-liter 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. 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:



Reactant and product concentrations were monitored using in situ Fourier transform infrared 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. Calibrated reference spectra were acquired by expanding known volumes of reference materials into the chamber. Analysis of the IR spectra was achieved through a process of spectral

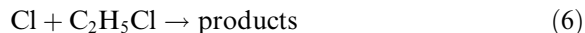
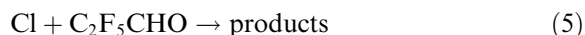
stripping in which small fractions of the reference spectrum were subtracted incrementally from the sample spectrum.

Experiments were performed at 296 ± 2 K in 700 Torr of air diluent. All reactants were obtained from commercial sources at purities $>99\%$. Ultra-high purity nitrogen and air diluent gases were used as received. In smog chamber experiments unwanted loss of reactants and products via photolysis and heterogeneous reactions has to be considered. Control experiments were performed in which product mixtures obtained after UV irradiation of $\text{C}_2\text{F}_5\text{CHO}$ /reference/ CH_3ONO / NO /air mixtures were allowed to stand in the dark in the chamber for 30 min. There was no observable ($<2\%$) loss of reactants or products. Samples of $\text{C}_2\text{F}_5\text{CHO}$ were subjected to UV irradiation in 700 Torr of air diluent for 15 min without any observable loss ($<1\%$), suggesting that photolysis of $\text{C}_2\text{F}_5\text{CHO}$ is not a significant complication in the present work.

3. Results and discussion

3.1. Relative rate study of the $\text{Cl} + \text{C}_2\text{F}_5\text{CHO}$ reaction in 700 Torr of air

The kinetics of reaction (5) were measured relative to reactions (6) and (7):



Reaction mixtures consisted of 5.9–18 mTorr of $\text{C}_2\text{F}_5\text{CHO}$, 140–241 mTorr of Cl_2 , and 9.3–29 mTorr of either $\text{C}_2\text{H}_5\text{Cl}$ or CH_3Cl in 700 Torr of N_2 . The observed loss of $\text{C}_2\text{F}_5\text{CHO}$ versus that of the reference compounds in the presence of Cl atoms is shown in Fig. 1. Linear least-squares analysis of the data in Fig. 1 gives $k_5/k_6 = 0.258 \pm 0.021$ and $k_5/k_7 = 3.86 \pm 0.28$, quoted uncertainties are two standard deviations from the linear regressions. Using $k_6 = 8.04 \times 10^{-12}$ [14] and $k_7 = 4.8 \times 10^{-13}$ [2] we derive $k_5 = (2.07 \pm 0.17) \times 10^{-12}$ and $(1.85 \pm 0.11) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

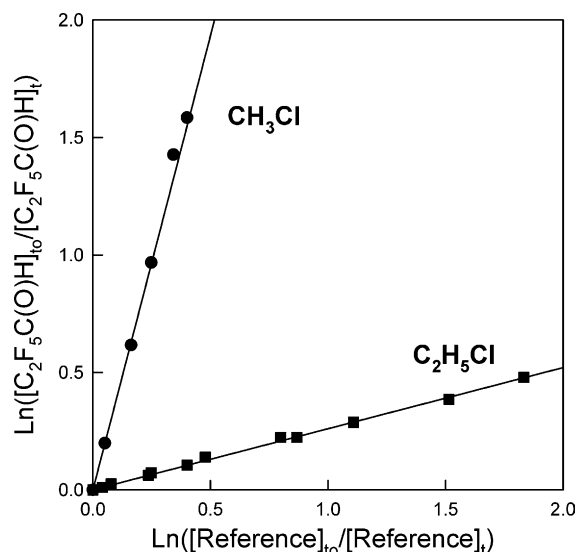


Fig. 1. Decay of $\text{C}_2\text{F}_5\text{CHO}$ versus $\text{C}_2\text{H}_5\text{Cl}$ (squares) or CH_3Cl (circles) in the presence of Cl atoms in 700 Torr of N_2 diluent at 296 ± 2 K.

Consistent results were obtained using both references. We choose to cite a final value for k_5 , which is the average of those, determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k_5 = (1.96 \pm 0.28) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

While there are no previous determinations of k_5 , Wallington and Hurley [15] have reported $k(\text{Cl} + \text{CF}_3\text{CHO}) = (1.8 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is indistinguishable from the value of $k(\text{Cl} + \text{C}_2\text{F}_5\text{CHO})$ reported herein. In contrast, Scollard et al. [16] have reported $k(\text{Cl} + \text{CF}_3\text{CHO}) = (2.70 \pm 0.11) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is substantially greater than the value of $k(\text{Cl} + \text{C}_2\text{F}_5\text{CHO})$ measured in the present work. It is of interest to note that in all cases for which data are available (CF_3H , $\text{C}_2\text{F}_5\text{H}$, $\text{CF}_3\text{CH}_2\text{OH}$, $\text{C}_2\text{F}_5\text{CH}_2\text{OH}$, $\text{CF}_3\text{C(O)OH}$, and $\text{C}_2\text{F}_5\text{C(O)OH}$ [2,11]) the rate of H-atom abstraction by Cl atoms and OH radicals from CF_3X is equal to, or slower than, that from $\text{C}_2\text{F}_5\text{X}$, where X is a hydrogen containing substituent. The value of $k(\text{Cl} + \text{C}_2\text{F}_5\text{CHO}) = (1.96 \pm 0.28) \times 10^{-12}$ measured in the present work is thus not consistent with expectations based upon the value of

$k(\text{Cl} + \text{CF}_3\text{CHO})$ value reported by Scollard et al. [16]. Wallington and Hurley [15] have argued that loss of CF_3CHO via reaction with CF_3O radicals caused Scollard et al. to overestimate $k(\text{Cl} + \text{CF}_3\text{CHO})$. The results from the present work lend support to, but do not prove, this argument.

Finally, it is worth noting that CF_3CHO and $\text{C}_2\text{F}_5\text{CHO}$ are factors of 40 and 70 less reactive towards Cl atoms than their non-fluorinated counterparts CH_3CHO and $\text{C}_2\text{H}_5\text{CHO}$ [17]. Reaction of Cl atoms with CH_3CHO proceeds essentially exclusively (>99%) via abstraction of the aldehydic hydrogen [17]. Abstraction of the aldehydic hydrogen is also important in the reaction of Cl atoms with $\text{C}_2\text{H}_5\text{CHO}$. It is clear that CF_3 and C_2F_5 groups have a strong deactivating effect on the aldehydic functional group. This effect presumably reflects an increase in the $\text{C}(\text{O})\text{--H}$ bond

strength upon fluorination (fluorination typically leads to increased C–H bond strengths on adjacent carbon atoms [18]).

3.2. Product study of the $\text{Cl} + \text{C}_2\text{F}_5\text{CHO}$ reaction in the presence of NO_x in 700 Torr of air

To investigate the mechanism of Cl atom initiated oxidation of $\text{C}_2\text{F}_5\text{CHO}$ in the presence of NO_x , mixtures containing 9 mTorr $\text{C}_2\text{F}_5\text{CHO}$, 148 mTorr Cl_2 and 53 mTorr NO in 700 Torr of air diluent were introduced into the reaction chamber and irradiated using the UV blacklamps. Fig. 2 shows spectra acquired before (A) and after (B) a 165 s irradiation of the gas mixture described above. The consumption of $\text{C}_2\text{F}_5\text{CHO}$ was 36%. Comparison of the IR features in Fig. 2B with the reference spectra of COF_2 and ClNO given in Figs. 2C and D shows the formation of these species.

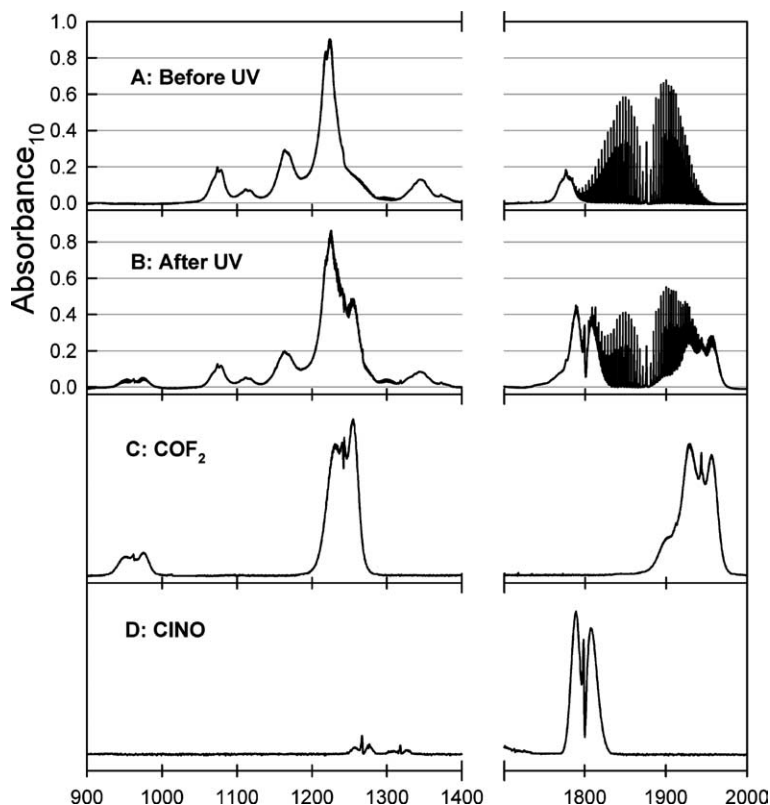


Fig. 2. IR spectra obtained before (A) and after (B) a 110 s irradiation of a mixture of 9.3 mTorr $\text{C}_2\text{F}_5\text{CHO}$, 148 mTorr Cl_2 and 53 mTorr NO in 700 Torr of air. The consumption of $\text{C}_2\text{F}_5\text{CHO}$ was 36%. (C and D) Reference spectra of COF_2 and ClNO , respectively.

Product features attributable to CF_3ONO_2 and $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$ were also detected.

Fig. 3 shows the observed formation of COF_2 , CF_3ONO_2 , and $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$ versus loss of $\text{C}_2\text{F}_5\text{CHO}$ following UV irradiation of $\text{C}_2\text{F}_5\text{CHO}/\text{Cl}_2/\text{NO}$ mixtures in 700 Torr of air diluent. The straight lines in Fig. 3 are linear least-squares fits which give the following molar yields: COF_2 , $(180 \pm 20)\%$; CF_3ONO_2 , $(6.1 \pm 0.6)\%$; and $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$, $(1.0 \pm 0.3)\%$. Quoted errors are two standard deviations from the regression analysis. We estimate that potential systematic errors associated with uncertainties in calibrations of the reference spectra contribute an additional 10% uncertainty. Within the experimental uncertainties, the observed formation of COF_2 , CF_3ONO_2 , and $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$ accounts for 100% of the loss of $\text{C}_2\text{F}_5\text{CHO}$.

The simplest explanation for the observed conversion of $\text{C}_2\text{F}_5\text{CHO}$ into COF_2 is that reaction (5) is followed by (8)–(16):

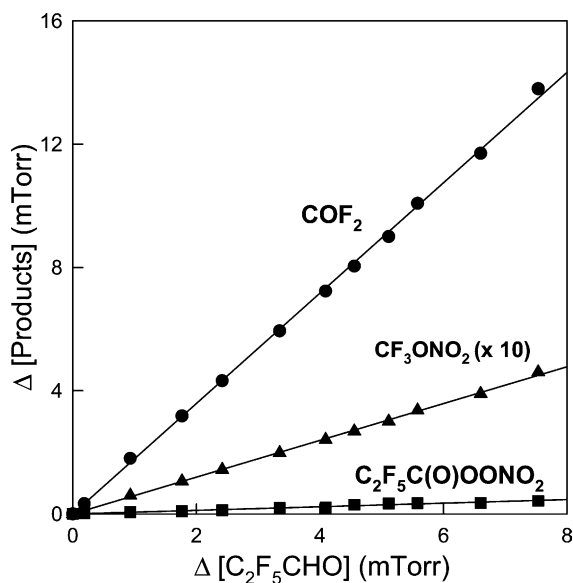
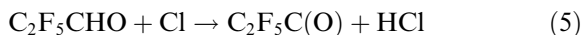
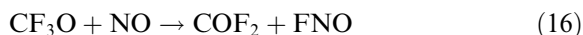
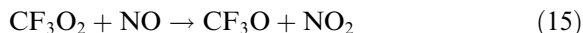
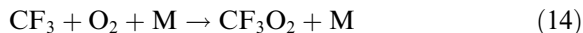
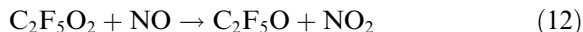
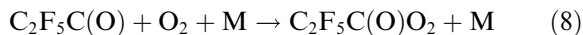
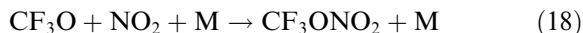
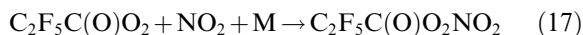


Fig. 3. Yield of COF_2 (circles), CF_3ONO_2 (triangles, values multiplied by 10 for clarity) and $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$ (squares) versus loss of $\text{C}_2\text{F}_5\text{CHO}$ following Cl atom initiated oxidation in the presence of NO_x in 700 Torr of air.



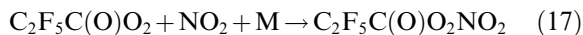
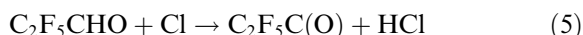
NO_2 is formed during the reaction sequence given above. In the presence of NO_2 , $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$, and CF_3ONO_2 will be formed via reactions (17) and (18).



Evidence for the formation of $\text{C}_2\text{F}_5\text{C(O)OH}$ was sought in the product spectra but not found. An upper limit for the molar formation of $\text{C}_2\text{F}_5\text{C(O)OH}$ of 2% was established.

3.3. Infrared spectrum of $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$

To record the IR spectrum of $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$ a mixture of 8.52 mTorr $\text{C}_2\text{F}_5\text{CHO}$, 228 mTorr Cl_2 and 8.53 mTorr NO_2 in 700 Torr of O_2 diluent was subjected to UV irradiation. The reaction of Cl atoms with $\text{C}_2\text{F}_5\text{CHO}$ in the presence of O_2 leads to the formation of $\text{C}_2\text{F}_5\text{C(O)O}_2$ radicals. By analogy to the behavior of other acetyl peroxy radicals, it is expected that $\text{C}_2\text{F}_5\text{C(O)O}_2$ radicals will react rapidly with NO_2 to give the peroxy nitate $\text{C}_2\text{F}_5\text{C(O)O}_2\text{NO}_2$.



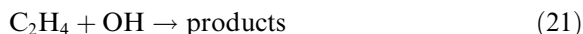
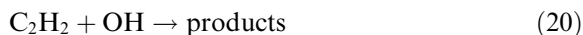
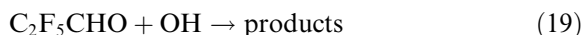
Peroxy nitrates are thermally unstable and decompose to reform acetyl peroxy radicals and NO_2 . It seems reasonable to assume that $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ will decompose at a rate similar to that of $\text{CF}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ and hence will have a lifetime at 296 K of approximately 5 h [19]. In the presence of excess NO_2 thermal decomposition of $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ is masked by its reformation via reaction (17). Following UV irradiation of $\text{C}_2\text{F}_5\text{CHO}/\text{NO}_2/\text{Cl}_2/\text{O}_2$ mixtures two carbon containing products were observed; COF_2 and a product with IR features at 791, 970, 990, 1086, 1111, 1201, 1243, 1301, 1761, and 1849 cm^{-1} whose spectrum is shown in Fig. 4A. The features shown in Fig. 4A increased linearly with the loss of $\text{C}_2\text{F}_5\text{CHO}$. The product features at 791, 1301, 1761, and 1849 cm^{-1} are characteristic of the NO_2 deformation, NO_2 symmetric stretch, NO_2 asymmetric stretch, and CO stretching modes in acetyl peroxy nitrates and we ascribe this product to

$\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$. We assign the spectrum in Fig. 4A to $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$. For comparison the spectrum of $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ is shown in Fig. 4B. The inset in Fig. 4A shows a plot of the observed formation of $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ and COF_2 versus loss of $\text{C}_2\text{F}_5\text{CHO}$. Calibration of $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ was achieved by assuming that reaction (5) leads to the formation of $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ and COF_2 in a combined molar yield of 100%.

The integrated band strength ($1700\text{--}1800\text{ cm}^{-1}$) of the NO_2 asymmetric stretching feature in $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ was $(5.25 \pm 1.04) \times 10^{-17}\text{ cm molecule}^{-1}$ (we attribute 20% uncertainty to the integrated band strength). This value is indistinguishable from that of $(5.14 \pm 0.10) \times 10^{-17}\text{ cm molecule}^{-1}$ for the corresponding feature in $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ [20].

3.4. Relative rate study of the $\text{OH} + \text{C}_2\text{F}_5\text{CHO}$ reaction in 700 Torr of air

The kinetics of reaction (19) were measured relative to reactions (20) and (21):



Initial reactant concentrations were 10–34 mTorr of $\text{C}_2\text{F}_5\text{CHO}$, 89–162 mTorr of CH_3ONO , 15–31 mTorr NO , and either 3–4 mTorr of C_2H_2 or 9 mTorr of C_2H_4 in 700 Torr of air diluent. When working with compounds such as $\text{C}_2\text{F}_5\text{CHO}$ which have modest reactivity towards OH radicals an indirect variation of the relative rate technique can be useful [13]. As discussed above, in the presence of excess NO the oxidation of $\text{C}_2\text{F}_5\text{CHO}$ gives COF_2 and CF_3ONO_2 in essentially quantitative yield. COF_2 and to a lesser extent CF_3ONO_2 , have intense characteristic IR features that are convenient to monitor. In the present work the loss of $\text{C}_2\text{F}_5\text{CHO}$ was inferred by the formation of its oxidation products COF_2 and CF_3ONO_2 .

The calculated loss of $\text{C}_2\text{F}_5\text{CHO}$ versus that of the reference compounds in the presence of OH atoms is shown in Fig. 5. Linear least-squares

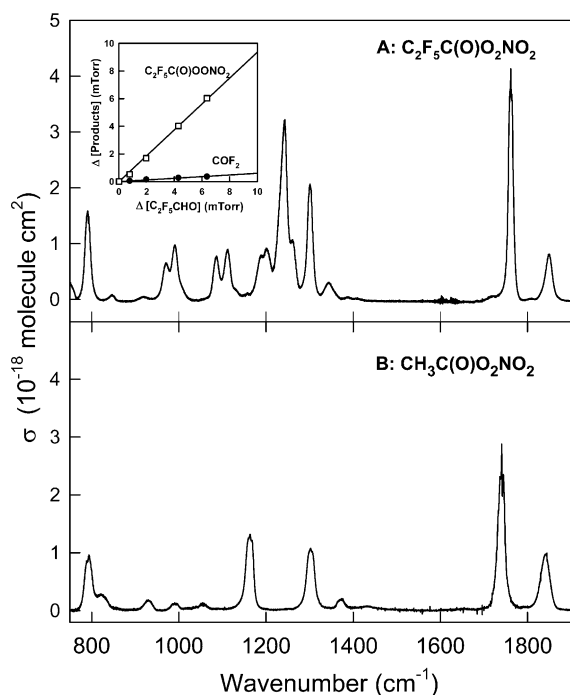


Fig. 4. Infrared spectra of $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ (A) and $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ (PAN) (B). The inset in (A) shows the yield of $\text{C}_2\text{F}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$ (squares) and COF_2 (circles) versus loss of $\text{C}_2\text{F}_5\text{CHO}$ (see text for details).

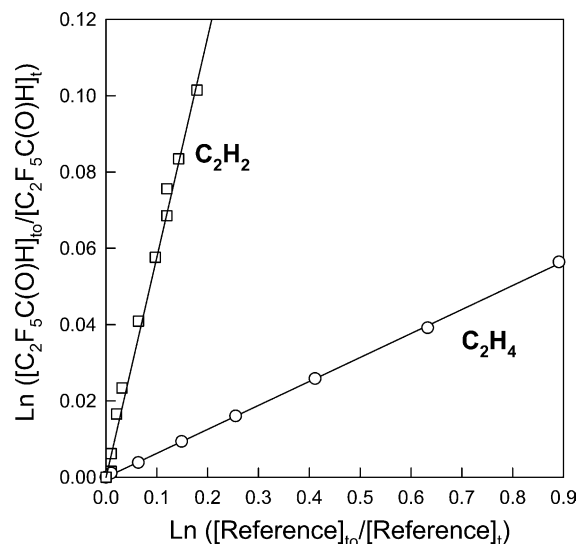


Fig. 5. Decay of $\text{C}_2\text{F}_5\text{CHO}$ versus C_2H_2 (squares) or C_2H_4 (circles) in the presence of OH radicals in 700 Torr of air diluent at 296 ± 2 K.

analysis of the data in Fig. 5 gives $k_{19}/k_{20} = 0.593 \pm 0.065$ and $k_{19}/k_{21} = 0.0646 \pm 0.0037$, where the quoted uncertainties are two standard deviations from the linear regressions. Using $k_{20} = 8.45 \times 10^{-13}$ [21] and $k_{21} = 8.52 \times 10^{-12}$ [22] $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ we derive $k_{19} = (5.01 \pm 0.55) \times 10^{-13}$ and $k_{19} = (5.50 \pm 0.32) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We choose to quote a final value for k_4 which is the average of those determined using the two reference compounds together with error limits which encompass the extremes of the individual determinations, hence, $k_{19} = (5.26 \pm 0.80) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. There are no literature data for k_{19} to compare with our results.

While there have been no previous studies of the reactivity of OH radicals towards $\text{C}_2\text{F}_5\text{CHO}$, we can compare our results with previous studies of the reactivity of CF_3CHO . Dóbe et al. [23] have measured $k(\text{OH} + \text{CF}_3\text{CHO}) = (1.1 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ using discharge flow techniques while Scollard et al. [16] have reported $k(\text{OH} + \text{CF}_3\text{CHO}) = (6.5 \pm 0.5) \times 10^{-13}$ and $(5.4 \pm 1.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on pulsed laser photolysis resonance fluorescence and relative rate experiments, respectively. The IUPAC data evaluation committee recommends $k(\text{OH} + \text{CF}_3\text{CHO}) = (6.0 \pm 1.2) \times 10^{-13} \text{ cm}^3 \text{ mole-}$

cule $^{-1} \text{ s}^{-1}$ [24] at 298 K. The reactivity of $\text{C}_2\text{F}_5\text{CHO}$ towards OH radicals measured in the present work is indistinguishable from that reported previously for CF_3CHO . This observation is consistent with the general pattern noted in Section 3.1 that the rate of H-atom abstraction by Cl atoms and OH radicals from CF_3X is equal to, or slower than, that from $\text{C}_2\text{F}_5\text{X}$.

4. Implications for atmospheric chemistry

The present work serves to improve our understanding of the atmospheric chemistry of $\text{C}_2\text{F}_5\text{CHO}$ and, by analogy, other perfluorinated aldehydes of the general formula $\text{C}_n\text{F}_{2n+1}\text{CHO}$. Cl atoms and OH radicals react with $\text{C}_2\text{F}_5\text{CHO}$ with rate constants of $(1.96 \pm 0.28) \times 10^{-12}$ and $(5.26 \pm 0.80) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Reaction occurs at the aldehydic H-atom. On progressing through the series of fluorinated aldehydes of the general formula $\text{C}_n\text{F}_{2n+1}\text{CHO}$, the greatest change in chemical environment of the aldehydic H-atom occurs on moving from CF_3CHO to $\text{C}_2\text{F}_5\text{CHO}$. Given the finding in the present work that the reactivity of Cl atoms and OH radicals towards $\text{C}_2\text{F}_5\text{CHO}$ are indistinguishable from the corresponding reactions with CF_3CHO , it seems reasonable to generalize our results to all members of the $\text{C}_n\text{F}_{2n+1}\text{CHO}$ series. By taking the average of the results obtained herein for $\text{C}_2\text{F}_5\text{CHO}$ and literature data for $k(\text{Cl} + \text{CF}_3\text{CHO})$ [15] and $k(\text{OH} + \text{CF}_3\text{CHO})$ [17] we arrive at $k(\text{Cl} + \text{C}_n\text{F}_{2n+1}\text{CHO}) = (1.9 \pm 0.5) \times 10^{-12}$ and $k(\text{OH} + \text{C}_n\text{F}_{2n+1}\text{CHO}) = (5.6 \pm 1.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Quoted uncertainties were chosen to encompass the extremes of the individual determinations.

The value of $k(\text{OH} + \text{C}_n\text{F}_{2n+1}\text{CHO})$ derived above can be used to provide an estimate of the atmospheric lifetime of $\text{C}_n\text{F}_{2n+1}\text{CHO}$ with respect to reaction with OH radicals. Assuming an atmospheric lifetime for CH_3CCl_3 with respect to reaction with OH radicals of 5.7 years [25] and a rate constant for the $\text{CH}_3\text{CCl}_3 + \text{OH}$ reaction of $1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [2] leads to an estimate of the atmospheric lifetime of $\text{C}_n\text{F}_{2n+1}\text{CHO}$ of $(1.0 \times 10^{-14}) / (5.6 \times 10^{-13}) \times 5.7 \times 365 \approx 40$ days.

The optimal temperature for such a scaling analysis is 272 K [26] (rather than 296 K used here) but we do not have any data for $k(\text{OH} + \text{C}_n\text{F}_{2n+1}\text{CHO})$ at 272 K. By analogy to other fluorinated organics [25], the temperature dependence of reaction (1) is expected to be similar to that for reaction of OH radicals with CH_3CCl_3 . Hence, the use of 296 K rather than 272 K is not expected to have any material impact on the estimated atmospheric lifetime.

As discussed elsewhere [16], photolysis is likely to be of comparable importance to reaction with OH as an atmospheric loss mechanism of $\text{C}_n\text{F}_{2n+1}\text{CHO}$. The published UV cross-section data for $\text{C}_2\text{F}_5\text{CHO}$ [27,28] suggests that this molecule has an absorption spectrum which is indistinguishable from that of $\text{C}_2\text{F}_5\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ [29]. $\text{C}_2\text{F}_5\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ has an atmospheric lifetime with respect to photolysis of 1–2 weeks [29]. It seems likely that $\text{C}_2\text{F}_5\text{CHO}$ will have a lifetime with respect to photolysis of the order of a few weeks. The absence of photodissociation quantum yield data for $\text{C}_2\text{F}_5\text{CHO}$ under atmospheric conditions prevents a more quantitative assessment of the photolysis rate at this time. Finally, there are two interesting points to note with regard to the atmospheric photolysis of $\text{C}_n\text{F}_{2n+1}\text{CHO}$. First, it has been reported that photolysis of $\text{C}_2\text{F}_5\text{CHO}$ using a high pressure Hg lamp gives a significant yield of $\text{C}_2\text{F}_5\text{H}$ [30]. Second, the intensity of the UV spectra increase substantially with increasing chain length for $n = 1, 2$, and 3 [27,28]. Compounds of the general formula $\text{C}_n\text{F}_{2n+1}\text{H}$ have high global warming potentials. If photolysis is a major atmospheric loss for $\text{C}_n\text{F}_{2n+1}\text{CHO}$ and if photolysis produces $\text{C}_n\text{F}_{2n+1}\text{H}$ this could have important environmental consequences.

The experiments conducted in the present work show that the reaction of Cl atoms with $\text{C}_2\text{F}_5\text{CHO}$ in air in the presence of excess NO initiates a sequence of reactions in which the molecule “unzips” to give COF_2 fragments. It seems likely that a similar fate awaits larger members of the $\text{C}_n\text{F}_{2n+1}\text{CHO}$ series. No evidence for the formation of perfluorocarboxylic acids was observed in the present experiments. We conclude that the gas-phase atmospheric oxidation of $\text{C}_n\text{F}_{2n+1}\text{CHO}$ in the presence of excess NO is not a significant

source of perfluorocarboxylic acids, $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{OH}$. At this point it is germane to note the existence of several other potential routes for conversion of $\text{C}_n\text{F}_{2n+1}\text{CHO}$ into $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{OH}$ in the atmosphere. These include: (i) conversion of $\text{C}_n\text{F}_{2n+1}\text{CHO}$ into the peroxy nitrate $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{O}_2\text{NO}_2$ followed by hydrolysis of $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{O}_2\text{NO}_2$ to give $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{OH}$, (ii) reaction of $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{O}_2$ with HO_2 radicals to give $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{OH}$ and O_3 , and (iii) addition of water to $\text{C}_n\text{F}_{2n+1}\text{CHO}$ to give the hydrate $\text{C}_n\text{F}_{2n+1}\text{CH}(\text{OH})_2$, reaction of the hydrate with OH radicals to give the $\text{C}_n\text{F}_{2n+1}\text{C}(\text{OH})_2$ radical which will probably react with O_2 to give $\text{C}_n\text{F}_{2n+1}\text{C}(\text{O})\text{OH}$ and HO_2 . These possibilities are under investigation in our laboratories.

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