Atmospheric Chemistry of $C_2F_5C(O)CF(CF_3)_2$: Photolysis and Reaction with Cl Atoms, OH Radicals, and Ozone

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Smog-chamber Fourier-transform infrared (FTIR) techniques were used to study the kinetics and photochemistry of $C_2F_5C(O)CF(CF_3)_2$ in 50−700 Torr of air at 296 K. Upper limits for the rate constants of reactions of Cl atoms, OH radicals, and ozone with $C_2F_5C(O)CF(CF_3)_2$ were established: $k_{Cl} < 1.7 \times 10^{-19}$, $k_{OH} < 5 \times 10^{-16}$, and $k_{O_3} < 4 \times 10^{-22}$ cm^3 molecule^{-1} s^{-1}. The ultraviolet absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ has a maximum at 305 nm where $\sigma_e = 6.8 \times 10^{-20}$ cm^2 molecule^{-1}. $C_2F_5C(O)CF(CF_3)_2$ is removed from the atmosphere by photolysis, which occurs on a time scale of approximately 1−2 weeks. As a result of its short atmospheric lifetime, the global warming potential of $C_2F_5C(O)CF(CF_3)_2$ is negligible.

1. Introduction

CF_2ClBr (Halon-1211) and CF_3Br (Halon-1301) are effective and widely used fire-suppression agents. Unfortunately, the release of Halons into the atmosphere leads to stratospheric ozone depletion.[1,2] International agreements, outlined in the Montreal Protocol, 1987 and subsequent amendments, are now in place to phase out the use of such compounds. Alternative fire-suppression agents are needed. Perfluoro-(4-methylpentan-3-one), $C_2F_5C(O)CF(CF_3)_2$, is under consideration as an environmentally friendly fire-suppression agent. This material has a boiling point of 48 °C and a vapor pressure of 304 Torr at 25 °C and will be released into the atmosphere during use. Prior to its large-scale industrial use, an assessment of the atmospheric chemistry, and hence the environmental impact, of this compound is needed. We report herein the results of the first investigation of the atmospheric chemistry of $C_2F_5C(O)CF(CF_3)_2$. The ultraviolet (UV) absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ and kinetics of its reaction of OH radicals were measured at MIT. The kinetics of the reactions of Cl atoms and ozone with $C_2F_5C(O)CF(CF_3)_2$ and the rate and mechanism of UV photolysis were measured in a smog chamber at Ford. The results are reported herein and discussed with respect to the atmospheric chemistry of $C_2F_5C(O)CF(CF_3)_2$.

2. Experimental Section

The experimental systems used are described in detail elsewhere.[3,4] All samples of $C_2F_5C(O)CF(CF_3)_2$ used in this work were supplied by the 3M Company at a purity of >99.99% (by $^1H/^{19}F$ NMR). Samples of $C_2F_5C(O)CF(CF_3)_2$ were degassed at liquid-nitrogen temperature and used without further purification. Uncertainties reported in this paper are two standard deviations unless stated otherwise.

2.1. Fourier-Transform Infrared (FTIR) Photolysis System at MIT. An upper limit to the rate constant for the OH + $C_2F_5C(O)CF(CF_3)_2$ reaction was established by monitoring the rate of $C_2F_5C(O)CF(CF_3)_2$ loss relative to CH_4 and CH_3Cl in the presence of OH radicals at 296 K. OH radicals were generated by photolysis of ozone at 254 nm in the presence of water vapor.

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (1)$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad (2)$$

The long-path absorption cell, made of Pyrex glass, had a volume of 7.6 L and a base length of 60 cm, which was adjusted to give a total of 24 passes, and an optical path length of 14.4 m. Concentrations of the reactants and products were monitored using a FTIR spectrometer (Nicolet 20SX). The mercury photolysis lamp (Ace Hanovia 450-W medium-pressure mercury lamp) was enveloped in a Vycor tube that transmits 254-nm radiation but absorbs the 185-nm Hg line and was placed inside the absorption cell. Control experiments performed in the absence of O_3 established that photolysis of $C_2F_5C(O)CF(CF_3)_2$ occurs in the chamber at a rate of $\sim 2 \times 10^{-4}$ s^{-1}. Appropriate corrections were applied to the data acquired in the relative rate study of $k(OH+C_2F_5C(O)CF(CF_3)_2)$ to account for such photolytic loss of $C_2F_5C(O)CF(CF_3)_2$.

The organic reactants were mixed with helium in a 3-L glass reservoir to yield mole fractions of ~1%. Ozone was prepared by first trapping the effluent from an ozonizer in cold silica gel and then desorbing the sample into a 12-L glass reservoir and subsequently mixing it with helium. Experiments were performed at room temperature in ~200 Torr of helium as a buffer gas in the presence of 3−5 Torr of ozone and 2−3 Torr of water vapor.

2.2. UV Spectrometer System at MIT. The UV absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ was recorded using a Cary 219 double-beam spectrophotometer by placing gaseous samples of the compound in a 14.5 cm long quartz cell at 296 K. Average

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absorption cross sections in the 200−400 nm wavelength range were obtained by measuring absorbances at four different pressures in the 1−5 Torr range.

2.3. FTIR Smog-Chamber System at Ford Motor Company. Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[4] The reactor was surrounded by 22 fluorescent lamps, which were used to photochemically initiate the experiments. In the present experiments, eight of the lamps were GE FS40 "sunlamps" with a phosphor coating, which has a maximum emission at approximately 310 nm, while the other 14 lamps were GE F15T8-BL "blacklamps", which have a maximum emission at approximately 360 nm. Cl atoms were generated by the photolysis of molecular chlorine in air diluent at 700 Torr total pressure at 296 ± 2 K.

$$Cl_2 + h\nu \rightarrow 2Cl \qquad (3)$$

The loss of $C_2F_5C(O)CF(CF_3)_2$ and $^{13}CH_3{}^{13}CHO$ and the formation of products (COF_2, $CF_3C(O)F$, and ^{13}CO) were monitored by FTIR spectroscopy using an infrared path length of 27.4 m, and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms.

Three sets of experiments were performed at Ford. First, the rate of $C_2F_5C(O)CF(CF_3)_2$ photolysis was measured relative to $^{13}CH_3{}^{13}CHO$ using the UV output of either 8 sunlamps or 14 blacklamps. Second, relative rate techniques were used to investigate the reactivity of Cl atoms with $C_2F_5C(O)CF(CF_3)_2$. Third, the reactivity of ozone with $C_2F_5C(O)CF(CF_3)_2$ was investigated. All experiments were performed at 296 K.

3. Results and Discussion

3.1. Relative Rate Study of $k(OH+C_2F_5C(O)CF(CF_3)_2)$. The kinetics of reaction 4 were measured relative to reactions 5 and 6 using the experimental system at MIT.

$$OH + C_2F_5C(O)CF(CF_3)_2 \rightarrow \text{products} \qquad (4)$$

$$OH + CH_4 \rightarrow \text{products} \qquad (5)$$

$$OH + CH_3Cl \rightarrow \text{products} \qquad (6)$$

Following the generation of OH radicals in the system, CH_4 and CH_3Cl were observed to decay, but there was no discernible loss (<2%) of $C_2F_5C(O)CF(CF_3)_2$ (over and above that ascribed to photolysis, see section 2.1). Using $k_5 = (6.3 \pm 0.6) \times 10^{-15}$ and $k_6 = (3.6 \pm 0.7) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1},[5] we derive upper limits of $k_4 < 5 \times 10^{-16}$ and $< 2 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. We cite a final value of $k_4 < 5 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. Perfluoroalkanes (CF_4, C_2F_6, etc.) do not react with OH radicals,[6] the results from the present work suggest that $C_2F_5C(O)CF(CF_3)_2$ is similarly unreactive toward OH radicals. There has been some recent discussion in the literature that a significant fraction of the reaction of OH radicals with ketones proceeds via addition to the C═O group followed by displacement of one of the alkyl groups.[7−9] We observe no evidence of such a channel for reaction 4.

3.2. UV Absorption Cross Sections of $C_2F_5C(O)CF(CF_3)_2$ and CH_3CHO. Figure 1 and Table 1 give the UV absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ measured at MIT. The complete spectrum is available in digital form upon request to ltmolina@mit.edu or mmolina@mit.edu. The absorption spectrum has a maximum at 305 nm where $\sigma_{max} = 6.8 \times 10^{-20}$ cm^2 $molecule^{-1}$. For comparison, the absorption spectrum of CH_3CHO[10] is also shown in Figure 1. As seen from Figure 1, $C_2F_5C(O)CF(CF_3)_2$ has an absorption spectrum that is shifted approximately 20 nm to the red and is somewhat more intense than that of CH_3CHO.

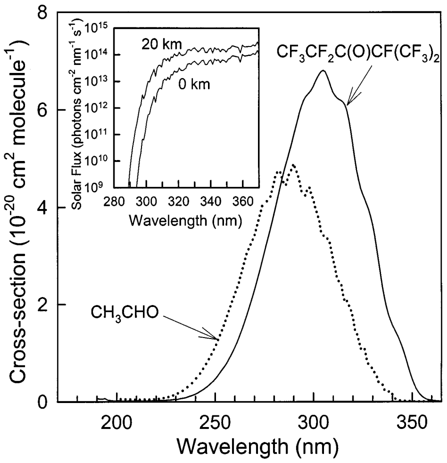

Figure 1. UV absorption cross sections of $C_2F_5C(O)CF(CF_3)_2$ (solid line) and CH_3CHO (dotted line) over the wavelength range 190−365 nm at 296 K. The insert shows the solar flux at sea level (0 km) and at 20 km altitude in the atmosphere.

TABLE 1: Measured UV Absorption Cross Section Data for $CF_3CF_2C(O)CF(CF_3)_2$

wavelength[a]	cross section[b]	wavelength[a]	cross section[b]
230	0.05	300	6.48
235	0.09	305	6.81
240	0.16	310	6.36
245	0.29	315	6.16
250	0.47	320	5.30
255	0.75	325	4.27
260	1.13	330	3.65
265	1.65	335	2.36
270	2.30	340	1.57
275	3.07	345	1.12
280	3.87	350	0.47
285	4.72	355	0.11
290	5.47	360	0.03
295	6.19	300	6.48

[a] In nanometers. [b] In 10^{-20} cm^2 $molecule^{-1}$.

3.3. Photolysis of $C_2F_5C(O)CF(CF_3)_2$: Rate and Mechanism. The rate and mechanism of the photolysis of $C_2F_5C(O)CF(CF_3)_2$ were studied in the smog chamber at Ford. Control experiments were performed in which $C_2F_5C(O)CF(CF_3)_2$/air mixtures were allowed to stand in the chamber in the dark to check for heterogeneous loss of $C_2F_5C(O)CF(CF_3)_2$. There was neither any discernible (<2%) loss of $C_2F_5C(O)CF(CF_3)_2$ nor any discernible formation of products (<0.02% molar yield of COF_2) when $C_2F_5C(O)CF(CF_3)_2$/air mixtures were allowed to stand in the dark for 16 h. Upon irradiation of $C_2F_5C(O)CF(CF_3)_2$/air mixtures with the output from UV fluorescent lamps (see section 2.3 for details), loss of $C_2F_5C(O)CF(CF_3)_2$ and formation of products were observable in the IR spectra.

Figure 2 shows typical IR spectra in the wavenumber region 1850−2000 cm^{-1} obtained before (panel A) and after (panel B) a 90 min UV irradiation of a mixture of 1.54 Torr of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of synthetic air at 296 K. Panel C shows the residual spectrum of panel A from panel B, which corresponds to the photoproducts produced from a mixture of $C_2F_5C(O)CF(CF_3)_2$ in air by UV radiation. Comparison of panel C with reference spectra of $CF_3C(O)F$ and COF_2 in panels D and E, respectively, shows that these species are products. $CF_3O_3CF_3$ and CF_3OH were also identified as products by virtue of their characteristic IR features at 897[11] and 3664 cm^{-1}, respectively.[12] When photolysis mixtures were left in the dark

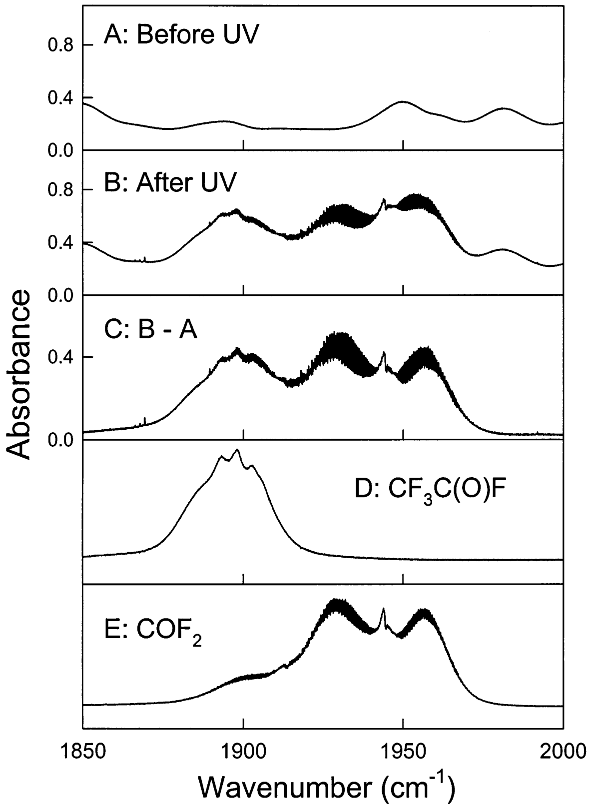

Figure 2. IR spectra acquired (A) before and (B) after a 90 min UV irradiation of a mixture containing 1.54 Torr of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air diluent at 296 K. Panel C shows the result of subtracting panel A from panel B. Reference spectra of $CF_3C(O)F$ and COF_2 are given in panels D and E.

for 90 min, there was no observable change in $CF_3C(O)F$ or $CF_3O_3CF_3$ concentrations while, consistent with previous observations,[12] there was a 20% loss of CF_3OH (first-order loss rate $k_{loss} = 4 \times 10^{-5}$ s^{-1}) and a corresponding increase in the amount of COF_2 in the chamber. In the present work, the half-life of CF_3OH with respect to decomposition into COF_2 was 4−5 h (consistent with the range of 1−5 h reported previously).[12]

$$CF_3OH \rightarrow COF_2 + HF \tag{7}$$

Figure 3 shows the observed formation of COF_2 and $CF_3C(O)F$ during the UV irradiation (blacklamps) of a mixture of 154 mTorr of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air diluent. As seen from Figure 3, for short irradiation times, the yields of COF_2 and $CF_3C(O)F$ were indistinguishable, while at longer irradiation times, the yield of COF_2 exceeds that of $CF_3C(O)F$. It is also evident from Figure 3 that the formation of $CF_3C(O)F$ scales linearly with irradiation time consistent with its formation as a primary product following photolysis of $C_2F_5C(O)CF(CF_3)_2$. After 7 h of irradiation, the loss of $C_2F_5C(O)CF(CF_3)_2$ was determined to be 2.5% ± 1.0%, that is, 3.9 ± 1.5 mTorr, indistinguishable from the $CF_3C(O)F$ yield.

The simplest explanation of the experimental observations is that photolysis of $C_2F_5C(O)CF(CF_3)_2$ occurs via cleavage of one of the C−C bonds associated with the carbonyl group to yield a perfluoroalkyl radical and a perfluoroacetyl radical. By analogy to similar alkyl radicals, these radicals will add O_2 to give the corresponding peroxy radicals and undergo self- and cross-reactions to give alkoxy radicals. For example, if photolysis occurs via rupture of the $C_2F_5{-}C(O)CF(CF_3)_2$ bond then, by analogy to the substantial database concerning the

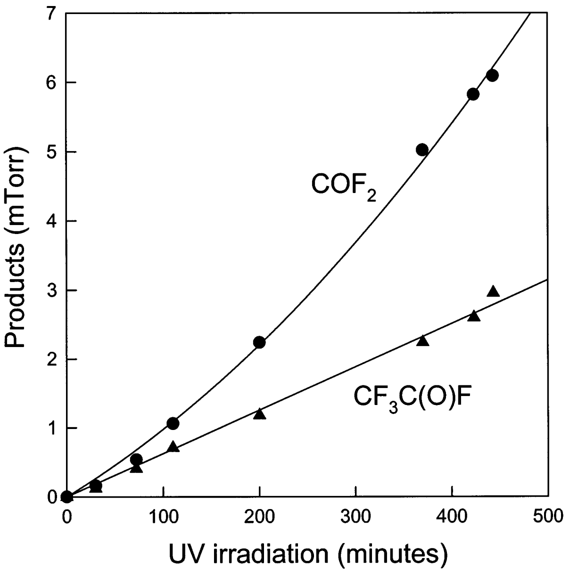

Figure 3. Formation of (●) COF_2 and (▲) $CF_3C(O)F$ as a function of irradiation time (using blacklamps) of a mixture of 154 mTorr of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air diluent at 296 K. The lines through the $CF_3C(O)F$ and COF_2 data are first- and second-order regressions.

atmospheric oxidation mechanisms of hydrofluorocarbons,[13] the chemistry is expected to be

$$C_2F_5C(O)CF(CF_3)_2 + h\nu \rightarrow C_2F_5 + C(O)CF(CF_3)_2 \tag{8}$$

$$C_2F_5 + O_2 + M \rightarrow C_2F_5O_2 + M \tag{9}$$

$$C(O)CF(CF_3)_2 + O_2 + M \rightarrow OOC(O)CF(CF_3)_2 + M \tag{10}$$

$$C_2F_5O_2 + RO_2 \rightarrow C_2F_5O + RO + O_2 \tag{11}$$

$$OOC(O)CF(CF_3)_2 + RO_2 \rightarrow OC(O)CF(CF_3)_2 + RO + O_2 \tag{12}$$

$$C_2F_5O + M \rightarrow CF_3 + COF_2 + M \tag{13}$$

$$OC(O)CF(CF_3)_2 + M \rightarrow CO_2 + CF(CF_3)_2 + M \tag{14}$$

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \tag{15}$$

$$CF(CF_3)_2 + O_2 + M \rightarrow OOCF(CF_3)_2 + M \tag{16}$$

$$OOCF(CF_3)_2 + RO_2 \rightarrow OCF(CF_3)_2 + RO + O_2 \tag{17}$$

$$CF_3O + CF_3O_2 + M \rightarrow CF_3O_3CF_3 + M \tag{18}$$

$$OCF(CF_3)_2 + M \rightarrow CF_3C(O)F + CF_3 + M \tag{19}$$

If photolysis occurs via rupture of the $C_2F_5C(O){-}CF(CF_3)_2$ bond, then reactions 20−23 will be followed by reactions 9, 11, 13, and 15−19:

$$C_2F_5C(O)CF(CF_3)_2 + h\nu \rightarrow C_2F_5C(O) + CF(CF_3)_2 \tag{20}$$

$$C_2F_5C(O) + O_2 + M \rightarrow C_2F_5C(O)O_2 + M \tag{21}$$

$$C_2F_5C(O)O_2 + RO_2 \rightarrow C_2F_5C(O)O + RO + O_2 \tag{22}$$

$$C_2F_5C(O)O + M \rightarrow C_2F_5 + CO_2 + M \tag{23}$$

In the above scheme, there is only one loss mechanism for CF_3O radicals, namely, association with CF_3O_2 to give the trioxide,

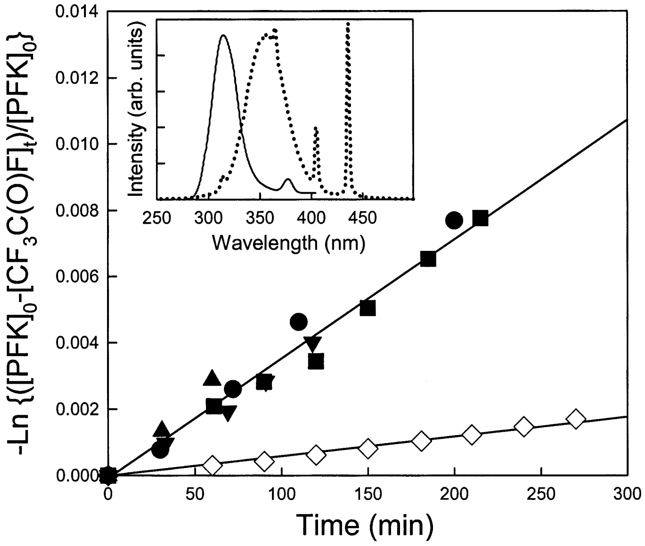

Figure 4. Decay of $C_2F_5C(O)CF(CF_3)_2$ inferred from the formation of $CF_3C(O)F$ as a function of irradiation time of $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air diluent at 296 K using either 8 sunlamps (filled symbols) or 14 blacklamps (open symbols). Initial concentrations of $C_2F_5C(O)$-$CF(CF_3)_2$ were (○) 154 mTorr, (□) 481 mTorr, (◇) 745 mTorr, (▽) 1.54 Torr, and (△) 1.83 Torr. The insert shows the spectral distribution (arbitrary units) of the sunlamps (solid curve) and blacklamps (dotted curve).

$CF_3O_3CF_3$. In smog-chamber experiments, there is another loss mechanism for CF_3O radicals, reaction with hydrogen-containing compounds present in the chamber (e.g., HCHO desorbing from the chamber walls, impurities in the air diluent, or both) to give CF_3OH, [13] which was an observed product in the present work.

The loss of $C_2F_5C(O)CF(CF_3)_2$ was small (2.5% loss after 7 h of irradiation) and difficult to monitor directly. To provide greater precision in the measurement of the photolysis of C_2F_5C-$(O)CF(CF_3)_2$, its loss was monitored indirectly by measuring the formation of $CF_3C(O)F$. Upon the basis of the mechanism outlined above, it seems reasonable to assume that the photolysis of $C_2F_5C(O)CF(CF_3)_2$ gives $CF_3C(O)F$ in a molar yield of unity. Accordingly, Figure 4 shows the loss of $C_2F_5C(O)CF(CF_3)_2$ as inferred from the formation of $CF_3C(O)F$ as a function of irradiation time for several different $C_2F_5C(O)CF(CF_3)_2$/air mixtures using either sunlamps (filled symbols) or blacklamps (open symbols). Within the admittedly significant data scatter evident from inspection of the data represented by filled symbols in Figure 4, there is no evidence for any systematic dependence of the first-order loss rate with variation of the initial C_2F_5C-$(O)CF(CF_3)_2$ concentration over the range 0.154−1.83 Torr. The line through the filled data in Figure 4 is a linear least-squares fit to the composite data set, which gives a photolysis rate of $J(C_2F_5C(O)CF(CF_3)_2) = (6 \pm 2) \times 10^{-7}\ s^{-1}$ for eight sunlamps. Similarly, a least-squares fit to the data obtained using blacklamps gives $J(C_2F_5C(O)CF(CF_3)_2) = (1.0 \pm 0.1) \times 10^{-7}\ s^{-1}$ for 14 blacklamps.

The insert in Figure 4 shows the spectral distribution of the output from the sunlamps (solid curve) and blacklamps (dotted curve) taken from the manufacturers specifications. The data in the insert provide an indication of the spectral region over which the lamps emit and not the absolute intensity of the lights. The maximum of both output curves has been scaled to the same value for display purposes. Finally, it should be noted that absorption by the Pyrex walls (Pyrex cuts off at ~300 nm) will modify the spectrum of UV light within the chamber. It is evident from Figure 4 that the sunlamps, although less numerous than the blacklamps, are much more effective in photolyzing $C_2F_5C(O)CF(CF_3)_2$. This behavior presumably reflects the better spectral overlap of emission from the sunlamps with the spectrum of $C_2F_5C(O)CF(CF_3)_2$ (compare insert in Figure 4 with spectrum in Figure 1).

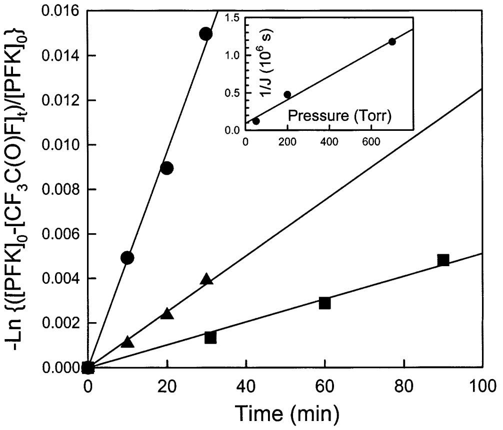

Figure 5. Decay of $C_2F_5C(O)CF(CF_3)_2$ during UV irradiation (sunlamps) of mixtures of 1.5 Torr of $C_2F_5C(O)CF(CF_3)_2$ in (■) 700, (▲) 200, or (●) 50 Torr of air diluent at 296 K. Lines are linear least-squares fits. The insert is a plot of the reciprocal of the photolysis rate versus the pressure of air diluent.

Figure 5 shows the loss of $C_2F_5C(O)CF(CF_3)_2$ following the irradiation (sunlamps) of mixtures containing 1.5 Torr of C_2F_5C-$(O)CF(CF_3)_2$ in either 700 (squares), 200 (triangles), or 50 (circles) Torr of air diluent. It is clear from Figure 5 that as the total pressure of air is decreased, the rate of photolysis increases. This observation suggests that the photolytically excited state of $C_2F_5C(O)CF(CF_3)_2$ has a lifetime that is sufficiently long that collisions with diluent gas can cause significant quenching. This can be represented as follows:

$$C_2F_5C(O)CF(CF_3)_2 + h\nu \rightarrow [C_2F_5C(O)CF(CF_3)_2]^* \quad (24)$$

$$[C_2F_5C(O)CF(CF_3)_2]^* \rightarrow \text{photolysis products} \quad (25)$$

$$[C_2F_5C(O)CF(CF_3)_2]^* + M \rightarrow C_2F_5C(O)CF(CF_3)_2 + M^* \quad (26)$$

Assuming that processes 25 and 26 are the only loss mechanisms for $[C_2F_5C(O)CF(CF_3)_2]^*$, it can be shown that $1/J = 1/k_{24} + [k_{26}/(k_{24}k_{25})][M]$, where J is the observed photolysis rate, k_{25} and k_{26} are the rate constants for processes 25 and 26, and [M] is the pressure of the diluent gas. Least-squares analysis of the data in Figure 5 leads to values of $J = 8.5 \times 10^{-7}$, 2.1×10^{-6}, and $8.3 \times 10^{-6}\ s^{-1}$ in the presence of 700, 200, and 50 Torr of air. The insert in Figure 5 shows a plot of $1/J$ versus the pressure of diluent gas; the linearity of this plot is consistent with the simple Stern−Volmer-type analysis given above. It was not the intention in the present work to map out the details of quenching of the excited state of $C_2F_5C(O)CF(CF_3)_2$ by air diluent, and hence, the data in Figure 5 are rather sparse. Nevertheless, it is evident from Figure 5 that quenching of the excited state is significant and in one atmosphere of air leads to substantial reduction in the photolysis rate from that observed in the presence of little, or no, diluent.

To provide a means of translating the measured photolysis rate of $C_2F_5C(O)CF(CF_3)_2$ in the chamber to an estimate of its photolysis rate in the atmosphere, a series of experiments were conducted to measure the rate of photolysis of CH_3CHO in the chamber. The UV spectrum, photolysis quantum yield, and

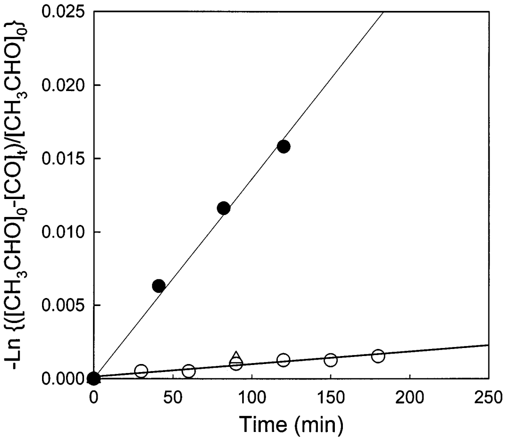

Figure 6. Loss of $^{13}CH_3{}^{13}CHO$ as a function of irradiation time using either sunlamps (filled symbols) or blacklamps (open symbols) of mixtures of $^{13}CH_3{}^{13}CHO$ in 700 Torr of air diluent at 296 K. Initial concentrations of $^{13}CH_3{}^{13}CHO$ were (●) 12 mTorr, (△) 30 mTorr, or (○) 40 mTorr.

photolysis lifetime of CH_3CHO in the atmosphere are well understood.[10,14] If the rate of $C_2F_5C(O)CF(CF_3)_2$ photolysis is measured relative to that of CH_3CHO, the known photolysis rate of CH_3CHO can be used as a scaling factor to provide an estimate of the atmospheric photolysis rate of $C_2F_5C(O)CF(CF_3)_2$. For the portion of the solar spectrum present in the troposphere, photolysis of CH_3CHO gives CH_3 and HCO radicals. Reaction of HCO radicals with O_2 gives CO.

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO \tag{27}$$

$$HCO + O_2 \rightarrow HO_2 + CO \tag{28}$$

As with $C_2F_5C(O)CF(CF_3)_2$, the photolysis of CH_3CHO was slow and difficult to measure directly in the chamber. For increased precision, the loss of CH_3CHO was measured indirectly by monitoring the formation of CO. To avoid potential complications caused by other sources of CO in the system, istopically labeled $^{13}CH_3{}^{13}CHO$ was used and the formation of ^{13}CO was monitored. Figure 6 shows the loss of $^{13}CH_3{}^{13}CHO$, inferred from the observed formation of ^{13}CO when mixtures containing $^{13}CH_3{}^{13}CHO$ in 700 Torr of air were irradiated using the sunlamps or blacklamps. Linear least-squares regressions to the data in Figure 6 give photolysis rates of 2.3×10^{-6} s^{-1} (sunlamps) and 1.5×10^{-7} s^{-1} (blacklamps). Comparing these values to the results obtained for $C_2F_5C(O)CF(CF_3)_2$ (6×10^{-7} s^{-1} for sunlamps and 1.0×10^{-7} s^{-1} for blacklamps), we can see that photolysis of CH_3CHO is 4 and 1.5 times more rapid than photolysis of $C_2F_5C(O)CF(CF_3)_2$ using sunlamps and blacklamps, respectively. The qualitative difference in the effectiveness of the two different types of fluorescent lamps is consistent with the relative overlap of their spectral output (see insert in Figure 4) with the spectra of $C_2F_5C(O)CF(CF_3)_2$ and CH_3CHO (see Figure 1).

From Figure 1, it is clear that the absorption cross sections of $C_2F_5C(O)CF(CF_3)_2$ are greater than those of CH_3CHO at all wavelengths transmitted by the Pyrex walls of the chamber. From the absorption cross section data alone, it would be reasonable to predict that $C_2F_5C(O)CF(CF_3)_2$ would photolyze more rapidly than CH_3CHO. Interestingly, the opposite is observed, namely, that $C_2F_5C(O)CF(CF_3)_2$ photolyzes more slowly than CH_3CHO. This observation indicates that the photolysis quantum yield for $C_2F_5C(O)CF(CF_3)_2$ in 700 Torr of air at 296 K is significantly less than unity. This conclusion is consistent with the observation that the photolysis rate in 50 Torr of air diluent is approximately a factor of 10 greater than that in 700 Torr of air (see insert in Figure 5). A similar effect has been observed in studies of CH_3CHO in which the photolysis quantum yield decreases from 0.96 to 0.40 (for 300 nm radiation) and 0.74 to 0.15 (for 313 nm radiation) as the total pressure of air diluent is increased from 50 to 700 Torr of air.[10,15]

The solar flux at sea level and 20 km altitude in the atmosphere is given in the insert in Figure 1. The solar flux drops dramatically at wavelengths below 300 nm. For purposes of discussing the atmospheric photolysis of $C_2F_5C(O)CF(CF_3)_2$ and CH_3CHO, we need only consider the wavelength range 295−350 nm. The UV fluorescent lamps used in the present study provide a broad coverage of this spectral region. The sunlamps provide output rich in the blue part of this region, while light from the blacklamps is rich in the red part of the range. The atmospheric photolysis rate of CH_3CHO at 0.5 km altitude is 7×10^{-6} s^{-1} for a solar zenith angle of 0° and 5×10^{-6} s^{-1} for a solar zenith angle of 40°,[10] and CH_3CHO has an atmospheric lifetime with respect to photolysis of approximately 3−4 days. Upon the basis of the relative photolysis rates in the chamber, it seems reasonable to conclude that the lifetime of $C_2F_5C(O)CF(CF_3)_2$ with respect to photolysis will be 1.5−4 times that of CH_3CHO, that is, approximately 1−2 weeks. At this point, the approximate nature of the estimated photolysis lifetime should be stressed. A more precise determination would require a study of the photolysis quantum yield as a function of wavelength, diluent pressure, and temperature. Such a study is beyond the scope of the present study and is unlikely to change the important conclusion of the present work, namely, that photolysis is an effective process by which $C_2F_5C(O)CF(CF_3)_2$ is removed from the atmosphere.

3.4. Kinetics of Reaction of $C_2F_5C(O)CF(CF_3)_2$ with Cl Atoms and O_3. The reaction of $C_2F_5C(O)CF(CF_3)_2$ with Cl atoms was studied by relative rate experiments at Ford, in which CF_3OCF_2H was used as a reference compound for the Cl reaction:

$$Cl + C_2F_5C(O)CF(CF_3)_2 \rightarrow \text{products} \tag{29}$$

$$Cl + CF_3OCF_2H \rightarrow \text{products} \tag{30}$$

Reaction mixtures consisted of 1.8 mTorr of $C_2F_5C(O)CF(CF_3)_2$, 2.08 Torr of Cl_2, and 2.4 mTorr of CF_3OCF_2H in 700 Torr of N_2 diluent. UV radiation for 140 min typically led to no discernible loss (<1%) of $C_2F_5C(O)CF(CF_3)_2$, while the consumption of CF_3OCF_2H was 8−80%. Using the literature value of $k_{30} = (2.3 \pm 0.3) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1},[16] we derive an upper limit of $k_{29} < 1.7 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 296 K.

To investigate the reaction of O_3 with $C_2F_5C(O)CF(CF_3)_2$, a mixture containing 3 mTorr of $C_2F_5C(O)CF(CF_3)_2$ and 74 mTorr of O_3 in 700 Torr of air was introduced into the chamber. The mixture was allowed to stand in the dark in the chamber for 360 min. There was no discernible loss of $C_2F_5C(O)CF(CF_3)_2$ (<2%) during this period, while there was a small (9%) decrease in the ozone in the chamber, which we attribute to decomposition on the chamber walls. From this experiment, we derive an upper limit for the rate constant of reaction of O_3 with $C_2F_5C(O)CF(CF_3)_2$ of $k_{O_3} < 4 \times 10^{-22}$ cm^3 molecule^{-1} s^{-1} at 296 K.

4. Conclusions

The results presented here comprise the first study of the atmospheric degradation mechanism of $C_2F_5C(O)CF(CF_3)_2$. There was no discernible reaction of $C_2F_5C(O)CF(CF_3)_2$ with

OH radicals, Cl atoms, or O_3. It seems likely that homogeneous gas-phase reactions do not play any role in the atmospheric loss of $C_2F_5C(O)CF(CF_3)_2$. The ultraviolet absorption spectrum of $C_2F_5C(O)CF(CF_3)_2$ is similar in shape and magnitude to that of CH_3CHO but is red-shifted by approximately 20 nm. The atmospheric lifetime of $C_2F_5C(O)CF(CF_3)_2$ with respect to photolysis is estimated to be 1−2 weeks. Photolysis of $C_2F_5C(O)CF(CF_3)_2$ in air gives $CF_3C(O)F$ and COF_2. $CF_3C(O)F$ will be incorporated into rain/cloud/seawater where it will undergo hydrolysis to give trifluoroacetic acid.[13] Similarly, COF_2 will undergo hydrolysis to give CO_2 and HF. At the concentrations expected in the environment, none of these degradation products is considered harmful. With an atmospheric lifetime of 1−2 weeks (or less if processes other than photolysis contribute), $C_2F_5C(O)CF(CF_3)_2$ will have a global-warming potential that, for all practical purposes, is negligible.

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