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Photochemistry of fluorinated compounds: reaction between FCO and CF_3CF_2 radicals

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Abstract

$CF_3CF_2C(O)F$ is a suitable source to generate the title radicals which can recombine to give back the precursor or lead to the formation of C_4F_{10}, CF_2O and CO. We performed the photolysis of $CF_3CF_2C(O)F$ pure and in the presence of c-C_6H_{12} or $(FCO)_2$ (oxalylfluoride), following the concentration of the different species by FTIR spectroscopy. The rate constant for the reaction $CF_3CF_2 + FCO \rightarrow CF_3CF_2C(O)F$ was obtained through a simulation using both our experimental data and bibliography data available. The value found is $(6.8 \pm 0.8) \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$ and it is not substantially different from the rate constant $(4.2 \pm 0.5) \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$ obtained for the reaction of CF_3 and FCO radicals. Thus, it was concluded that the length of the carbon chain does not affect the mechanism nor the rate constant value when it is compared with the CF_3 + FCO system. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: $CF_3CF_2C(O)F$; Photolysis; Rate constant; Fluorinated compounds

1. Introduction

In the last years, it has been of great interest in atmospheric chemistry to know the impact of the substitutes of CFCs and their degradation products. In fact, the radicals CF_3O_x and FCO_x originated from the decomposition of HFCs are involved in a great deal of reactions in the stratosphere [1–3] and have been the subject of much laboratory work comprising not only their kinetic properties [4–14] but also their spectroscopic properties [15–19].

In previous works has been reported the gas-phase photolysis of the simplest perfluoroacyl halides derived from the tropospheric degradation of some HFCs, that is $CF_3C(O)F$ [20,21], $CF_3C(O)Cl$ [22,23], as well as the corresponding ones bearing one additional CF_2 group in the alkylic moiety [24]. In these works, the quantum yields of the photolysis and the products formed were identified.

It was found that $CF_3C(O)Cl$ and $CF_3CF_2C(O)Cl$ photolyze with a quantum yield of unity. The primary radicals formed are C_nF_{2n+1} ($n = 1$, 2, respectively) and ClCO, which can also decompose into Cl and CO [24,25].

The $CF_3C(O)F$ photolysis produces as the first step, CF_3 and FCO radicals, but at variance with $CF_3C(O)Cl$ and $CF_3CF_2C(O)Cl$, the FCO radicals are stable and do not decompose, allowing the recombination reaction with CF_3 radicals to give again $CF_3C(O)F$

$$CF_3 + FCO \rightarrow CF_3C(O)F \tag{R1}$$

Besides, CF_3 radicals react to give C_2F_6 and the FCO radicals react to give CF_2O and CO. Because of this direct recombination (R1), a quantum yield for $CF_3C(O)F$ disappearance lower than unity ($\phi = 0.4$) and a rate constant of $(4.2 \pm 0.5) \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$ were obtained [21].

The quantum yield for the disappearance of $CF_3CF_2C(O)F$ gave the same value as that for $CF_3C(O)F$ and so we believe that a similar radical recombination reaction occurs. The subject of this paper is thus an attempt to explain the formation of products such as C_4F_{10}, CF_2O and CO, the low quantum yield as a consequence of the direct recombination of both primary radicals CF_3CF_2 and FCO and to give a value for their recombination rate constant.

We performed the photolysis of $CF_3CF_2C(O)F$ alone and in the presence of either c-C_6H_{12} or oxalylfluoride, $(FCO)_2$, to determine the value of the direct CF_3CF_2 and FCO radical recombination rate constant, which to the best of our knowledge has not been reported.

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2. Experimental details

2.1. Materials

Commercially available samples of perfluoropropionyl fluoride, $CF_3CF_2C(O)F$ (PCR Research Chemicals), were trap-to-trap distilled in vacuum before use and the purity was checked by IR spectroscopy. Samples of commercial cyclohexane (98%) were used as-received. Oxygen was condensed by flowing O_2 at atmospheric pressure through a trap immersed in liquid air and later pumped under vacuum several times and transferred to a glass bulb whilst the trap was still immersed in liquid air. Oxalylfluoride, $(FCO)_2$, was synthesized by fluorination of oxalylchloride with NaF in sulfolane as solvent and purified by trap-to-trap distillation [26].

2.2. Procedure

Reactants and products were manipulated in a conventional high-vacuum system. The photolyses were carried out using low-pressure Hg lamps that surrounded a quartz cell fitted with KCl windows. The cell was located in the optical path (23 cm) of a Fourier transform IR (FTIR) spectrometer which was used to follow the evolution of the reaction with time. This approach has been discussed elsewhere [22].

3. Results and discussion

The photolysis of $CF_3CF_2C(O)F$ leads to the formation of C_4F_{10}, CF_2O and CO [24]. These products are explained on the basis of the C–$C_{\text{carbonylic}}$ bond breaking to give CF_3CF_2 and FCO radicals [24]:

$$CF_3CF_2C(O)F \rightarrow CF_3CF_2 + FCO \qquad \text{(R2)}$$

followed by the radical recombination reactions:

$$CF_3CF_2 + CF_3CF_2 \rightarrow C_4F_{10} \qquad \text{(R3)}$$

$$FCO + FCO \rightarrow CF_2O + CO \qquad \text{(R4)}$$

The photolysis of $CF_3CF_2C(O)F$ (1.7 Torr) in the presence of $c\text{-}C_6H_{12}$ (90.0 Torr) leads, as can be seen in the IR spectra portrayed in Fig. 1, to the formation of CF_3CF_2H, HFCO and very small quantities of CO as well as HF (which is not shown in the wavelength range displayed). In these experiments, it was not observed C_4F_{10} nor CF_2O; this fact indicating that all the CF_3CF_2 and FCO radicals formed reacted with $c\text{-}C_6H_{12}$:

$$CF_3CF_2 + c\text{-}C_6H_{12} \rightarrow CF_3CF_2H + c\text{-}C_6H_{11} \qquad \text{(R5)}$$

$$FCO + c\text{-}C_6H_{12} \rightarrow HFCO + c\text{-}C_6H_{11} \qquad \text{(R6)}$$

and therefore their participation is hindered in reactions (R3) and (R4).

Furthermore, a difference between the disappearance rate of $CF_3CF_2C(O)F$ was observed when the photolysis is carried out in presence and in absence of $c\text{-}C_6H_{12}$, as is shown in Fig. 2. As can be seen, the rate is faster in the presence of $c\text{-}C_6H_{12}$. This suggests that in the absence of $c\text{-}C_6H_{12}$, a reaction that leads back to the formation of $CF_3CF_2C(O)F$ is present, thus making its disappearance slower. It is evident that the only radicals that can lead to the formation of $CF_3CF_2C(O)F$ in our system are CF_3CF_2 and FCO through

$$CF_3CF_2 + FCO \rightarrow CF_3CF_2C(O)F \qquad \text{(R-2)}$$

In order to prove the occurrence of the direct recombination reaction of radicals (R-2), we carried out a new set of experiments by photolysing $CF_3CF_2C(O)F$ in the presence

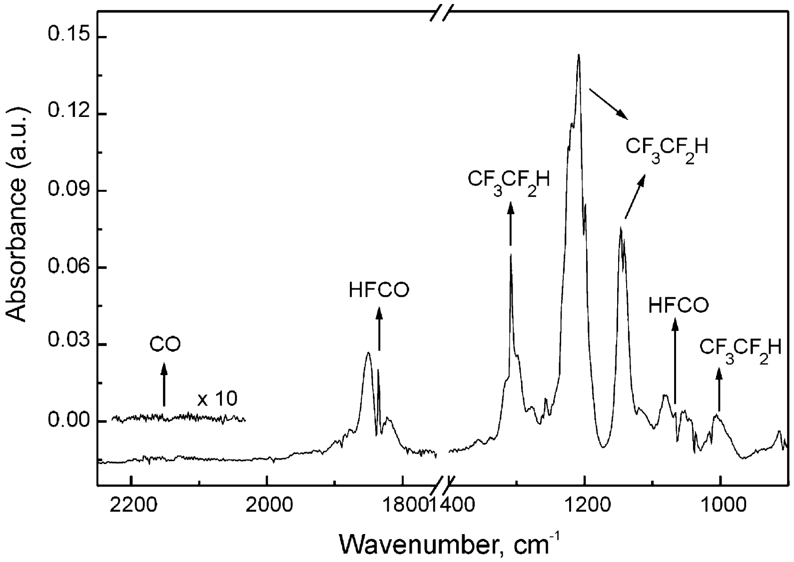

Fig. 1. IR spectrum of the products obtained after the photolysis at 254 nm of $CF_3CF_2C(O)F$ in the presence of $c\text{-}C_6H_{12}$.

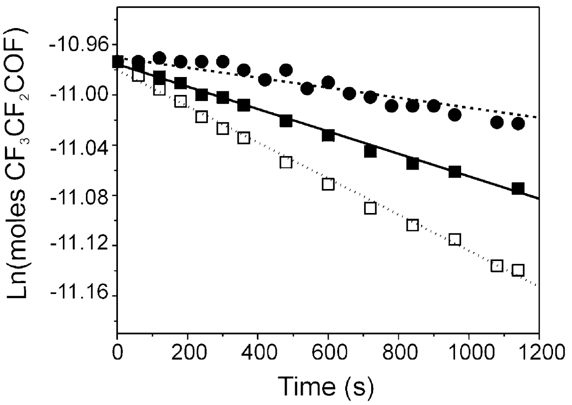

Fig. 2. Plot of ln(moles $CF_3CF_2C(O)F$) vs. photolysis time: (●) in the presence of $(FCO)_2$; (■) pure; (☐) in the presence of c-C_6H_{12}. Each line corresponds to the least-squares fitting to the experimental points. The slope of the dotted line is k_2.

of FCO radicals. As source of such radicals, we used the photolysis of oxalylfluoride, $(FCO)_2$ [27]:

$$(FCO)_2 + h\nu \rightarrow FCO + FCO \qquad \text{(R7)}$$

Fig. 2 also shows the disappearance of $CF_3CF_2C(O)F$ in the presence of $(FCO)_2$. As can be seen, its disappearance rate (see the dashed line) is smaller than when $CF_3CF_2C(O)F$ is photolyzed alone. The IR spectra of the products obtained in the photolysis of $CF_3CF_2C(O)F$ alone and in the presence of an excess of FCO radicals are shown in Fig. 3. The comparison of both spectra reveals that the formation of C_4F_{10} is higher when $CF_3CF_2C(O)F$ is photolyzed alone. When the photolysis is carried out in the presence of $(FCO)_2$, the CF_3CF_2 radicals are diverted from reaction (R3) by means of reaction (R-2) with the decrease in C_4F_{10} concentration.

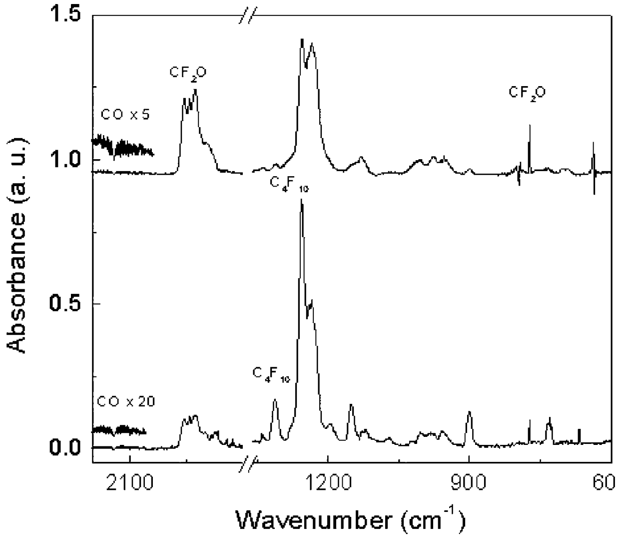

Fig. 3. IR spectra of the products obtained for the photolysis at 254 nm of $CF_3CF_2C(O)F$ alone (lower trace) and in the presence of $(FCO)_2$ (upper trace).

All this evidence suggests that the mechanism involves reactions (R2), (R-2), (R3) and (R4) when the photolysis is carried out in the absence of any added gas.

According to this mechanism, the temporal variation of $[CF_3CF_2C(O)F]$ is given by

$$-\frac{d[CF_3CF_2C(O)F]}{dt} = k_2[CF_3CF_2C(O)F] - k_{-2}[CF_3CF_2][FCO] \qquad (1)$$

Solving the differential equations for the intermediate species and substituting into the proper equations, the temporal variation of $[CF_3CF_2C(O)F]$ is given by

$$\ln[CF_3CF_2C(O)F] = -k_{obs}t + \ln[CF_2C(O)F]_0 \qquad (2)$$

where k_{obs} (full line in Fig. 2) equals

$$k_{obs} = \frac{2k_2(k_3k_4)^{1/2}}{k_{-2} + 2(k_3k_4)^{1/2}} \qquad (3)$$

This equation was used to obtain a first approximation to k_{-2} for which we used the rate constants k_3 and k_4 obtained from the literature. In the case of k_4, there are four values reported up to now but only the work of Behr and Heydtmann [27] was carried out at pressures comparable to those used in our experiments (1.7 Torr), and so we took the value $(1.7 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. For k_3 the value informed is 2.85×10^{-12} cm^3 molecule^{-1} s^{-1} [28].

The rate of $CF_3CF_2C(O)F$ disappearance (k_2) was obtained from the slope of Fig. 2 for the case where the photolysis was carried out in the presence of c-C_6H_{12}. In the conditions prevailing in those experiments where an excess of c-C_6H_{12} was present, it is clear that the presence of an effective radical scavenger, able to trap radicals that participate in reactions (R2) and (R3), prevents reaction (R-2) from taking place, and the variation of the $CF_3CF_2C(O)F$ concentration is only due to the photolysis reaction (R2). From the slope of $\ln[CF_3CF_2C(O)F]$ vs. time (see Fig. 2, dotted line), a value of $(1.4 \pm 0.1) \times 10^{-4}$ s^{-1} for the photolysis rate constant under our experimental conditions, k_2, is obtained.

The concentration of $CF_3CF_2C(O)F$ at different times was obtained (always through the IR spectra) in two different ways, i.e. either looking at the reactant remaining (1334 cm^{-1} band) or quantifying the appearance of CF_2O (1928 cm^{-1} band) and using a 2:1 stoichiometry governed by the mechanism assumed.

The rate constants k_2, k_3, k_4 and k_{-2} were used to simulate the time variation of the concentration of $CF_3CF_2C(O)F$ and CF_2O by a numerical method of coupled differential equations using the above-discussed mechanism and recovering in that way, as an adjustable parameter, the value for k_{-2} that best fits the experimental points. This method is reliable since it takes into account the simultaneous variation in the concentration of reactants and products for a sufficiently long time. The best fit to the k_{-2} value gives $(6.8 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} which is slightly

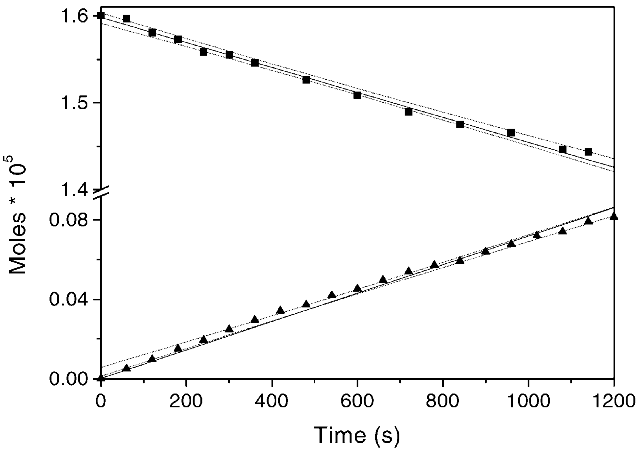

Fig. 4. Fitting to the experimental concentration of species ((■) $CF_3CF_2C(O)F$; (▲) CF_2O) with $k_{-2} = (6.8 \pm 0.8) \times 10^{-12}\,cm^3$ molecule^{-1} s^{-1}. Dotted lines represent the 95% confidence limits.

smaller than the value derived using Eq. (3). The experimental (symbols) and simulated (solid line) results are shown in Fig. 4. To assess the influence that the errors associated with the rate constants used in the simulation have on k_{-2}, a series of simulations using the limiting values for each rate constant was carried out. It was observed that the value of k_2 is the one that most affects the numerical result on k_{-2}. However, the error ascribed to k_{-2} was estimated so as to represent the experimental points with a 95% confidence. A larger variation of k_2 makes the results fall beyond these limits.

The value of the recombination rate constant also explains why, in the $CF_3CF_2C(O)F$ photolysis in the presence of oxalylfluoride, the C_4F_{10} concentration drops and the $CF_3CF_2C(O)F$ concentration decreases more slowly than when it is photolyzed alone. This is a consequence of the presence of an excess of FCO radicals, which favors reactions (R-2) and (R4) over reaction (R3). The rate constant for the recombination of CF_3 and FCO radicals reported by Bierbrauer et al. [21] had a value of $(6.9 \pm 0.8) \times 10^{-12}\,cm^3$ molecule^{-1} s^{-1}. Nevertheless, the value of $1.7 \times 10^{-11}\,cm^3$ molecule^{-1} s^{-1} for k_3 leads to a rate constant of $(4.2 \pm 0.5) \times 10^{-12}\,cm^3$ molecule^{-1} s^{-1} for the recombination reaction (R1).

Comparing both rate constants for radical recombination (i.e. (R-2) for CF_3CF_2 and (R1) for CF_3), there is no substantial difference. This and other similarities between $CF_3C(O)F$ and $CF_3CF_2C(O)F$ photolyses such as their rupture (in the two cases the scission is the $C–C_{carbonylic}$ bond) and the products formed by the recombination reaction when they are photolyzed alone (C_2F_6, CF_2O, CO and C_4F_{10}, CF_2O, CO, respectively) and in the presence of c-C_6H_{12} (CF_3H and CF_3CF_2H, respectively) lead us to suggest that the length of the perfluoroalkylic chain does not affect the mechanism of the reaction nor the recombination rate of radicals formed by the primary step in the photolysis.

4. Conclusions

In the study of the $CF_3CF_2C(O)F$ photolysis in the presence of c-C_6H_{12}, an increase in the reactant disappearance rate is observed. In our experimental conditions k_2 was $(1.4 \pm 0.1) \times 10^{-4}\,s^{-1}$. When $(FCO)_2$ is added, an excess of FCO produces a reduction of the disappearance rate of $CF_3CF_2C(O)F$. The two former findings are compatible with a mechanism mediated by radicals.

The low quantum yield for the $CF_3CF_2C(O)F$ disappearance and our results in this work suggest that a CF_3CF_2 and FCO radical recombination reaction is taking place and the calculated rate constant obtained for this recombination is $(6.8 \pm 0.8) \times 10^{-12}\,cm^3$ molecule^{-1} s^{-1}. The value found is not substantially different within experimental error from the rate constant obtained for CF_3 and FCO radicals. We then conclude that the mechanism of reaction and the rate constant are not substantially changed by the length of the perfluoroalkyl chain.

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