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Photochemistry of perfluoroacyl halides in the presence of O_2 and CO

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Abstract

Photolyses of $CF_3C(O)X$ and $C_2F_5C(O)X$ ($X = Cl$, F) at 254 nm in the presence of O_2 yield the perfluorinated radicals C_2F_5O (C_2) and CF_3O (C_1), respectively. The C_2 radicals decompose to give CF_3 radicals:

$$C_2F_5O \rightarrow CF_3 + CF_2O$$

which, in turn, react with O_2 leading to the formation of C_1 radicals. When in addition to O_2, CO is present, the C_1 radicals react with it leading to its catalytic oxidation to CO_2. The trioxide $CF_3OC(O)O_3C(O)OCF_3$ was observed following the photolysis of all four halides in the presence of O_2 and CO.

The other radical partners coming from the initial step in the photolysis (XC(O)) as well as the products of their reaction with O_2 ($XC(O)O_y$, $y = 1, 2$) do not react with CO but when $X = F$ they lead to the formation of a new stable peroxy molecule with the formula $CF_3OC(O)O_2C(O)F$. Some of the properties of this new molecule, its stability and its IR features are presented in this work. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photochemistry; Perfluoroacyl halide; Photolysis

1. Introduction

The tropospheric reactions of HCFCs, HFCs and their degradation products have received much attention recently. CF_2O, CFClO, CFHO, $CF_3C(O)X$ ($X = Cl$, F) are some of these degradation products. In particular, $CF_3C(O)F$ forms through the tropospheric degradation of CF_3CHFCl and CF_3CH_2F [1]. $CF_3C(O)Cl$ in turn is the product of the tropospheric degradation of CF_3CHCl_2 [2].

The photochemical rupture of $CF_3C(O)X$ at 254 nm was studied by several groups [3–12] and there is a general agreement that the primary step is:

$$CF_3C(O)Cl \rightarrow CF_3 + CO + Cl \quad (1)$$

$$CF_3C(O)F \rightarrow CF_3 + FCO \quad (2)$$

In addition, the photochemistry of perfluoroacyl molecules with a longer carbon chain (i.e. $C_2F_5C(O)X$) was studied to compare the effect of the length of the carbon chain in the primary photochemical path and the mechanism of reaction. The results showed that the primary step is [13,14]:

$$C_2F_5C(O)Cl \rightarrow C_2F_5 + CO + Cl \quad (3)$$

$$C_2F_5C(O)F \rightarrow C_2F_5 + FCO \quad (4)$$

respectively and that the length of the chain does not indicate a mechanism different from the accepted for $CF_3C(O)X$ molecules.

The $CF_3C(O)Cl$ photochemistry was studied for the compound alone [8,9,12], in the presence of the major reactive component of the atmosphere (i.e. O_2) [4,12], and in the presence of mixtures of O_2/CO both at room and low temperatures (close to 5 °C) [10]. The results obtained, specially in the presence of O_2/CO at low temperatures, lead to the formation and identification of a new compound ($CF_3OC(O)O_2C(O)OCF_3$) and a new intermediate molecule proposed as $CF_3OC(O)O_3C(O)OCF_3$ [10,15].

The photolysis of $CF_3C(O)F$ was studied for the compound alone [6,11] and in the presence of several gases ($c\text{-}C_6H_{12}$, $(FCO)_2$ and O_2) [11]. The results lead to the determination of the rate constant between CF_3 and FCO radicals [11]. A similar study for the photolysis of $C_2F_5C(O)F$ allowed the determination of the rate constant of the reaction between C_2F_5 and FCO radicals [14].

The photolysis of $C_2F_5C(O)Cl$ was studied only for the compound alone, its photolytic rupture being reaction 3 [13].

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Due to the important results obtained in all these cases, and taking into account that the photolysis of $CF_3C(O)Cl$ was the only one studied in the presence of O_2/CO, we performed the photolyses of the other perfluoroacyl halides in the presence of O_2 and CO at room and low temperatures, to complete the set of measurements. Besides, the fact that two of the acyl halides studied yield the FCO radical leads to coupling reactions of two different fluorocarbon radicals and makes possible the formation of a new stable species that will be proved to be the peroxide $CF_3OC(O)O_2C(O)F$.

2. Experimental

2.1. Materials

Commercially available samples of $CF_3C(O)Cl$, $CF_3C(O)F$, $C_2F_5C(O)Cl$ and $C_2F_5C(O)F$ (PCR Research Chemicals) were distilled in vacuum before use. Oxygen was condensed by passing it at atmospheric pressure through a trap immersed in liquid air. The condensate was then pumped under vacuum several times and transferred to a glass bulb whilst the trap was immersed in liquid air. CO was passed through a trap maintained at liquid nitrogen temperature and stored in a glass bulb.

2.2. Procedure

A quartz walled cell fitted with KCl windows was used to conduct the photochemical experiments. Photolyses were carried out using low-pressure 10 W Hg lamps arranged around the cell, which was mounted in the light path of an FTIR spectrophotometer to allow us to monitor the appearance of products and the disappearance of reagents as a function of time. The characteristic bands used to follow the concentration of a particular compound appear in Section 3 as numbers between brackets.

The measurements were performed at room and at low temperature (close to 5 °C). The lower temperature was used in experiments aimed at increasing the amount of intermediates or marginally stable compounds.

A typical experiment at room temperature involved photolyzing the sample for a certain period of time, then turning off the lights, and continuing to monitor the variation of the products concentration for around 120 min. For experiments carried out at low temperature, we extended the observation time up to 2 days after having turned off the photolysis lamps. For details see Ref. [10].

3. Results

3.1. Perfluoropropionyl chloride

The photolysis of $C_2F_5C(O)Cl$ (1.5 Torr) in the presence of O_2 (10.0 Torr), shown in Fig. 1, leads to the formation of CF_2O (1928 and 774 cm^{-1}), $CF_3O_3CF_3$ (1170 cm^{-1}), $CF_3O_3C_2F_5$ (1081 cm^{-1}), CO_2 (2340 and 667 cm^{-1}) and small quantities of CO. The identification and quantification of $CF_3O_3C_2F_5$ were carried out through the spectra presented in Refs. [16,17]. The analysis of the IR spectra does not reveal the formation of other products. The UV spectra obtained after the photolysis shows the formation of Cl_2. A ratio of 2:1 between the $C_2F_5C(O)Cl$ consumed and the Cl_2 formed is determined.

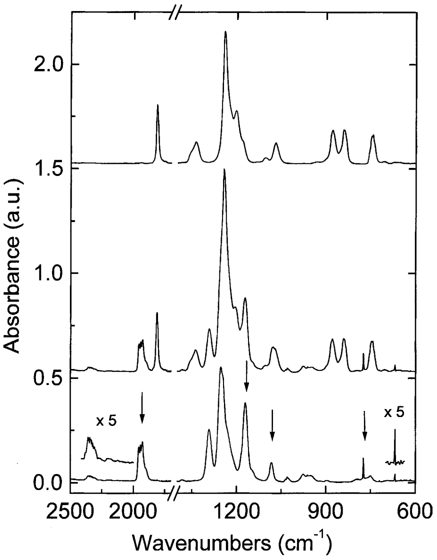

Fig. 1. Spectra obtained in the photolysis of a mixture of $C_2F_5C(O)Cl/O_2$. Upper, before the photolysis; middle, after photolysis; lower trace, corresponds to spectrum of the products. The arrows indicate the bands used for the identification of the products.

The photolysis of $CF_3C(O)Cl/O_2/CO$ mixtures leads to the formation of an intermediate [10] after a series of reactions between CF_3O, CO and O_2. In order to check that in the photolysis of $C_2F_5C(O)Cl/O_2/CO$ mixtures the same intermediate is formed, we photolyzed $C_2F_5C(O)Cl$ (1.5 Torr), O_2 (10.0 Torr) and CO (5.0 Torr) at room and low temperatures. The room temperature spectra are shown in Fig. 2. The comparison between the upper (before the photolysis) and middle traces (taken immediately after the lights were turned off, following 12 min of irradiation) clearly reveals the formation of CF_2O, $CF_3O_3CF_3$, the disappearance of CO and the appearance of CO_2. It can also be observed that several peaks appear (975, 1137 and 1881 cm^{-1} marked with arrows) and disappear within 2 h after the lights are turned off (see the lower trace), whereas CF_2O and CO_2 increase. This is an evidence of the existence of an intermediate in the reaction. An analysis of the spectra taken after the photolysis (not showed in the figure) reveals that the stability of the intermediate is of the order of a few minutes. Both its spectrum, and its thermal stability are the same as those observed in the photolysis of $CF_3C(O)Cl/O_2/CO$ mixtures referred to as Intermediate I by Malanca et al. [10]. Also, after subtraction of the reagent itself, CF_2O

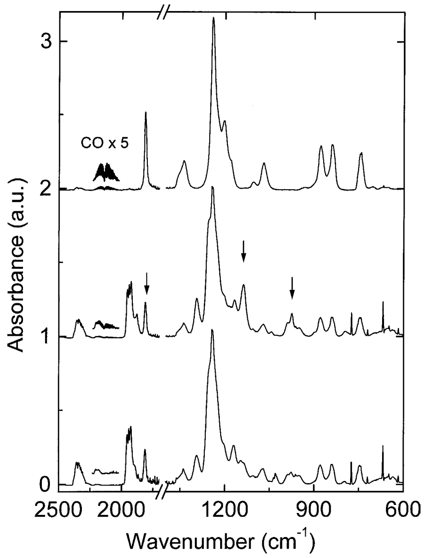

Fig. 2. Spectra obtained in the photolysis of a mixture of $C_2F_5C(O)Cl/O_2/CO$ at room temperature for different times. Upper, before the photolysis; middle, immediately after turning off the lights; lower trace, taken 2 h later. The arrows indicate the peaks corresponding to the intermediate. Note how the concentration of CO drops steadily with time. Its concentration has been magnified for a clearer understanding.

and CO_2, the formation of $CF_3OC(O)O_2C(O)OCF_3$ and $CF_3OC(O)O_2CF_3$ was observed. These products were identified using the reference spectra shown in Ref. [15].

The results obtained when the photolysis is carried out at low temperature were also coincident with the results obtained for $CF_3C(O)Cl/O_2/CO$ mixtures. As long as the system is kept at low temperature, several features can be observed, such as a smaller formation of both CF_2O and CO_2 and constancy in the concentration of the intermediate. When the system is allowed to warm up to room temperature (20 min after the photolysis) the catalytic oxidation of CO to CO_2, the formation of CF_2O and the decay of the intermediate can be observed.

3.2. *Perfluoroacetyl fluoride*

The photolysis of perfluoroacyl chloride as well as fluoride gives the perfluorinated radicals (C_1 or C_2), but only in the perfluoroacyl fluorides photolysis the formyl halogenated fragment (FCO) does not break apart after the primary absorption of the photon into F + CO. Due to this substantial difference, some differences in the nature of the products should also be expected. In order to establish whether the FCO radicals modify either the mechanism, the intermediates or the products, mixtures of $CF_3C(O)F$ (1.4 Torr), O_2 (10.0 Torr) and CO (5.0 Torr) were photolyzed at room temperature. Again, the catalytic conversion from CO to CO_2, the formation of CF_2O and of the same intermediate as in the experiments with $C_2F_5C(O)Cl$ were clearly observed. As in the photolyses of $C_2F_5C(O)Cl$ and $CF_3C(O)Cl$, the intermediate decays and the formation of CF_2O and CO_2 was observed after the lamps were turned off.

Nevertheless, the appearance of a peak at 1152 cm^{-1} (see Fig. 3) was also observed. The subtraction of the spectra of $CF_3C(O)F$, CF_2O, CO_2, $CF_3O_3CF_3$, $CF_3OC(O)O_2$-

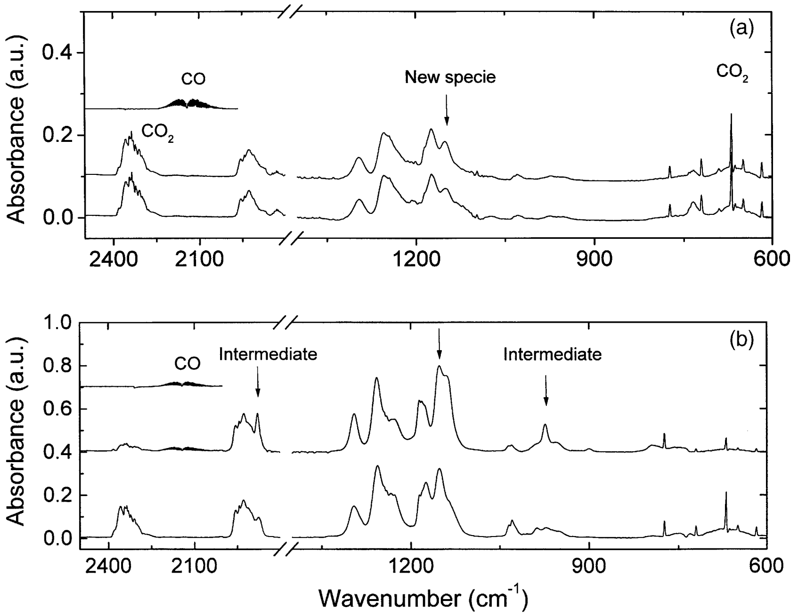

Fig. 3. Spectra obtained in the photolysis of a mixture of $CF_3C(O)F/O_2/CO$ at: (a) room; (b) low temperature. In each subset the traces are: upper, spectrum of CO added initially; middle, spectrum of the products immediately after the lights were turned off; lower, spectrum of the products 2 h later and allowing the system to reach room temperature. The arrows indicate some of the peaks corresponding to the intermediate and the new species. Notice that both increase in the photolysis at low temperature.

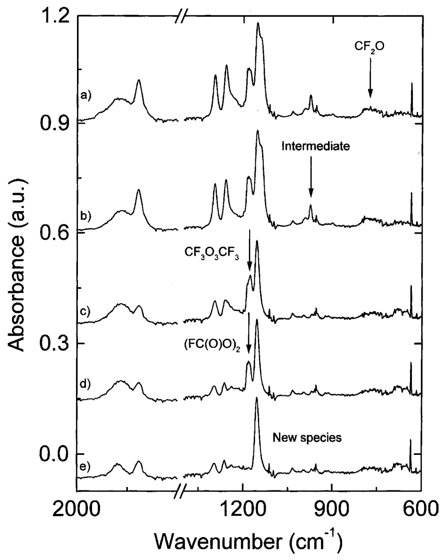

Fig. 4. Spectra obtained in the photolysis of a mixture of $CF_3C(O)F/O_2/CO$ showing: (a) the products after 20 min of photolysis; (b)–(e) what is left after the consecutive subtraction of the compounds indicated by each arrow. The last trace corresponds to the spectrum of the new species.

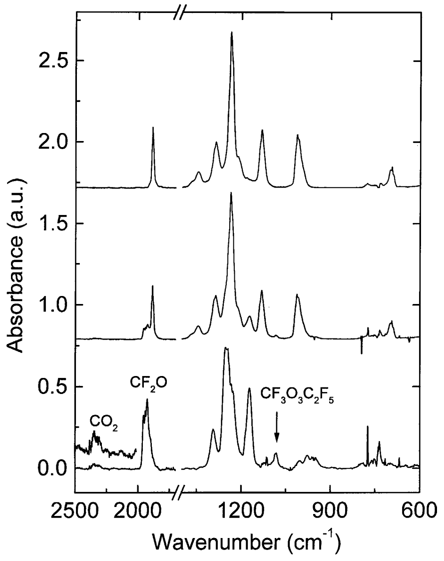

Fig. 5. Spectra of the products obtained in the photolysis of a mixture of $C_2F_5C(O)F/O_2$. Upper, before the photolysis; middle, after photolysis, lower trace, corresponds to the products.

$C(O)OCF_3$ and $CF_3OC(O)O_2CF_3$ to the spectrum obtained 2 h after the lights were turned off, reveals the formation of $(FC(O)O)_2$ proving the existence of $FC(O)O_x$ radicals in the dark. Taking into account that the only peaks that decay after the lights are turned off are those corresponding to the intermediate and the new species, but having in mind that the intermediate is also formed in experiments without FCO radicals, the $(FC(O)O)_2$ must be originated from the decay of the new species. As can be seen in Fig. 4, the spectrum of the new species contains bands that could be assigned to C–O, C=O and C–F stretchings.

In order to establish the fragments that lead to the formation of this new species, three different mixtures were photolyzed, namely: (1) 1.5 Torr of $(FC(O))_2$, 20.0 Torr of O_2 and 7.0 Torr of CO; (2) 1.5 Torr of $(CF_3C(O))_2O$, 20.0 Torr of O_2 and 7.0 Torr of CO; (3) 0.5 Torr of $(CF_3C(O))_2O$, 1.5 Torr of $(FC(O))_2$, 20.0 Torr of O_2 and 7.0 Torr of CO. Only the photolysis of the third mixture leads to the formation of the new species. These observations allow us to discard that the formation of the new species was the result of the participation of only the FCO radical, O_2 and CO or the participation of only the CF_3 radical, O_2 and CO. Therefore, it is established that its formation requires the participation of both CF_3 and FCO radicals together with O_2 and CO.

The photolysis of $(CF_3C(O))_2O/(FC(O))_2/O_2/CO$ mixtures provides better yields for formation of the new species than the photolysis of $CF_3C(O)F/O_2/CO$ mixtures. This could be explained on account of the values of the absorption cross-sections at 254 nm that show: $\varepsilon_{CF_3C(O)F} = 2.5\,M^{-1}\,cm^{-1} < \varepsilon_{(FC(O))_2} = 30.6\,M^{-1}\,cm^{-1} < \varepsilon_{(CF_3C(O))_2O} = 59.2\,M^{-1}\,cm^{-1}$. Also, a lowering in temperature acts helping the formation of the new species with a substantially better yield.

3.3. Perfluoropropionyl fluoride

In order to compare the results of the photolyses of chlorides –$CF_3C(O)Cl$ and $C_2F_5C(O)Cl$– with those of the fluorides –$CF_3C(O)F$ and $C_2F_5C(O)F$–, mixtures of $C_2F_5C(O)F/O_2$ and $C_2F_5C(O)F/O_2/CO$ were photolyzed to complete the set of measurements.

Fig. 5 shows the spectra obtained in the photolysis of $C_2F_5C(O)F$ (1.7 Torr) in the presence of O_2 (3.0 Torr). The formation of CF_2O, CO_2 and $CF_3O_3C_2F_5$ is very clear. The other two products namely $(FC(O)O)_2$ and $CF_3O_3CF_3$ were identified after further distillation of the mixture between -100 and $-186\,^{\circ}C$ to improve the separation. As in the photolysis of $C_2F_5C(O)Cl/O_2$ no other products were observed.

The photolyses of mixtures of $C_2F_5C(O)F$ (1.7 Torr)/O_2 (10.0 Torr)/CO (5.0 Torr) at room and at low temperatures show results similar to those obtained in the photolysis of $CF_3C(O)F$ under the same conditions: catalytic conversion of CO to CO_2 in the photolysis at room temperature; small disappearance of CO when the photolysis is carried out at low temperatures; noticeable formation of Intermediate I and the new species; and the formation of CO_2, CF_2O and $(FC(O)O)_2$ during the dark period following the photolysis as a consequence of the decay of the intermediate and the new species.

4. Discussion

The photochemical rupture of $CF_3C(O)X$ and $C_2F_5C(O)X$ at 254 nm leads to the formation of perfluorinated radicals CF_3 and C_2F_5 respectively (reactions 1–4) [3–14].

In the presence of an excess of O_2 they are converted into CF_3O_2 and $C_2F_5O_2$ radicals respectively [17–19]

$$CF_3 + O_2 \rightarrow CF_3O_2 \qquad (5)$$

$$C_2F_5 + O_2 \rightarrow C_2F_5O_2 \qquad (6)$$

and therefore into CF_3O and C_2F_5O radicals [17,20]

$$CF_3O_2 + CF_3O_2 \rightarrow CF_3O + CF_3O + O_2 \qquad (7)$$

$$C_2F_5O_2 + C_2F_5O_2 \rightarrow C_2F_5O + C_2F_5O + O_2 \qquad (8)$$

The C_2F_5O radicals are expected either: (a) to decompose leading to the formation of CF_2O and CF_3 radicals [17]:

$$C_2F_5O \rightarrow CF_3 + CF_2O \qquad (9)$$

which in the presence of O_2 are converted to CF_3O_2 and CF_3O radicals through reaction 5 and 7 or (b) to react with the abundant CF_3O_2 radicals to give $CF_3O_3C_2F_5$ [17]

$$C_2F_5O + CF_3O_2 \rightarrow CF_3O_3C_2F_5 \qquad (10)$$

according to reaction 10. There exists necessarily another pathway that ends up with the same product, namely

$$C_2F_5O_2 + CF_3O \rightarrow CF_3O_3C_2F_5 \qquad (11)$$

The only product containing the $C_2F_5O_x$ moiety that we observed experimentally is the trioxide $CF_3O_3C_2F_5$. Therefore, we believe that a discussion on the relative occurrence of reactions 10 and 11 is appropriate at this point. As Sehested et al. [17] in their study of the kinetics of the reaction between $C_2F_5O_2$ radicals, we observed in all the photolyses with propionyl halides and O_2 an important formation of CF_2O and a minor formation of trioxide $CF_3O_3C_2F_5$. This suggests that the majority of the C_2F_5O radicals follow the unimolecular decomposition path (reaction 9) and that the trioxide is formed mainly by reaction 11. This statement could be corroborated having in mind that the formation of $CF_3O_3C_2F_5$ was not observed in the photolyses of mixtures of $C_2F_5C(O)Cl/O_2/CO$, or $C_2F_5C(O)F/O_2/CO$, basically due to the fact that the CF_3O radical participates in the catalytic conversion to CO_2 and therefore, it is not readily available to react with the $C_2F_5O_2$ radical.

The other trioxide –$CF_3O_3CF_3$– formed both in the photolyses of $C_2F_5C(O)Cl/O_2$ and $C_2F_5C(O)F/O_2$ mixtures, is explained through the reaction between CF_3O_2 and CF_3O radicals [20]:

$$CF_3O_2 + CF_3O \rightarrow CF_3O_3CF_3 \qquad (12)$$

The disappearance of CO and the formation of CO_2 is evident when the photolysis of $C_2F_5C(O)Cl$ is carried out in the presence of 10 Torr of O_2 and 5 Torr of CO (cf. Fig. 2). Its catalytic conversion can be explained through the participation of two catalytic cycles namely: through Cl atoms [4]

$$Cl + CO \Leftrightarrow ClCO \qquad (13)$$

$$ClCO + O_2 \rightarrow ClC(O)O_2 \qquad (14)$$

$$2ClC(O)O_2 \rightarrow 2ClCOO + O_2 \qquad (15)$$

$$ClCOO \rightarrow Cl + CO_2 \qquad (16)$$

and through CF_3O radicals [10]

$$CF_3O + CO \rightarrow CF_3OCO \qquad (17)$$

$$CF_3OCO + O_2 \rightarrow CF_3OC(O)O_2 \qquad (18)$$

$$2CF_3OC(O)O_2 \rightarrow 2CF_3OCOO + O_2 \qquad (19)$$

$$CF_3OCOO \rightarrow CF_3O + CO_2 \qquad (20)$$

The low yield of CO and the formation of CO_2 in the photolysis of mixtures of $C_2F_5C(O)Cl/O_2$ is somewhat more subtle to observe but these results are in agreement with the ones obtained in the photolysis of $CF_3C(O)Cl/O_2$ mixtures [4] and can also be explained in a similar way.

The photolysis of $C_2F_5C(O)Cl/O_2/CO$ mixtures lead to the formation of the same intermediate observed in the photolysis of $CF_3C(O)Cl/O_2/CO$ mixtures. Argüello et al. also observed this intermediate in the photolysis of $(CF_3C(O))_2O/O_2/CO$ mixtures and they proposed its molecular formula as $CF_3OC(O)O_3C(O)OCF_3$. Its formation is explained by the reaction between CF_3OCOO and $CF_3OC(O)O_2$ radicals:

$$CF_3OCOO + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O_3C(O)OCF_3 \qquad (21)$$

Although the CF_3OCOO radicals are unstable [17], reaction 20 being the most important channel for their disappearance [21], we realize that at the high pressures of O_2 and CO used in all the experiments carried out there exists the possibility of having a small concentration that allows reaction 21 to compete. The other products formed in the photolysis were $CF_3OC(O)O_2C(O)OCF_3$ and $CF_3OC(O)O_2CF_3$. Their formation was explained by the following reactions [15]:

$$CF_3OC(O)O_2 + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O_2C(O)OCF_3 + O_2 \qquad (22)$$

$$CF_3O_2 + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O_2CF_3 + O_2 \qquad (23)$$

The intermediate ($CF_3OC(O)O_3C(O)OCF_3$) was observed in the photolysis of all the perfluoroacyl halides studied up to now in the presence of O_2 and CO, as a consequence of the formation of CF_3O radicals in all these systems. Also, the products formed as a consequence of the decomposition of the intermediate were the same in all the cases: CF_2O, CO_2, $CF_3OC(O)O_2C(O)OCF_3$ and $CF_3OC(O)O_2CF_3$.

The photolysis of perfluoroacyl fluorides, $CF_3C(O)F$ and $C_2F_5C(O)F$, causes the formation of the FCO radical as a consequence of the rupture of the molecule (reactions 2 and 4) and introduces a new series of reactions in the presence of O_2:

$$FCO + O_2 \rightarrow FC(O)O_2 \qquad (24)$$

$$2FC(O)O_2 \rightarrow 2FCOO + O_2 \qquad (25)$$

$$2FCOO \rightarrow (FC(O)O)_2 \qquad (26)$$

$$FCOO \rightarrow F + CO_2 \tag{27}$$

leading to the formation of $(FC(O)O)_2$ and CO_2.

Considering that the IR spectrum of the new species shows two bands at around 1850 cm^{-1} pointing to two different carbonylic stretchings and that FCOO radicals could couple to CF_3OCOO radicals according to

$$FCOO + CF_3OCOO \rightarrow CF_3OC(O)O_2C(O)F \tag{28}$$

the new stable species should be fluoroformyl trifluoromethoxyacetyl peroxide. Nevertheless, the IR spectrum of the new species could also have been assigned to a very similar molecule that could be produced in this system as well, by any of these two reactions

$$FC(O)O_2 + CF_3OCOO \rightarrow CF_3OC(O)O_3C(O)F \tag{29}$$

or

$$FCOO + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O_3C(O)F \tag{30}$$

leading to the trioxide. We could not detect experimentally any indication of the existence of this particular molecule, especially we could not prove that when it decomposes, another compound bearing the FCOO and CF_3OCOO moieties is formed. Moreover, the new species has a lifetime of 2 days; that is, it is a relatively stable substance. The stability of some trioxides bearing a C=O bond has been reported to be smaller than the corresponding peroxides. $FC(O)O_3C(O)F$ [22,23] has a lifetime of some minutes while the peroxide $FC(O)O_2C(O)F$ is a fairly stable molecule. In a similar form, the stability of $CF_3OC(O)O_3C(O)OCF_3$ is around a few minutes [15, this work], again lower than that of the peroxide, $CF_3OC(O)O_2C(O)OCF_3$. Based on these facts, we conclude that the new species is fluoroformyl trifluoromethoxyacetyl peroxide.

Acknowledgements

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