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Gas phase photochemistry of perfluoropropyl fluoride and perfluoropropyl chloride

Santiago A. Cariati, Daniel E. Weibel*, Eduardo H. Staricco

Instituto de Investigaciones en Físico Química de Córdoba (INFIQC), Departamento de Físico Química, Facultad de Ciencias Químicas,
Universidad Nacional de Córdoba. Agencia Postal 4, C.C. 61, 5000 Córdoba, Argentina

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Abstract

The photolysis of perfluoropropyl fluoride and perfluoropropyl chloride vapour was studied in the 12.9–79.0 Torr and 6.1–40.7 Torr pressure ranges, using light of 232–240 and 254 nm, respectively. The products found were CF_3CF_2COF: CO, C_4F_{10} and COF_2; CF_3CF_2COCl: CO, CF_3CF_2Cl, C_4F_{10} and Cl_2. The quantum yield for the decomposition of CF_3CF_2COF was 0.4 ± 0.06, independently of the total pressure and light intensity while for CF_3CF_2COCl it was 1.01 ± 0.06 at 254 nm taken as $\phi_{(C_2F_5Cl+2C_4F_{10})}$. When the photolysis was made in the presence of hydrogenated compounds, a clear hydrogen abstraction took place in both the reactions, indicating the existence of radicalary mechanisms. No net effect of mechanisms and quantum yields were found on the length of the carbon chain with respect to the perfluoro acetyl halides. Mechanisms for the decomposition of perfluoroacyl halides are discussed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the last 25 years several studies have been reported on the photolysis of perhalogenated carbonyl compounds [1–3] [4–7]. Recently, the interest in the study of this kind of compounds has received special attention because some of them have been found in the tropospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). It is well known that they are being used instead of the traditional chlorofluorocarbons (CFCs) in refrigerant fluids, cleaning agents, etc. [8]. For example, it has been found that perfluoroacetyl chloride is a product of the tropospheric degradation of HCFC 123 (CF_3CHCl_2) [9]. Recent studies have started the photochemical investigation of this kind of compounds with the addition of different gases which are present in the atmosphere, like O_2 [10,11]. These studies were concerned with the degradation processes that occur in the atmosphere after photolysis of the parent molecules.

In previous papers [6,7], we have reported the gas-phase photolysis of the simplest perfluoro compounds of this family, that is, perfluoroacetyl fluorine and perfluoroacetyl chloride. The difference found in the quantum yields and in the nature of the photochemical products was related to the relative strengths of the C–X bonds (X = F, Cl). In order to obtain a better understanding of the photochemical mechanism of this kind of compounds, we carried out the investigation of the propyl family of fluorine and chlorine perhalogenated compounds, that is, perfluoropropyl fluoride and perfluoropropyl chloride.

2. Experimental details

2.1. Materials

Commercially available samples of perfluoropropyl fluoride (CF_3CF_2COF) and perfluoropropyl chloride (CF_3CF_2COCl) (P.C.R. Research Chemicals) were trap-to-trap distilled twice and the purity was verified by gas chromatography and IR spectrophotometry before use. Samples of commercially available cyclohexane (98%) and *n*-hexane (98%) were used as received.

2.2. System and procedure

The experiments were performed in a similar equipment to that described before [6]. Briefly, the experiments were carried out in a conventional grease-free high-vacuum system with a 126-ml quartz cylinder as the reaction vessel. The

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*Corresponding author.

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Table 1
Photolysis of CF_3CF_2COF with unfiltered light

Initial amount of CF_3CF_2COF (mol × 10^4)	Amount of CO (mol × 10^6)	Amount of COF_2 (mol × 10^6)	Amount of C_4F_{10} (mol × 10^6)	Conversion to CO (%)
0.992	1.12	1.06	1.17	2.3
1.57	1.76	1.88	1.82	2.2
1.92	2.88	2.97	3.00	3.0
3.1	1.28	1.31	1.14	0.8
5.2	2.86	2.80	2.65	1.1

Note: Ratio CO : COF_2 : C_4F_{10} = 1 :(1.01 ± 0.06) :(1.00 ± 0.07).

pressure was measured with a capacitance manometer within ±0.1 Torr.

The light source was a high-pressure 500 HBO OSRAM mercury lamp. In some cases, a similar lamp with lower power (200 W) was also used. The wavelengths were selected using a high-intensity monochromator with a 9.6-nm bandwidth in most cases. CF_3CF_2COF was photolysed using light of 240 and 232 nm, while CF_3CF_2COCl was photolysed at 254 nm. Similar runs were also made with the full arc of the lamp. The intensity of the lamp was measured using potassium ferrioxalate solution as actinometer. The procedure was described in detail in a previous paper [12]. After a period of illumination, the reactant and the products were condensed in a liquid-air cold trap and the non-condensable product was transferred to a gas burette by a Toepler pump and then measured. The fraction condensed at −186°C was quantitatively transferred to the inlet of a gas chromatograph (Konic KNK-3000-HRGC) for the quantitative analysis using a 6-m silica–gel column. The products were identified by IR spectrometry (FT IR Nicolet 5SX) and in some cases chromatographically by using known standard samples.

The UV spectra of CF_3CF_2COF and CF_3CF_2COCl were obtained using a UV spectrophotometer Shimadzu 260 or Shimadzu UV-1601. The maximum absorption coefficient for CF_3CF_2COF was (56.8 ± 0.3) l mol^{-1} cm^{-1} at 214 nm, and for CF_3CF_2COCl it was (28.7 ± 0.3) l mol^{-1} cm^{-1} at 258 nm.

3. Results

3.1. Photolysis of CF_3CF_2COF

When CF_3CF_2COF was photolysed with the full arc of the lamp, CO, C_4F_{10} and COF_2 were obtained as the main products. COF_2 was quantitatively converted to CO_2 by the silica–gel column [6,13,14]. The experimental results in the photolysis of CF_3CF_2COF with unfiltered light are shown in Table 1.

Table 2 shows the mass balance of the carbon atoms. Taking into account the results shown in Table 1 and that the total C decomposed is the same as the amount of quantified C (within the experimental error), the following stoichiometric equation can be deduced:

$$2CF_3CF_2COF + h\nu \rightarrow C_4F_{10} + CO + COF_2 \ (a)$$

3.2. Quantum yield of the photolysis of CF_3CF_2COF at 232 and 240 nm

The values of the quantum yields of CO, C_4F_{10} and COF_2 at 232 and 240 nm are shown in Table 3. Two runs were also carried out with the addition of c-C_6H_{12}. When 26. Torr of CF_3CF_2COF were photolysed at 240 nm in the presence of 9.5 and 20.0 Torr of c-C_6H_{12}, the yields of C_4F_{10} and COF_2 showed a drastic decrease to zero with the concurrent formation of CF_3CF_2H in increasing amounts. This behaviour was also found previously in the photolysis of trifluoroacetyl fluoride [6].

3.3. Photolysis of CF_3CF_2COCl

When the CF_3CF_2COCl photolysis was performed with the light of the full arc of the lamp, CO, CF_3CF_2Cl, and C_4F_{10} were obtained as the main products.

The experimental results in the photolysis of CF_3CF_2COCl with unfiltered light are shown in Table 4. $COCl_2$ was not found in significant amounts and this is in accordance with the relation:

Table 2
Mass balance of carbon atoms in the photolysis of CF_3CF_2COF with unfiltered light

Initial amount of CF_3CF_2COF (mol × 10^4)	Conversion to CO (%)	CF_3CF_2COF decomposed (mol × 10^6)	Total C decomposed (mol × 10^6)	Amount of C quantified (mol × 10^5)	Difference between C decomposed and quantified (%)
0.992	2.3	2.28	6.84	6.86	0.3
1.57	2.2	3.45	10.35	10.92	5.2
1.92	3.0	5.76	17.28	17.85	3.2
3.1	0.8	2.48	7.44	7.15	−3.9
5.2	1.1	5.72	17.16	16.26	−5.2

Table 3
Photolysis of CF_3CF_2COF at 232 and 240 nm

λ (nm)	PCF_3CF_2COF (Torr)	I_{abs} (%)	ϕ_{CO}	ϕ_{COF_2}	$\phi_{C_4F_{10}}$
232	15.3	46.0	0.27	0.15	0.16
	30.2	70.4	0.23	0.18	0.20
	51.3	87.3	0.25	0.16	0.19
240	12.9	24.5	0.16	0.15	0.22
	27.0	44.5	0.16	0.16	0.22
	27.5 [a]	45.1	—	0.19	0.20
	29.9	47.9	0.23	0.19	0.21
	32.7	51.0	0.18	0.17	0.19
	52.3	68.1	0.20	0.18	0.21
	79.0	82.1	0.25	0.22	0.25

[a] 350 Torr of N_2 added.

Table 4
Photolysis of CF_3CF_2COCl with unfiltered light

Initial amount of CF_3CF_2COCl (mol × 10^4)	Amount of CO (mol × 10^6)	Amount of CF_3CF_2Cl (mol × 10^6)	Amount of C_4F_{10} (mol × 10^6)	$\frac{C_4F_{10} + C_2F_5Cl}{CO}$
1.29	1.41	0.801	0.287	0.98
1.99	2.19	1.31	0.42	0.98
1.79	1.25	0.667	0.33	1.06
2.73	0.94	0.60	0.16	0.97

$$\frac{C_4F_{10} + C_2F_5Cl}{CO} = 1.03 \pm 0.06$$

Table 5 shows the mass balance of carbon atoms and in Table 6 can be seen the mass balance of chlorine atoms. Taking into account that the total C decomposed is the same as the amount of quantified C (within the experimental error) and the following relation:

$$\frac{\text{defect of mol of Cl}}{\text{mol of } C_4F_{10}} = 2.03 \pm 0.02$$

then, the following stoichiometric equations can be deduced:

$$CF_3CF_2COCl + h\nu \rightarrow CF_3CF_2Cl + CO \ (b)$$

$$2CF_3CF_2COCl + h\nu \rightarrow C_4F_{10} + CO + Cl_2 \ (c)$$

3.4. *Quantum yield of the photolysis of CF_3CF_2COCl at 254 nm*

Some runs were made to check the quantum yield in the photodecomposition of CF_3CF_2COCl. The values of quantum yields of CF_3CF_2Cl, C_4F_{10}, and $[CF_3CF_2Cl + 2C_4F_{10}]$ are shown in Table 7. In those runs, the amounts of CO were below the limit of the Toepler pump sensitivity and, therefore, could not be measured. In addition, when 32.9 Torr of CF_3CF_2COCl were photolysed with the full arc of the lamp in the presence of 10.3 Torr of *n*-hexane, a similar behaviour to the photolysis of CF_3CF_2COF with c-C_6H_{12} was found, that is an important decrease in the amount of CF_3CF_2Cl and C_4F_{10} was observed with a subsequent appearance of C_2F_5H in greater amounts.

4. Discussion

From the experimental results obtained and shown in Tables 1 and 2 and Tables 4–6, the stoichiometric equations (a), (b) and (c) can be deduced for CF_3CF_2COF and CF_3CF_2COCl respectively.

In addition, the following mean value for the quantum yields of CF_3CF_2COF (232–240 nm) and CF_3CF_2COCl (254 nm), respectively, can be seen from Tables 3 and 7:

Table 5
Mass balance of carbon atoms in the photolysis of CF_3CF_2COCl with unfiltered light

Initial amount of CF_3CF_2COCl (mol × 10^4)	Conversion to $2C_4F_{10} + C_2F_5Cl$ (%)	CF_3CF_2COCl decomposed (mol × 10^6)	Total C decomposed (mol × 10^6))	Amount of C quantified (mol × 10^5)	Difference between C decomposed and quantified (%)
1.29	1.07	1.38	4.14	4.16	0.5
1.99	1.08	2.15	6.45	6.19	0.6
1.79	0.75	1.34	4.02	3.90	−3.0
2.73	0.34	0.93	2.79	2.78	−0.4

Table 6
Mass balance of chlorine atoms in the photolysis of CF_3CF_2COCl with unfiltered light

Initial amount of CF_3CF_2COCl (mol × 10^4)	Cl [a] decomposed (mol × 10^6)	Amount of Cl quantified (mol × 10^6)	Defect of Cl (mol × 10^6)	Amount of C_4F_{10} quantified (mol × 10^6)	$\frac{\text{defect of ml of Cl}}{\text{mol of } C_4F_{10}}$
1.29	1.38	0.801	0.579	0.287	2.02
1.99	2.15	1.31	0.84	0.42	2.00
1.79	1.34	0.667	0.673	0.33	2.04
2.73	0.93	0.60	0.33	0.16	2.06

[a] Taking into account the same conversion as in Table 4 and assuming that the amount of Cl atoms is the same as the amount of CF_3CF_2COCl photolysed.

For the CF_3CF_2COF photolysis:

$$\phi_{CO} = 0.22 \pm 0.04$$

$$\phi_{COF_2} = 0.19 \pm 0.03$$

$$\phi_{C_4F_{10}} = 0.20 \pm 0.04$$

$$\phi_{CF_3CF_2COF} = 0.40 \pm 0.06$$

For the CF_3CF_2COCl photolysis:

$$\phi_{C_4F_{10}} = 0.052 \pm 0.017$$

$$\phi_{C_2F_5Cl} = 0.90 \pm 0.05$$

$$\phi_{(C_2F_5Cl+2C_4F_{10})} = \phi_{CF_3CF_2COCl} = 1.01 \pm 0.06$$

Taking into account our previous results obtained with the smaller members of this family of compounds [6,7]:

$$\phi_{CF_3COF} \cong 0.4 \ (240\text{–}232 \text{ nm})$$

$$\phi_{CF_3COCl} = 0.98 \pm 0.13 \ (254\text{–}280 \text{ nm})$$

and the similar results obtained by Maricq et al. [10] for CF_3COCl:

$$\phi_{CF_3COCl} = 1.01 \pm 0.11 \ (193 \text{ nm})$$

$$\phi_{CF_3COCl} = 0.92 \pm 0.08 \ (248 \text{ nm})$$

a general mechanism for the photodecomposition of perhalogenated carbonyl compounds can be proposed:

$$RCOX + h\nu \rightarrow A^* \quad (1)$$

$$A^* \rightarrow RCOX^\# \quad (2)$$

$$A^* \rightarrow RCO + X \quad (3)$$

$$A^* \rightarrow R + COX \quad (4)$$

$$A^* \rightarrow R + CO + X \quad (5)$$

$$RCO + M \rightarrow R + CO + M \quad (6)$$

$$R + X + M \rightarrow RX + M \quad (7)$$

$$COX + M \rightarrow CO + X + M \quad (8)$$

$$X + X + M \rightarrow X_2 + M \quad (9)$$

$$R + R \rightarrow R_2 \quad (10)$$

$$COX + COX \rightarrow CO + COX_2 \quad (11)$$

where A^* denotes the lowest singlet excited state; R = CF_3, CF_3CF_2, X = F, Cl, and $RCOX^\#$ denotes the ground state with an excess of vibrational energy.

Table 7
Photolysis of CF_3CF_2COCl at 254 nm

$P_{CF_3CF_2COCl}$ (Torr)	I_{abs} (%)	$\phi_{C_4F_{10}}$	$\phi_{CF_3CF_2Cl}$	$\phi_{[2C_2F_{10}+C_2F_5Cl]}$
6.1	19.1	0.052	0.93	1.03
10.0	29.3	0.070	0.85	0.99
20.2	50.4	0.030	0.88	0.94
40.7	75.7	0.060	0.95	1.07

An RCOX molecule is excited by one-photon absorption to a singlet excited state, from which it can form $RCOX^\#$ by internal conversion or by the recombination of R + COX radicals, or it can decompose by primary dissociation by steps (3), (4) and (5). The presence of radicals was verified by adding c-C_6H_{12} or n-C_6H_{14} gas to the system.

From the obtained results, it can be shown that when

4.1. (I) X = F

Steps 3 and 5 can be ruled out and, therefore, steps 6, 7, 8 and 9 do not occur.

The value of 0.4 for the quantum yields indicates that either the internal conversion of step (2) is very effective or that the recombination of radicals:

$$CF_3 + COF \rightarrow CF_3COF \ (2')$$

is an efficient process. This last recombination is more consistent with the experimental results obtained with the addition of hydrogenated compounds, which shows the presence of radicals. In a recent study carried out by Argüello et al. [15] they obtained interesting results which demonstrate that reaction (2′) would take place very efficiently. With the addition of oxygen to the system, the quantum yield of decomposition of CF_3COF tends to be unity when the amount of oxygen increases. These results show that after absorption of a photon by the reactive and its dissociation, an efficient recombination process between CF_3 and COF radicals takes place. Therefore, this recombination reaction should be responsible for the quantum yields lower than unity.

4.2. (II) X = Cl

No evidence of Step (11) was found. If the primary process is Step (4), COCl radicals would be formed after absorption of one photon. An estimation of the ΔH for Step (4) of 100.4 KJ mol^{-1} was obtained taking into account a ΔH_f for CF_3CF_2COCl estimated as -1011.6 KJ mol^{-1} [16–18]. If the photon energy at 254 nm is 471.09 KJ mol^{-1}, the energy to be distributed among the radical products of Step (4) would be ca. 370.7 KJ mol^{-1}. Thus, according to a statistical distribution of energy, the COCl radical would have >40 KJ mol^{-1} of energy in excess. Considering the following reaction [19]:

$$\mathrm{COCl} + M \rightarrow \mathrm{CO} + \mathrm{Cl} + M \quad \Delta H = 25.1\ \mathrm{KJ\,mol^{-1}}$$

the COCl fragment will decompose readily if the primary process is Step (4) and, therefore, no recombination process of COCl (Step (11)) should take place.

Step (3) cannot be ruled out on the basis of previous results [11,20,21] obtained in the CF_3COCl photolysis, because the CF_3CO radical may dissociate to CF_3 and CO ($R = CF_3$) giving the same species as Step (5). In a recent work by Mariqc et al. [10], they pointed out that their experiments do not indicate which bond breaks first, C–Cl or C–C, although they suggested to consider first a cleavage C–Cl leading to a vibrationally excited CF_3CO fragment that rapidly dissociates. Whichever bond breaks first, the remaining fragment CF_3CO or COCl has sufficient internal energy to dissociate prior to stabilization by collision. A similar argument can be applied when $R = CF_3CF_2$. In summary, if Step (3) occurs, the RCO radical should have a very short lifetime and it would decompose immediately.

Step (5) should be considered due to the experiments obtained by photodissociation of CF_3COCl by time-resolved IR and UV spectroscopy [10]. From the results obtained by excitation with a UV light pulse from an excimer laser, the authors concluded that Step (5) (for CF_3COCl) is the major dissociation pathway at both, 190 and 248 nm. The results indicate that both, the C–C and C–Cl bonds break each time a photon is adsorbed, in particular, at 193 nm.

From our experimental results and the technique used, it is not possible to distinguish between steps (3), (4) and (5).

The stable products COF_2, C_4F_{10}, CO, and CF_3CF_2Cl, Cl_2 can be explained by steps (10), (11) and steps (7), (8), (9) and (10) when X = F and X = Cl, respectively.

The difference found in the nature of the products and in the quantum yields in the RCOF and RCOCl photolysis can be related to the relative strengths of the C–X bonds. In the RCOF photolysis in which the C–F ($\approx$485 KJ mol^{-1}) bond is the strongest, no product yielded by F atoms were found, while in the irradiation of RCOCl a relatively similar C–Cl and C–C bond dissociation energy allowed steps (3), (4) and (5) to take place. These arguments can also be applied to explain the difference in the value of the quantum yields obtained.

Finally, the effect of the length of carbon chain on the photochemical mechanisms and on the values of the quantum yields was not observed for the shortest member of the family, i.e. $R = CF_3$, CF_3CF_2. The photodecomposition products, quantum yields and mechanisms seem to be similar in this kind of compounds. Therefore, it could be expected that the environmental impact of these related compounds will be similar, independent of the length of the carbon chain.

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