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Quantum yield in the gas phase photolysis of perfluoroacetyl chloride: a comparison with related compounds

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Abstract

The photolysis of perfluoroacetyl chloride vapour was studied in the pressure range 4.6–59.9 Torr and with addition of inert gas up to 535.2 Torr using light of 254 and 280 nm. The quantum yield for the decomposition of CF_3COCl taken as $\Phi[CF_3Cl+2C_2F_6]=0.98\pm0.13$ was not affected by the total pressure, the intensity and the wavelength of the light within the studied range of conditions. In the presence of $c\text{-}C_6H_{12}$ a clear hydrogen abstraction reaction took place indicating the presence of CF_3 radicals. An upper limit for the rate of hydrogen abstraction of $\log k_H(cm^3\ mol^{-1}\ s^{-1})=7.9$ at 298 K was obtained. Light emission was not observed over the range 330–600 nm. Mechanisms for the decomposition of perfluoroacyl halides are discussed.

Keywords: Quantum yield; Gas phase photolysis

1. Introduction

In previous papers we reported the results of the photolysis of perfluoroglutaryl dichloride (PFGDCl), 4-chloroperfluorobutanoyl chloride (4-ClPFBCl) [1,2] and perfluoroacetyl fluoride (CF_3COF) vapour [3]. The 4-ClPFBCl is a stable intermediate product in the photolysis of PFGDCl, whose overall reaction decomposition occurs stepwise:

$$ClCO(CF_2)_3COCl+h\nu \longrightarrow Cl(CF_2)_3COCl \qquad (I)$$

$$Cl(CF_2)_3COCl+h\nu \longrightarrow Cl(CF_2)_3Cl \qquad (II)$$

The experimental conditions were established in order to study reactions (I) and (II) separately finding quantum yields of unity for both reactions at different wavelengths. A concerted process has therefore been proposed to explain these results [1,2].

On the contrary, a quantum yield of $\Phi=0.4$ was determined in the photolysis of CF_3COF [3]. A radical process was assumed in this case owing to the fact that when the pressure of $c\text{-}C_6H_{12}$ added was increased, the yields of C_2F_6 and COF_2 decreased dramatically to zero with the concurrent formation of CF_3H in increasing amounts.

In order to find out whether the different behaviour is due to F-substitution of Cl atoms or the length of the carbon chain, we undertook to study the photolysis of CF_3COCl. In addition, a few irradiations of PFGDCl in presence of a chemical quencher, $c\text{-}C_6H_{12}$, were performed to check the mechanism proposed before [1].

2. Experimental details

2.1. Materials

A commercially available sample of trifluoroacetyl chloride (CF_3COCl) (PCR Research Chemicals Inc.) and perfluoroglutaryl dichloride (PFGDCl) (PCR Research Chemicals Inc.) were twice trap-to-trap distilled and the purity was verified by gas chromatography. Samples of commercially available cyclohexane (98%) and $c\text{-}C_4F_8$ (98%) were used as received.

2.2. System and procedure

The equipment was similar to that used before [3]. Briefly, the experiments were carried out in a con-

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ventional grease-free high-vacuum system with 126 ml quartz cylinder as the reaction vessel. The light source was a high pressure 500 HBO OSRAM mercury lamp. The selected wavelengths were isolated by a high intensity monochromator using a bandwidth of 9.6 nm in most cases. CF_3COCl was photolysed using light of 254 and 280 nm. Similar runs were also made with the full arc of the lamp. The actinometric measurements with potassium ferrioxalate solution were performed using the technique previously described in detail [4].

After photolysis, the contents of the reaction vessel were condensed in a liquid air cold trap and CO was transferred to a gas burette by a Toepler pump and then measured (the system is not affected by the presence of Hg traces). The fraction condensed at −186 °C was quantitatively transferred to the inlet of a gas chromatograph (Varian 1420) for the quantitative analysis using a 6m silica gel column. The products were identified by IR spectrophotometry (FT IR Nicolet 5SX). In some cases attempts were made to quantify $COCl_2$ chromatographically by conversion to CO_2 on a silica–gel column [5]. This was unsuccessful because the amount produced was perhaps lower than the limit of detection (see discussion section).

The UV spectra of CF_3COCl was obtained using a Shimadzu 260 UV spectrophotometer. The maximum absorption coefficient for CF_3COCl was (17.8 ± 0.2) l mol^{-1} cm^{-1} at 254 nm.

Light emission was not observed when 180 Torr of CF_3COCl was irradiated at 254 nm and the emission spectra was scanned in the range 300–600 nm using a SLM 4800C spectrofluorometer.

Some experiments were carried out at 270 nm photolysing PFGDCl in an identical way as described elsewhere [2] but in the presence and absence of a radical scavenger. Indeed, a fixed pressure of PFGDCl was photolysed in the presence and absence of c-C_6H_{12} as radical scavenger. The products were quantitatively analysed using a 3m Silicone Q–F column attached to a Varian 1420 gas chromatograph.

3. Results

3.1. Photolysis of CF_3COCl

3.1.1. Determination of the stoicheometric equation

When the CF_3COCl photolysis was performed with the light of the full arc of the lamp, CO, CF_3Cl and C_2F_6 were obtained as principal products.

The experimental results in the photolysis of CF_3COCl with unfiltered light is shown in Table 1. $COCl_2$ was not found in significant amounts and this is in accordance with the relation

Table 1
Photolysis of trifluoroacetyl chloride with unfiltered light

P CF_3COCl (Torr)	CO (10^6 mol)	CF_3Cl (10^6 mol)	C_2F_6 (10^6 mol)	$\frac{2C_2F_6+CF_3Cl}{CO}$
7.6	6.25	5.76	0.520	1.09
9.0	8.90	6.88	0.877	0.97
15.1	5.52	4.00	0.687	0.97
24.8	11.30	9.24	0.765	0.95
30.8	14.40	12.50	0.986	1.01
59.9	10.00	7.80	0.830	0.95

$$\frac{2C_2F_6+CF_3Cl}{CO} = 0.99 \pm 0.05$$

Table 2 shows the mass balance of the carbon atoms and in Table 3 can be seen the mass balance on 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 ratio

$$\frac{\text{mol of Cl in defect}}{\text{mol of } C_2F_6} = 2.00 \pm 0.04$$

the following stoicheometric equations are deduced:

$$CF_3COCl \longrightarrow CF_3Cl + CO \qquad (a)$$

$$2CF_3COCl \longrightarrow C_2F_6 + CO + Cl_2 \qquad (b)$$

3.1.2. Quantum yield at 254 and 280 nm

The values of ΦC_2F_6, ΦCF_3Cl and $\Phi[CF_3Cl+2C_2F_6]$ are shown in Table 4 and Table 5. The amounts of CO were not determined because they were under the limit of the Toepler pump sensitivity in these conditions of illumination. As can be seen in both Tables, the quantum yield is independent of the wavelength of radiation. The results of addition of inert gas (c-C_4F_8) are shown in Table 6. They indicate that the $\Phi[CF_3Cl+2C_2F_6]$ seems to be independent up to 535.2 Torr of the c-C_4F_8 added.

Irradiation of CF_3COCl at 254 nm emission was not observed over the range 330–600 nm up to 180 Torr of reactant.

When 5.2 Torr of CF_3COCl were photolysed with the full arc of the lamp in the presence of 20.0 Torr of c-C_6H_{12}, a drastic decrease in the amount of CF_3Cl and C_2F_6 was observed with a subsequent appearance of CF_3H in greater amounts. An upper limit of log $k_H = 7.9$ cm^3 mol^{-1} s^{-1} at 25 °C was calculated.

3.2. Effect of c-C_6H_{12} addition on the perfluoroglutaryl dichloride photolysis

The runs without c-C_6H_{12} were performed in the same way as described in [2]. These runs were compared

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

Initial amount of CF_3COCl (mol×10^5)	% Conversion to $2C_2F_6+CF_3Cl$	CF_3COCl decomposed (mol×10^6)	C Total decomposed (mol×10^5)	Amount of C quantified (mol×10^5)	Difference between C decomposed and quantified (%)
5.20	13.1	6.81	1.36	1.31	−3.7
6.15	14.0	8.61	1.72	1.75	1.7
10.33	5.2	5.37	1.06	1.09	1.8
16.96	6.4	10.80	2.16	2.20	1.8
21.06	6.9	14.50	2.90	2.89	−0.4
40.96	2.3	9.42	1.88	1.95	3.6

Table 3
Mass balance of chlorine atoms in the photolysis of trifluoroacetyl chloride with unfiltered light

Initial amounts of CF_3COCl (mol×10^5)	Cl[a] decomposed (mol×10^6)	Amount of Cl quantified (mol×10^6)	Defect of Cl (mol×10^6)	Amount of C_2F_6 quantified (mol×10^6)	mol in defect of Cl / mol of C_2F_6 (mol×10^6)
5.20	6.81	5.76	1.05	0.520	2.02
6.15	8.61	6.88	1.73	0.877	1.97
10.33	5.37	4.00	1.37	0.687	1.99
16.96	10.80	9.24	1.56	0.765	2.04
21.06	14.50	12.50	2.00	0.986	2.03
40.96	9.42	7.80	1.62	0.830	1.95

[a] Taking into account the same conversion as in Table 1 and assuming that the amount of Cl atoms is the same as the amount of CF_3COCl photolysed.

Table 4
Photolysis of trifluoroacetyl chloride at 254 nm

P CF_3COCl (Torr)	$\%I_{Abs}$	ϕC_2F_6	ϕCF_3Cl	$\phi(2C_2F_6+CF_3Cl)$
4.6	9.6	0.035	0.80	0.93
5.1	10.6	0.035	0.81	0.88
5.2	10.7	0.049	0.92	1.02
5.4	11.3	0.100	0.69	0.89
10.0	19.6	0.083	1.02	1.18
10.0	19.7	0.047	0.87	0.96
10.1	19.9	0.051	0.97	1.07
10.1	19.9	0.069	0.64	0.78
10.3	20.3	0.076	0.92	1.07
19.9	35.4	0.041	1.10	1.18
20.0	35.6	0.056	0.95	1.06
20.1	35.8	0.046	0.79	0.88
20.1	35.7	0.056	0.76	0.87
21.3	37.4	0.067	0.71	0.84
21.8	38.0	0.085	0.88	1.05
22.6	39.1	0.052	0.84	0.94
37.4	55.9	0.030	0.88	0.94
39.7	58.0	0.070	0.93	1.07
40.0	58.3	0.058	0.82	0.94
40.2	58.8	0.065	0.70	0.83
40.3	58.9	0.090	0.93	1.11
41.6	59.9	0.034	0.69	0.76

Table 5
Photolysis of trifluoroacetyl chloride at 280 nm

P CF_3COCl (Torr)	$\%_{Abs}$	ϕC_2F_6	ϕCF_3Cl	$\phi(2C_2F_6+CF_3Cl)$
27.5	22.7	0.088	0.99	1.17
39.2	30.8	0.044	0.75	0.84
46.9	35.4	0.052	0.89	0.99
53.8	39.4	0.130	0.95	1.17

with those where c-C_6H_{12} was added in the presence of 15.0 Torr of PFGDCl and photolysed at 270 nm during the same photolysis time. The results (see Table 7) show that the product of the photolysis, 4-chloroperfluorbutanoyl chloride (4-ClPFBCl), was unaffected by c-C_6H_{12} addition. The ratio 4-ClPFBCl_o:4-ClPFBCl_c was never found to be higher than unity. The amounts of 4-ClPFBCl were the same regardless of whether c-C_6H_{12} was added or not within the present experimental conditions.

4. Discussion

4.1. CF_3COCl

The experimental evidence presented in Tables 1–3 allowed us to deduce the stoicheometric equations (a) and (b). $COCl_2$ was not found in significant amounts because it photolyses easily during the illumination time [6], or probably because the following reaction:

$$COCl\cdot + M \longrightarrow CO + Cl + M \qquad \Delta H = +25.1\ \text{kJ mol}^{-1}$$

Table 6
Photolysis of trifluoroacetyl chloride at 254 nm with c-C_4F_8 added

P CF_3COCl (Torr)	$\%_{Abs}$	*P* c-C_4F_8 (Torr)	ϕC_2F_6	ϕCF_3Cl	$\phi(2C_2F_6+CF_3Cl)$
39.8	58.1	66.3	0.078	0.96	1.11
39.9	58.3	157.8	0.093	0.69	0.88
40.1	58.5	267.3	0.100	0.67	0.87
41.0	59.7	393.8	0.150	0.74	1.04
41.0	59.7	535.2	0.110	0.71	0.93

Table 7
Photolysis of trifluoroglutaryl dichloride in presence of c-C_6H_{12} at 270 nm

P PFGDCl (Torr)	*P* c-C_6H_{12} (Torr)	$\frac{4\text{-ClPFBCl}_0{}^{a}}{4\text{-ClPFBCl}_c}$
15.0	15.0	1.0
15.0	32.0	1.1
15.0	48.5	$<1^{b}$
15.0	55.1	$<1^{b}$

occurs easily as the excess of energy involved in the photochemical reaction would be higher than 25.1 KJ mol^{-1} [6,7].

In addition, it can be seen from Tables 4–6 that the quantum yields are independent of the radiation wavelength and are unaffected by the c-C_4F_8 added as inert gas.

The mean value for quantum yields between 254–280 nm are:

$$\Phi C_2F_6 = 0.062 \pm 0.023$$

$$\Phi CF_3Cl = 0.86 \pm 0.11$$

$$\Phi CF_3Cl + 2C_2F_6 = 0.98 \pm 0.13$$

The experimental results could be explained by the following mechanism:

$$CF_3COCl + h\nu \longrightarrow A^* \tag{1}$$

$$A^* \longrightarrow CF_3CO^{\bullet} + Cl \tag{2}$$

$$A^* \longrightarrow CF_3^{\bullet} + COCl \tag{3}$$

$$CF_3CO^{\bullet} \longrightarrow CF_3^{\bullet} + CO \tag{4}$$

$$CF^{\bullet} + Cl^{\bullet} + M \longrightarrow CF_3Cl + M \tag{5}$$

$$CF_3^{\bullet} + CF_3^{\bullet} \longrightarrow C_2F_6 \tag{6}$$

$$COCl^{\bullet} + M \longrightarrow CO + Cl + M \tag{7}$$

$$Cl^{\bullet} + Cl^{\bullet} + M \longrightarrow Cl_2 + M \tag{8}$$

where A* denotes the lowest singlet excited state.

A CF_3COCl molecule is excited by the absorption of one photon to a singlet state, from which it can decompose by primary dissociation steps (2) and (3). The presence of radicals was demonstrated by adding c-C_6H_{12} gas to the system.

From our results it is not possible to distinguish exactly if the primary dissociation is step (2) or (3). The stability of CF_3CO radicals is well known from the literature [8]. Specifically, Porter et al. [8] have shown that the principal products of primary photodissociation of hexafluoroacetone in a conventional flash apparatus are CF_3 radicals and CO rather than CF_3CO and CF_3 radicals. Nevertheless, if CF_3CO radicals were formed by step (2), they would dissociate spontaneously by step (4).

On the contrary, if the primary process is step (3), COCl radicals would be formed after absorption of one photon. The ΔH for this step was estimated as an upper limit of 351.1 KJ mol^{-1}, taking into account a ΔH_f for CF_3COCl estimated as -840.2 KJ mol^{-1} [9,10]. Assuming that the lower energy used in our experiments for the photolytic reaction is 427.2 KJ mol^{-1}, the energy to be distributed among the radical products of step (3) would be about 75.2 KJ mol^{-1}. Thus, according to a statistical distribution, the COCl radical would have about 16.7 KJ mol^{-1} in excess (lower limit). Therefore, if COCl radicals are formed in the primary process, they should decompose readily [6,7].

The formation of the products CF_3Cl, C_2F_6 and Cl_2 can be explained by steps (5), (6), (7) and (8).

Finally the presence of CF_3 radicals was tested with c-C_6H_{12} added to a radical scavenger. Assuming that the only sources of CF_3H and C_2F_6 are:

$$CF_3^{\bullet} + c\text{-}C_6H_{12} \longrightarrow CF_3H + c\text{-}C_6H_{11}^{\bullet}$$

and

$$CF_3^{\bullet} + CF_3^{\bullet} \longrightarrow C_2F_6$$

then

$$k_H = \frac{R_{CF_3H}}{R_{C_2F_6}^{1/2}[c\text{-}C_6H_{12}]}$$

where R_i is the rate of formation of the i-products and [c-C_6H_{12}] is the concentration of hydrocarbon.

The estimated upper limit of $k_H = 7.9 \times 10^7$ cm^3 mol^{-1} s^{-1} correlates quite well with the other values of the literature [3].

4.2. Decomposition in the gas phase photolysis of perfluoroacyl halides

In the photolysis of the CF_3COF [3], C_2F_6, COF_2 and CO were found as main products. CF_4 was detected in negligible amounts and $\Phi CF_3COF = 0.4$. In contrast, in the CF_3COCl photolysis (shown in the present study) CF_3Cl and CO were the main products, although C_2F_6, CO and Cl_2 appeared in significant amounts. The ΦCF_3COCl was close to unity.

The difference found in the nature of the products in the CF_3COF and CF_3COCl photolysis can be explained with arguments similar to those of the liquid phase photochemistry of polyfluoroacyl halides according to steps (2′) and (3′): C–X bonds. The different behaviour exhibited in the liquid phase photochemistry of polyfluoroacyl fluoride, chloride and bromide is related to the relative strengths of the C–X bonds [11].

$$A^* \longrightarrow CF_3CO^{\cdot} + X \qquad (2')$$

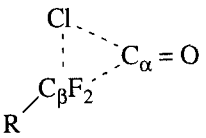
$$A^* \longrightarrow CF_3^{\cdot} + COX \qquad (3')$$

where X = F, Cl.

In the CF_3COF photolysis, in which the C–F (≈ 485 KJ mol^{-1}) bond is the strongest, no products yielded from fluorine atoms were found. Thus, step (2′) did not take place. In the irradiation of CF_3COCl, steps (2′) and (3′) can take place due to a relatively similar C–Cl and C–C bond dissociation energy.

The difference in the quantum yields can be explained with similar arguments. The weaker C–Cl bond with respect to C–F bond allows its breakage easily and the quantum yields obtained when X = Cl were unity (ΦDClPFG = 1, Φ4Cl-PFGCl = 1 [2]). When X = F an effective internal conversion was found. Similar results were also obtained in the perfluoropropionyl fluoride photolysis (CF_3CF_2COF) [12], where C_4F_{10}, COF_2 and CO were the main products and ΦCF_3CF_2COF was close to 0.4.

In the irradiation of PFGDCl, there is no evidence that free radicals were present as we can see in Table 7. As we suggested previously [1], a concerted process should be present in which the chlorine atom can migrate to the neighbouring carbon (C). The configuration proposed is as follows:



where R = $-CF_2CF_2COCl$.

Since C_β is strongly electrophilic, the chlorine atom could migrate to that carbon atom simultaneously with the C_α–C_β bond cleavage.

A similar behaviour is expected to be found in related compounds with different lengths of carbon chain. We have therefore undertaken the study of the photochemistry of perfluoropropyl halides [12].

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References

[1] D.E. Weibel, E.R. de Staricco and E.H. Staricco, *J. Photochem. Photobiol. A: Chem., 43* (1988) 11.
[2] D.E. Weibel, E.R. de Staricco and E.H. Staricco, *J. Photochem. Photobiol. A: Chem., 54* (1990) 181.
[3] D.E. Weibel, C.M. de Vöhringer, E.R. de Staricco and E.H. Staricco, *J. Photochem. Photobiol. A: Chem., 63* (1992) 1.
[4] D.E. Weibel, E.R. de Staricco and E.H. Staricco, *J. Photochem. Photobiol. A: Chem., 49* (1989) 279.
[5] J. Heicklen, *J. Am. Chem. Soc., 87* (1965) 445.
[6] (a) H. Okabe, *Photochemistry of small molecules*, Wiley, New York, 1978, p. 125. (b) S. Glicker and H. Okabe, *J. Phys. Chem., 91* (1987) 437. (c) H. Okabe, A.H. Laufer and J.J. Ball, *J. Chem. Phys., 55* (1971) 373.
[7] J. Heiklen, *J. Phys. Chem., 70* (1966) 2456.
[8] (a) B.G. Tucker and E. Whittle, *Trans. Faraday Soc. 61* (1965) 866. (b) J.C. Amphlett and E. Whittle, *Trans. Faraday Soc., 63* (1967) 80. (c) J.S.E. McIntosh and G.B. Porter, *Trans. Faraday Soc., 64* (1968) 119. (d) J.A. Kerr and J.P. Wright, *J. Chem. Soc., Faraday Trans. 1, 81* (1985) 1471.
[9] S.W. Benson, F.R. Cruickshank, D.M. Goldèn, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev., 69* (1969) 279.
[10] *Handbook of Chemistry and Physics*, 68th edn., CRC Press, 1987–1988.
[11] J.F. Harris, Jr., *J. Organomet. Chem., 30* (7) (1965) 2182.
[12] E.H. Staricco et al. (to be submitted).