THE KINETICS OF THE GAS PHASE PHOTOCHLORINATION OF HEXAFLUOROPROPENE

M. C. GONZALEZ and E. CASTELLANO

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Cas de Correo 16, Sucursal 4, 1900 La Plata (Argentina)

(Received July 24, 1980; in revised form October 16, 1980)

Summary

The gas phase photochlorination of hexafluoropropene (C_3F_6) was studied in a static system at temperatures between 30 and 80 °C. The rate was measured under both steady and intermittent light of wavelength 436 nm. $C_3F_6Cl_2$, the only final product, is formed according to the equation

$$+ \frac{d[C_3F_6Cl_2]}{dt} = k[Cl_2] J_{abs}^{1/2}$$

The rate constants of reactions (3)

$$C_3F_6Cl + Cl_2 \rightarrow C_3F_6Cl_2 + Cl$$

and (4)

$$2C_3F_6Cl \rightarrow products$$

are
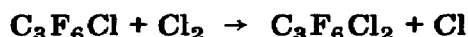
$$\log\{k_3(\text{l mol}^{-1} \text{ s}^{-1})\} = 8.8 - \frac{3600 \pm 200}{4.57T}$$

and

$$\log\{k_4(\text{l mol}^{-1} \text{ s}^{-1})\} = 9.14 \pm 0.21$$

At 30 °C, with a Cl_2 pressure of 100 Torr and $J_{abs} = 1.73 \times 10^{11} h\nu$ cm^{-3} s^{-1}, a quantum efficiency ϕ of 7529 molecules quanta^{-1} was obtained.

1. Introduction

The addition of atoms or radicals to olefins has been studied extensively. The photolysis of mixtures of chlorine and ethylene and of its simple chloro derivatives has been investigated systematically by Schumacher and

coworkers [1 - 4]. They have pointed out the variation of the reaction rate with structure.

The photochlorinations of perfluoroethylene [5] and perfluoro-2-butene [6] have also been studied. However, there appear to be no data available on the corresponding reaction between chlorine and perfluoropropene. Therefore in this work the gas phase photochlorination of perfluoropropene (C_3F_6) at temperatures between 30 and 80 °C under the influence of both steady and intermittent radiation was undertaken.

Preliminary experiments showed that in the absence of oxygen the reaction proceeds by a chain mechanism. In runs with excess chlorine and which were carried out to full conversion the analysis of the products using low temperature fractional distillation showed the existence of only one compound, which was identified as dichlorohexafluoropropane ($C_3F_6Cl_2$) by its vapour pressure and IR spectra. The pressure change in the system indicated that the stoichiometry of the reaction is

$$C_3F_6 + Cl_2 \rightarrow C_3F_6Cl_2$$
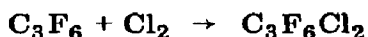
Under steady illumination the rate equation, the reaction mechanism and some of its kinetic parameters were established. The reaction was also studied with intermittent illumination. The rotating sector method enabled the absolute rate constants for each of the individual steps in the reaction mechanism to be calculated.

2. Experimental

Since the reaction occurs with a decrease in pressure, a manometric method at constant temperature and constant volume was employed to follow the course of the reaction. The apparatus for steady illumination described elsewhere [7] was used with minor modifications. The reactor was a quartz cylinder 5 cm long, 5 cm in diameter and 98.1 cm^3 in volume which had flat optical windows. A Q-700 end-on Hanau medium pressure mercury lamp (125 V, 500 W) was used as the light source. A small optical diaphragm 3 mm in diameter and covered by an unpolished glass plate was set in front of the lamp and in the focal plane of a quartz lens. By means of three collimating holes 45 mm in diameter and a system of Schott and Gen glass filters (BG 12.4 mm; GG 15.2 mm), a parallel homogeneous monochromatic light beam of wavelength 436 nm was obtained. In a series of experiments several different light intensities were applied using neutral glasses to reduce them.

Because of the large chain length, whenever possible the components of the system were blackened and those between the lamp housing and the reactor were enclosed in a blackened cardboard box. In order to prevent the entry of extraneous light into the reaction cell, all runs were carried out in a darkened room.

The light intensity was measured with a Hatchard and Parker [8] ferrioxalate actinometer and the absorbed light was calculated using the extinction coefficient [9] of chlorine. The light absorption was also measured with a Kipp and Zonen large-surface thermopile using up to 150 Torr Cl_2. The results were in good agreement with those calculated.

The experiments with intermittent light were performed following the suggestions given by Burnett and Melville [10]. A 90° blackened aluminium sector 30 cm in diameter was used to cut the light beam off at its narrowest cross section. A set of synchronous a.c. motors (Thamyr S.A., Buenos Aires, Argentina) at constant velocity was used for slow sector speeds. A low voltage d.c. motor connected to a power supply was used for high sector speeds and the rotation speed was controlled electronically [11].

C_3F_6 was supplied by PCR Research Chemicals, Florida, U.S.A. It was purified by repeated low pressure trap-to-trap distillation. Only the middle fraction was collected and was stored in a Pyrex trap cooled with liquid air. Cylinder chlorine was washed with water, was dried over sulphuric acid, was condensed, was trap-to-trap distilled at low pressure and was stored in a Pyrex trap cooled with liquid air. Tetrafluoromethane (CF_4) was supplied by Matheson Co., U.S.A. It was purified in the same way as the C_3F_6 and was stored in a 2 l Pyrex flask. Cylinder oxygen was circulated through a trap maintained at −130 °C and was stored in a 2 l Pyrex flask.

When possible all samples were carefully degassed before use. For continuous illumination most of the runs were followed up to 80% conversion. For intermittent light the reaction rate was generally measured up to a conversion of 40% and occasionally up to a conversion of 80%.

3. Results

3.1. Experiments with full light

Under the experimental conditions used no thermal reaction or induction period was observed. The run was discarded if a dark reaction occurred. The dark reaction disappeared after careful distillation of the reactants. From time to time a short induction period, presumably caused by the presence of some oxygen, was observed. In this case a degassing of the reactants was sufficient to eliminate it. The experiments showed very good reproducibility.

To determine the rate law numerous experiments were performed at 30 °C with a systematic variation of the variables involved. A series of runs was carried out at constant light intensity using an initial chlorine pressure of 50 Torr and a pressure of C_3F_6 between 20 and 200 Torr. Considering that the conversion was about 80%, the lowest C_3F_6 pressure investigated was about 4 Torr. The results showed that under these conditions the rate is independent of the C_3F_6 pressure.

Experiments performed using a chlorine pressure of 100 Torr and a C_3F_6 pressure of 50 Torr in the presence of up to 350 Torr CF_4 or up to

200 Torr reaction products showed that the rate is also independent of total pressure and of the presence of reaction products.

The influence of the light intensity on the rate was studied in a series of runs using an initial chlorine pressure of 100 Torr, an initial C_3F_6 pressure of 50 Torr and incident light intensities between 0.4×10^{16} and 3.8×10^{16} quanta min^{-1}. The rate was found to be proportional to $J_{abs}^{1/2}$.

In order to determine how the rate depends on chlorine pressure a series of experiments was carried out at approximately constant light intensity using an initial C_3F_6 pressure of 50 Torr and chlorine pressures between 15 and 150 Torr. Considering that the conversion was about 80%, the lowest chlorine pressure investigated was about 3 Torr. In analysing the results the fact that the rate depends on $J_{abs}^{1/2}$ was taken into account. The results showed that the rate is proportional to the chlorine pressure.

Consequently the course of the reaction can be represented by the equation

$$\frac{d[C_3F_6Cl_2]}{dt} = \frac{\Delta p}{\Delta t} = k[Cl_2]J_{abs}^{1/2} \tag{A}$$

To establish the temperature dependence of k a number of runs were also carried out at 60 and 80 °C. For the mean values of k the following were obtained: $k_{30\,°C} = 24.0 \; l^{1/2} \; mol^{-1/2} \; s^{-1/2}$; $k_{60\,°C} = 42.7 \; l^{1/2} \; mol^{-1/2} \; s^{-1/2}$; $k_{80\,°C} = 58.9 \; l^{1/2} \; mol^{-1/2} \; s^{-1/2}$. From these data the heat of activation E_0 for the overall reaction is 3.6 kcal mol^{-1} and $A_0 = 0.944 \times 10^4 \; l^{1/2} \; mol^{-1/2} \; s^{-1/2}$ (see Fig. 1).

The presence of oxygen inhibits the reaction and promotes a sensitized C_3F_6 oxidation.

Table 1 shows the results obtained during the course of the reaction in three typical experiments. It can be seen that the value of k remains constant throughout each experiment.

A summary of the most important results obtained under continuous illumination is given in Table 2. The constancy of the $\bar{k}$ value in spite of the great variation in the experimental conditions is remarkable.
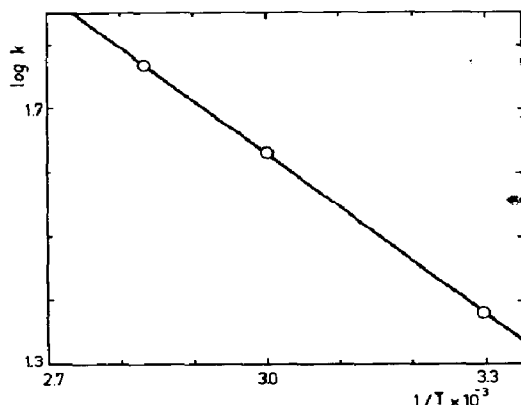

Fig. 1. An Arrhenius plot of the overall reaction (k in $l^{1/2} \; mol^{-1/2} \; s^{-1/2}$).

TABLE 1

Typical experimental results[a]

$\Sigma\Delta t$ (min)	$\Sigma\Delta p$ (Torr)	k ($l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$)
Experiment 48[b]		
5	1.4	22.5
13	3.6	24.8
31	7.5	25.1
50	10.3	22.8
72	12.9	24.5
102	15.5	24.8
144	17.7	22.5
216	20.0	22.8
355	22.2	23.9
Experiment 47[c]		
2	2.1	25.4
4.5	4.4	23.6
7	6.5	23.1
13	11.1	23.4
19	15.2	24.8
25.5	19	26
29	20.8	25.4
33.5	23	25.4
37.5	24.7	24.2
47	28.3	25.4
52	29.9	24.2
70	34.4	23.4
77	35.9	24.5
95	38.9	23.7
105	40.3	23.9
132	43.1	23.4
171	46	24.8
231	48.7	25.7
Experiment 58[d]		
6	6	22.8
11	10.7	24.8
17	15.5	24.5
23	19.5	23.9
26	21.2	22.5
35	25.9	23.7
40	28.1	23.1
45	30.1	23.4
52	32.5	22.5
73	37.8	20.7
103	43.6	23.1

[a] $\Sigma\Delta p$ is the decrease in total pressure corresponding to the illumination time $\Sigma\Delta t$. k is the rate constant calculated point to point using eqn. (A).
[b] T = 30 °C; incident light intensity J_0 = 1.1 × 10^{16} quanta min^{-1}; initial C_3F_6 pressure, 49.2 Torr; initial Cl_2 pressure, 24.7 Torr; mean rate constant value $\bar{k}_m$ = 23.7 $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$.
[c] T = 30 °C; incident light intensity J_0 = 1.1 × 10^{16} quanta min^{-1}; initial C_3F_6 pressure, 52.1 Torr; initial Cl_2 pressure, 54.5 Torr; mean rate constant value $\bar{k}_m$ = 24.5 $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$.
[d] T = 30 °C; incident light intensity J_0 = 1.1 × 10^{16} quanta min^{-1}; initial C_3F_6 pressure, 200.5 Torr; initial Cl_2 pressure, 59.1 Torr; mean rate constant value $\bar{k}_m$ = 23.2 $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$.

TABLE 2

Experiment	T (°C)	Initial Cl_2 pressure (Torr)	Initial C_3F_6 pressure (Torr)	$J_0 \times 10^{-16}$ (quanta min^{-1})	$\bar{k}$ ($l^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$)	
57	30	53.9	23.9	1.1	22.8	
58		59.1	200.5	1.1	23.2	
107		98.5	200.8	2.64	24.7	
109		97	124.2	2.45	24.6	
59		99.2	46.3	1.1	23.2	112.4 Torr $C_3F_6Cl_2$ added
60		115.4	51.3	1.01	23.2	197.3 Torr $C_3F_6Cl_2$ added
79		98.7	43.2	1.1	24.1	291.0 Torr CF_4 added
76		84.4	42.3	1.1	24.2	311.6 Torr CF_4 added
54		92.4	55.7	0.335	22.3	
55		113.8	43.6	0.335	24.2	
184		80.3	47.8	1.35	23.8	
97		63	62.7	2.26	24.6	
101		115.1	57.7	2.47	24.4	
98		73.3	43.8	2.63	24.8	
115		108	73.5	3.13	24.3	
99		78.8	43.9	2.6	24.4	
104		104.3	45.7	2.45	24.3	
113		53.9	46.6	3.13	23.2	
50		15.8	52.4	0.93	24.1	
52		15.2	53.9	1.03	24.0	
45		26.4	50.5	1.1	24.0	
48		24.7	49.2	1.1	23.7	
47		54.5	52.1	1.1	24.5	
51		97.7	49.1	1.03	23.8	
73		96	50.9	1.1	24.2	
61		112.0	53.0	1.01	25.3	
53		157.6	44.6	1.03	24.5	
85	60	45.4	52.4	3.4	42.4	
94		58.8	64.1	3.5	43.4	
90		84.1	54.8	3.14	42.9	
92		84.2	64.9	3.29	43.1	
87		79.8	31.8	6.21	43.1	
95	80	73.44	62.4	3.28	58.7	
96		66.6	57.3	3.28	59.3	
214		81.4	61.3	2.06	58.2	
215		82.8	67.4	2.06	58.3	

3.2. Experiments with intermittent light

Rotating sector experiments in which the light intensity and the sector speed were varied were carried out at temperatures of 30, 60 and 80 °C and the ratio

$$\rho = \frac{2(\text{rate with sector})}{\text{rate with continuous light}}$$
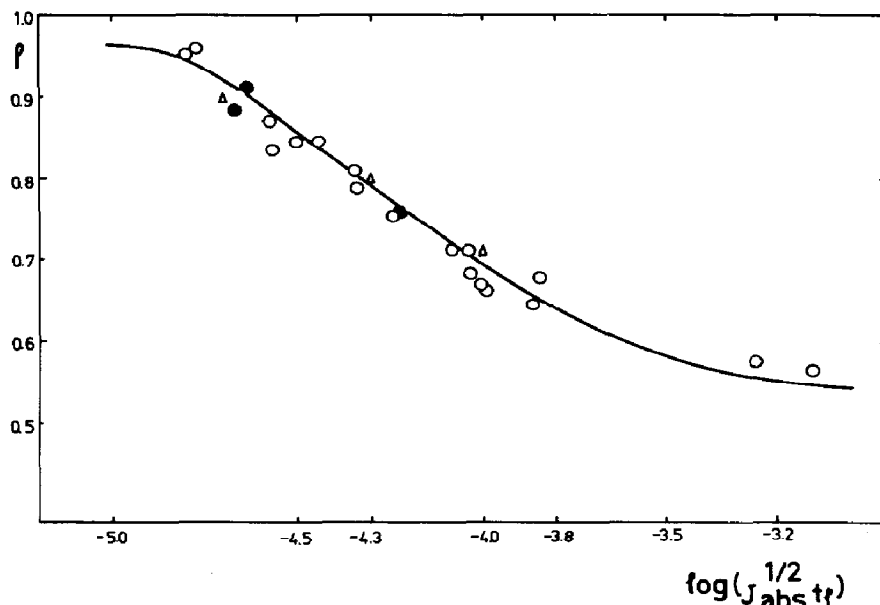
was determined.

Fig. 2. Rotating sector curve ρ vs. $\log_{10}(J_{abs}^{1/2} t_1)$: ——, theoretical curve, best fit to the experimental points with a Cl_2 pressure of 100 Torr and a C_3F_6 pressure of 50 Torr; $\bigcirc$, $T = 30$ °C; $\bullet$, $T = 60$ °C; $\triangle$, $T = 80$ °C.

At the beginning and at the end of each experiment the criterion $\rho_\infty = 1.00 \pm 0.01$, where ρ_∞ refers to conditions of limiting fast sector speed, was applied. If this value (valid for a 90° sector for the case when the rate is proportional to $J_{abs}^{1/2}$) was not found, the results of the experiment were discarded and the reactants were purified again.

A typical plot of ρ *versus* $\log_{10}(J_{abs}^{1/2} t_1)$, where t_1 is the duration of the light period in seconds and J_{abs} is the absorbed light, is shown in Fig. 2 with the theoretical curve in the position of the best fit to the experimental points. The maximum deviation observed was about 5%.

The calculation of the chain lifetime followed conventional practice. It was found that $\tau = 0.74$ s for $J_{abs} = 1.78 \times 10^{11}$ quanta cm^{-3} s^{-1}.

4. Discussion

The experimental results can be explained with the well-known chain mechanism, which is common to a series of substituted olefin photo-chlorinations ($CH_2{=}CHCl$ [1]; $CH_2{=}CCl_2$ [2]; $CHCl{=}CCl_2$ [3]; $CCl_2{=}CCl_2$ [4]; C_2F_4 [5]; C_4F_8 [6]).

$$Cl_2 + h\nu \quad \rightarrow \quad Cl + Cl \tag{1}$$

$$Cl + C_3F_6 \quad \rightarrow \quad C_3F_6Cl \tag{2}$$

$$C_3F_6Cl + Cl_2 \quad \rightarrow \quad C_3F_6Cl_2 + Cl \tag{3}$$

$$2C_3F_6Cl \quad \rightarrow \quad products \tag{4}$$

Stationary state treatment gives

$$\frac{d[C_3F_6Cl_2]}{dt} = \frac{k_3}{k_4^{1/2}} [Cl_2] J_{abs}^{1/2}$$

which is identical with the rate equation found when $k = k_3/k_4^{1/2}$.

Because of the high quantum efficiency of the reaction it was not possible to establish whether step (4) produces the dimer or whether it is a disproportionation reaction.

The reverse of steps (2) and (3) cannot take place to any appreciable extent since a dependence of the rate on the C_3F_6 pressure was not found. For the same reason reactions such as

$$C_3F_6Cl + Cl \rightarrow C_3F_6Cl_2$$

and

$$Cl + Cl + M \rightarrow Cl_2 + M$$

can be ruled out.

In the stationary state the lifetime of the chain is given by

$$\tau = \tfrac{1}{2} (J_{abs} k_4)^{1/2}$$

from which $k_4 = 1.55 \times 10^9$ l mol^{-1} s^{-1} was obtained. Within the experimental error this value does not depend on the temperature.

According to the mechanism proposed the energy of activation of the overall reaction is $E = E_3 - \tfrac{1}{2} E_4$ and, since k_4 is independent of temperature, E_4 must be zero. This is a usual value for the recombination of radicals in a photochlorination process [12]. Taking $E_4 = 0$, E_3 can be calculated, i.e. $E_3 = 3.60$ kcal mol^{-1}.

With the numerical value of k_4 we obtain $k_3 = 9.45 \times 10^5$ l mol^{-1} s^{-1}, i.e.

$$k_3 = 3.7 \times 10^8 \exp\left(-\frac{3600}{RT}\right)$$

Using 6.5 Å as the collision diameter of C_3F_6Cl and 3.6 Å for that of chlorine, the collision frequency $Z_3 = 1.68 \times 10^{11}$ l mol^{-1} s^{-1}. This corresponds to a probability factor $\alpha_3 = A_3/Z_3 = 2.42 \times 10^{-3}$. This value is similar to that corresponding to the reaction $C_2HCl_4 + Cl_2$ [13].

The value $Z_4 = 1.04 \times 10^{11}$ l mol^{-1} s^{-1} was also calculated and the probability factor $\alpha_4 = A_4/Z_4 = 1.5 \times 10^{-2}$ was determined. This is similar to that obtained in the recombination of similar radicals ($2C_2Cl_4H$ [13]; $2CH_3$ [14]; $2C_2H_5$ [15]; $2CF_3$ [16]).

The values for ϕ of 7.53×10^3 molecules quanta^{-1} and for E_3 of 3.60 kcal mol^{-1} determined in this work lie between $\phi = 2.5 \times 10^5$ and $E_3 = 0.8$ kcal mol^{-1} and $\phi = 2.8 \times 10^2$ and $E_3 = 5.35$ kcal mol^{-1} obtained in the photochlorination of C_2F_4 [5] and C_4F_8 [6] respectively.

The values $E_4 = 0$ and $\log_{10}A_4 = 9.19$ are similar to those obtained in the photochlorination of a series of substituted ethylenes [12]; in particular $\log_{10}A_4 = 9.19$ is in close agreement with the value of about 9.1 which can be derived from the empirical relation proposed by Bertrand *et al.* [17], whereas the values $E_3 = 3.60$ kcal mol^{-1} and $A_3 = 10^{8.6}$ resemble those of the $C_2H_2Cl_2$ photochlorination [12].

Since the k_4 values are similar for photochlorinations which occur with the same mechanism, the different values observed for the quantum yields must be attributed to a change in E_3.

Acknowledgment

References

1 H. Schmitz and H. J. Schumacher, *Z. Phys. Chem., Abt. B, 52* (1942) 72.
2 K. L. Muller and H. J. Schumacher, *Z. Phys. Chem., Abt. B, 35* (1937) 285.
3 K. L. Muller and H. J. Schumacher, *Z. Phys. Chem., Abt. B, 35* (1937) 455.
4 C. Schott and H. J. Schumacher, *Z. Phys. Chem., Abt. B, 49* (1941) 107.
5 E. Castellano, N. Bergamin and H. J. Schumacher, *Z. Phys. Chem. N.F., 27* (1961) 112.
6 M. E. Roselli and H. J. Schumacher, *Z. Phys. Chem. N.F., 28* (1963) 326.
7 K. L. Muller and H. J. Schumacher, *Z. Phys. Chem., Abt. B, 35* (1937) 285.
8 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A, 235* (1956) 518.
9 H. V. Halban and K. Siedentopf, *Z. Phys. Chem., 103* (1922) 71.
10 G. M. Burnett and V. H. Melville, in S. L. Friess, E. S. Lewis and A. Weissberger (eds.), *Techniques of Organic Chemistry*, Vol. VIII, Part II, Wiley–Interscience, New York, 2nd edn., 1963, pp. 1107 - 1137.
11 A. J. Arvía, S. L. Marchiano and J. J. Podestá, *Electrochim. Acta, 12* (1967) 259.
12 G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens and G. Verbeke, *Chem. Rev., 63* (1963) 355.
13 F. S. Dainton, D. A. Lomax and M. Weston, *Trans. Faraday Soc., 53* (1957) 460.
14 R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys., 19* (1957) 85.
15 K. J. Join and E. W. R. Steacie, *Proc. R. Soc. London, Ser. A, 208* (1951) 25.
16 P. B. Ayscough, *J. Chem. Phys., 24* (1956) 944.
17 L. Bertrand, G. R. De Maré, G. Huybrechts, J. Olbregts and M. Toth, *Chem. Phys. Lett., 5* (1970) 183.