Journal of Photochemistry, *38* (1987) 65 - 74

KINETICS AND MECHANISM OF THE GAS PHASE PHOTOCHLORINATION OF 1,2-DICHLORO-1,2-DIFLUOROETHYLENE

H. E. DI LORETO and E. CASTELLANO

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

(Received August 27, 1986; in revised form December 8, 1986)

Summary

The gas phase photochlorination of 1,2-dichloro-1,2-difluoroethylene was studied in a static system at temperatures between 30 and 90 °C. The rate was measured under both continuous and intermittent light of wavelength 436 nm. The only final product, $CFCl_2CFCl_2$, is formed according to the equation

$$+\frac{d[C_2F_2Cl_4]}{dt} = k[Cl_2]J_{abs}^{1/2}$$

where J is the intensity of the absorbed light.

The rate constants determined under continuous illumination are as follows: $k_{30\,°C} = 5.63 \pm 0.09$ $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$, $k_{60\,°C} = 10.43 \pm 0.02$ $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$ and $k_{90\,°C} = 21.26 \pm 1.4$ $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$.

The rate constants for the elementary reactions

$$CFCl_2\dot{C}FCl + Cl_2 \longrightarrow C_2F_2Cl_4 + Cl$$

and

$$2CFCl_2\dot{C}FCl \longrightarrow \text{products}$$

are

$$\log k_3 = 8.68 - \frac{4810 \pm 300}{4.57\,T}$$

and

$$\log k_4 = 8.91 \pm 0.21$$

respectively, where k_3 and k_4 are in litres per mole per second.

1. Introduction

The photochemical reaction of 1,1-dichloro-1,1-difluoroethylene (CCl_2CF_2) under continuous and intermittent light was investigated some time ago [1] and the rate constants for reactions

0047-2670/87/$3.50

$CF_2Cl\dot{C}Cl_2 + Cl_2 \longrightarrow CF_2ClCCl_3 + Cl$

and

$CF_2Cl\dot{C}CCl_2 + CF_2Cl\dot{C}Cl_2 \longrightarrow$ products

were determined.

By investigating the photochlorination of CFClCFCl the rate constants for the reactions

$CFCl_2\dot{C}FCl + Cl_2 \longrightarrow CFCl_2CFCl_2 + Cl$

and

$CFCl_2\dot{C}FCl + CFCl_2\dot{C}FCl \longrightarrow$ products

could presumably be measured and compared with those for the previously investigated reactions.

Consequently, the gas phase photochlorination of a cis–trans mixture of 1,2-dichloro-1,2-difluoroethylene under both steady and intermittent illumination in the range 30 - 90 °C was undertaken. Under steady illumination, the rate equation, the reaction mechanism and some of its kinetic parameters were established. Since, as will be shown, the rate depends on the square root of the intensity of the absorbed light, the rate constants included in the rate equation can be determined using intermittent illumination as provided by the rotating sector technique.

2. Experimental details

Preliminary experiments showed that the reaction proceeds by a chain mechanism. In runs with excess chlorine conducted to completion the pressure decrease was equal to the $C_2F_2Cl_2$ initial pressure. The analysis of the reaction products using low temperature fractionation and IR spectroscopy showed the existence of only one compound identified as $CFCl_2CFCl_2$. Therefore, the reaction stoichiometry is given by

$CFClCFCl + Cl_2 = CFCl_2CFCl_2$

and the reaction course could be monitored manometrically at a constant volume and temperature. The apparatus for continuous and intermittent illumination has been described elsewhere [2]. The reaction vessel was a quartz cylinder 5 cm long, 5 cm in diameter and 98.1 cm^3 in volume, with flat optical windows. As a light source an Osram HBO-200 high pressure mercury lamp fed by a stabilized a.c. power supply was used. A set of quartz lenses and stops was used to produce a parallel homogeneous light beam 4.5 cm in diameter. The 436 nm region was isolated with a system of glass filters (BG12 (2 mm) and GG15 (2 mm) (Schott and Gen., F.R.G.)). When necessary, the light intensity was reduced by means of calibrated wire gauzes.

In the experiments carried out under continuous illumination the light intensity was measured with a Hatchard and Parker potassium ferrioxalate actinometer [3] and the absorbed light was calculated using the extinction coefficient [4] of chlorine. The light absorption was also measured in the reaction vessel by means of a Kipp and Zonen large-surface thermopile at a chlorine pressure of 200 Torr. The results were in good agreement with those calculated.

The experiments with intermittent illumination were carried out according to the procedure suggested by Burnett and Melville [5]. A 90° blackened aluminium sector 30 cm in diameter was used to cut off the light beam at its narrowest cross-section, approximately 2 mm in diameter. A set of synchronous motors (Thamyr SA, Buenos Aires, Argentina) at constant speed was used for slow sector speeds. An electronically controlled d.c. motor [6] was used to produce high sector speeds.

Whenever possible the components of the system were blackened and those between the lamp housing and the reaction vessel were enclosed in a blackened cardboard box. In order to prevent the entry of stray light into the reaction cell, all runs were carried out in a darkened room.

CFClCFCl (cis–trans mixture), supplied by PCR Research Chemicals, Florida, U.S.A., was purified by repeated low pressure trap-to-trap distillation. Only the middle fraction was collected and stored in a Pyrex trap cooled with liquid air. IR analysis using the 990 cm^{-1} band and $\epsilon = 0.0035$ $Torr^{-1}$ cm^{-1} for the cis isomer and the 890 cm^{-1} band and $\epsilon = 0.014$ $Torr^{-1}$ cm^{-1} for the trans isomer [7] showed the mixture to consist of 48% cis isomer and 52% trans isomer. Cylinder chlorine was washed with water, dried over sulphuric acid, condensed and trap-to-trap distilled at low pressure and stored in a trap cooled with liquid air. CF_4, supplied by the Matheson Co., U.S.A., was circulated through a trap cooled at —120 °C and stored in a Pyrex flask (2 l). Cylinder oxygen was circulated through a trap cooled at —130 °C and stored in a Pyrex flask (2 l). CFClCFCl and Cl_2 were carefully degassed before use.

Under continuous illumination most of the runs were followed up to 80% conversion. Under intermittent illumination the reaction rate was generally measured up to 40% conversion.

3. Results

3.1. Experiments under continuous illumination

Under the experimental conditions used no dark reaction or induction period was observed. The experiments showed very good reproducibility. Most of them were conducted at 30 °C and some others at 60 and 90 °C. The light intensity was varied between 0.45×10^{16} and 4.02×10^{16} quanta min^{-1}; the initial chlorine pressure was varied between 25 and 200 Torr and that of C_2F_2Cl between 15 and 200 Torr. Considering that the conversion was up to 85% the lowest $C_2F_2Cl_2$ pressure investigated was about 2 Torr.

TABLE 1

Results of a typical experiment (number 55, see Table 2)[a]

$\Sigma\Delta t$[b] (min)	$\Sigma\Delta p$[c] (Torr)	k[d] ($l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$)
3	2.9	5.24
6	5.9	5.63
9	9.0	6.09
12	11.7	5.56
16	15.2	5.69
20	18.4	5.53
24	21.6	5.86
28	24.5	5.63

[a] $T = 30$ °C; $[Cl_2]_i = 100.6$ Torr; $[C_2F_2Cl_2]_i = 49.5$ Torr; $J_0 = 3.68 \times 10^{16}$ quanta min^{-1} where $[Cl_2]_i$ and $[C_2F_2Cl_2]_i$ are the initial reactant pressures.

[b] $\Sigma\Delta t$, illumination time.

[c] $\Sigma\Delta p$, decrease in total pressure corresponding to the illumination time $\Sigma\Delta t$.

[d] Mean value $\bar{k} = 5.65$ $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$.

Some experiments were carried out in the presence of up to 50 Torr of added reaction products and some others in the presence of up to 300 Torr CF_4. Oxygen effects were studied by adding up to 100 Torr oxygen.

At the end of some experiments, conducted to a conversion of up to 30% of the initial $C_2F_2Cl_2$ pressure, the reactor content was condensed and the excess chlorine distilled off at —110 °C. Thereafter the unreacted $C_2F_2Cl_2$ was separated from the $C_2F_2Cl_4$ by distillation at —80 °C and collected into an IR cell.

IR quantitative analysis showed the mixture to consist of 48.8% cis isomer and 51.2% trans isomer, identical, within the limits of the experimental errors, with the original mixture. Consequently, no difference in the reactivity of the two isomers could be detected.

The experimental results showed that the reaction rate is proportional to $J_{abs}{}^{1/2}$ and to the chlorine pressure and is independent of CFClCFCl pressure, at least up to pressures of about 2 Torr. It is also independent of the presence of reaction products or of the total pressure. Consequently, the reaction rate can be represented by the equation

$$\frac{d[C_2F_2Cl_4]}{dt} = \frac{\Delta p}{\Delta t} = k[Cl_2]J_{abs}{}^{1/2}$$

The mean values of k determined at 30, 60 and 90 °C were as follows: $k_{30\,°C} = 5.63 \pm 0.09$ $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$; $k_{60\,°C} = 10.43 \pm 0.02$ $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$; $k_{90\,°C} = 21.26 \pm 1.4$ $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$. From these data the activation energy E for the overall reaction was found to be 4.81 ± 0.3 kcal. The presence of oxygen inhibits the photochlorination reaction and promotes a sensitized CFClCFCl oxidation.

Table 1 shows the results of a typical experiment. Table 2 gives a summary of the most important results obtained under continuous illumination.

TABLE 2

Summary of results obtained under continuous illumination

Number	*Temperature* (°C)	*Initial* Cl_2 *pressure* (Torr)	*Initial* C_2F_2Cl *pressure* (Torr)	$J_0 \times 10^{-16}$ (quanta min^{-1})	$\bar{k}$ ($l^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$)
107	30	98.2	52.2	3.57	5.60
88	30	98.2	50.9	1.23	5.63
91	30	97.5	50.5	1.21	5.42
92	30	99.2	52.2	0.45	5.29
67	30	24.4	49.3	3.64	5.81
74	30	25.3	48.3	3.64	5.64
65	30	48.4	49.7	3.62	5.36
66	30	50.0	50.4	3.67	5.54
55	30	100.6	49.5	3.68	5.64
57	30	100.3	48.1	3.64	5.72
62	30	149.8	50.3	4.02	5.46
63	30	151.0	49.3	3.89	5.87
101	30	201.5	52.7	3.54	5.37
108	30	200.3	52.9	3.59	5.63
82	30	99.5	16.1	3.61	5.80
83	30	99.7	16.7	3.63	5.98
75	30	98.9	49.3	3.82	5.52
77	30	99.3	49.4	3.72	5.65
93	30	97.7	99.3	3.61	5.65
97	30	99.9	98.4	3.49	5.95
85	30	100.8	198.0	3.30	5.84
84	30	99.7	197.0	3.62	5.81
95[a]	30	97.6	50.9	3.48	5.47
96[b]	30	99.9	50.4	3.48	5.52
131[c]	30	98.2	50.5	3.50	5.94
132[d]	30	97.5	50.1	3.45	5.20

(continued)

TABLE 2 *(continued)*

Number	*Temperature* (°C)	*Initial* Cl_2 *pressure* (Torr)	*Initial* C_2F_2Cl *pressure* (Torr)	$J_0 \times 10^{-16}$ (quanta min^{-1})	$\bar{k}$ ($l^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$)
71	30	97.1	50.1	3.78	5.60
72	30	98.4	50.6	3.78	5.65
107	30	98.2	52.2	3.57	5.60
118	30	75.8	50.7	3.49	5.64
113	60	97.4	52.1	3.42	10.37
114	60	98.5	51.4	3.42	10.57
115	60	98.1	50.8	3.43	10.34
116	60	99.6	50.4	3.48	10.43
120	90	75.1	51.4	3.50	22.08
122	90	74.6	51.8	3.59	20.84
123	90	74.4	49.5	3.63	20.66
124	90	75.7	50.0	3.63	21.45

[a] 25.1 Torr added reaction products.

[b] 50.5 Torr added reaction products.

[c] 207.6 Torr added CF_4.

[d] 301.4 Torr added CF_4.

3.2. *Experiments under intermittent illumination*

Rotating sector experiments were carried out at 30 and 90 °C and the ratio

$$\rho = \frac{2 \times \text{rate with sector}}{\text{rate with continuous light}}$$

was determined.

In the experiments with the sector the light intensity was measured using the reaction itself as an actinometer. Accordingly, in each experiment the procedure was to measure the rate under continuous illumination followed by the rate at a previously fixed sector speed and, finally, the rate at high sector speed was measured. This sequence was repeated two or three times. In this way the light intensity could be calculated and at the same time the constancy of the lamp output could be checked.

The criterion $\rho_\infty = 1.00 \pm 0.01$ where ρ_∞ refers to conditions of limiting fast sector speeds was applied; $\rho_\infty = 1$ for a 90° sector when the rate is proportional to $J_{abs}^{1/2}$. When this value for ρ_∞ was not found, the results of the experiments were discarded and the reactants were subjected to further purification.

A typical plot of ρ *vs.* $\log_{10}(J_{abs}^{1/2} t_i)$, where t_i is the flash period, is given in Fig. 1. The k_4 value that results in the best fit of the theoretical $\rho = f(\log_{10} m)$ function, where $m = 2J_{abs}^{1/2}k_4^{1/2}t_i$, with the experimental ρ *vs.* $\log_{10}(J_{abs}^{1/2} t_i)$ points is $k_4 = 8.2 \times 10^8$ l mol^{-1} s^{-1} (the maximum deviation was then about 5%).

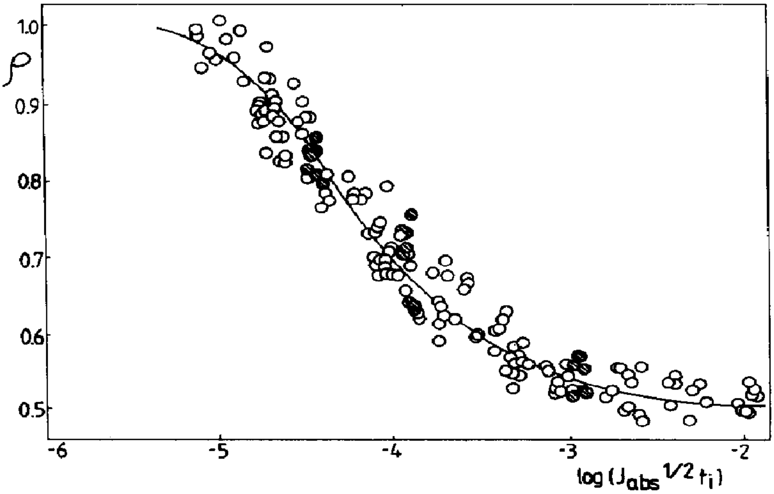

Fig. 1. Rotating sector curve for ρ *vs.* $\log_{10}(J_{abs}^{1/2} t_i)$ (initial chlorine pressure, 50 Torr; initial CFClCFCl pressure, 100 Torr): ——, theoretical curve best fit to the experimental points; ○, T = 30 °C; ●, T = 90 °C.

4. Discussion

The experimental results can be explained on the basis of the well-known chain mechanism which is common to a series of substituted olefin photochlorinations ($CH_2=CHCl$ [8]; $CHCl=CHCl$ [2]; $CHCl=CCl_2$ [9]; $CCl_2=CCl_2$ [10]; C_2F_4 [11]; $CF_2=CFCl$ [11]; $CF_2=CCl_2$ [12]; C_3F_6 [13]; C_4F_8 [14])

$$Cl_2 + h\nu \longrightarrow Cl + Cl \qquad (1)$$

$$Cl + C_2F_2Cl_2 \longrightarrow \dot{C}_2F_2Cl_3 \qquad (2)$$

$$\dot{C}_2F_2Cl_3 + Cl_2 \longrightarrow C_2F_2Cl_4 \qquad (3)$$

$$\dot{C}_2F_2Cl_3 + \dot{C}_2F_2Cl_3 \longrightarrow \text{products} \qquad (4)$$

The reverse reactions of steps (2) and (3), if present, are not important since the rate is independent of $C_2F_2Cl_2$ pressure.

For the same reason reactions such as

$$\dot{C}_2F_2Cl_3 + Cl \longrightarrow C_2F_2Cl_4$$

and

$$Cl + Cl + M \longrightarrow Cl_2 + M$$

can be ruled out.

Because of the high quantum efficiency of the overall reaction it was impossible to establish whether reaction (4) is a dimerization or a disproportionation.

Stationary state treatments give

$$\frac{d[C_2F_2Cl_4]}{dt} = \frac{k_3}{k_4^{1/2}} [Cl_2] J_{abs}^{1/2}$$

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

Within the experimental error, k_4 does not depend on the temperature. Therefore, E_4 must be close to zero as is usual for the recombination of radicals in the photochlorination of olefins [15]. According to the mechanism, $E = E_3 - (1/2)E_4$. Taking $E_4 = 0$, E_3 is calculated to be 4.81 ± 0.3 kcal mol^{-1}. From the numerical values determined for k and k_4, we obtain $k_3 = kk_4^{1/2} = 1.61 \times 10^5$ l mol^{-1} s^{-1} at 30 °C and hence

$$\log_{10} k_3 = 8.68 - \frac{4810 \pm 300}{4.57T}$$

If collision diameters of 6 Å and 3.6 Å are assumed for the $CFCl_2\dot{C}FCl$ radical and chlorine respectively, the collision frequency z_3 is found to be 1.56×10^{11} l mol^{-1} s^{-1} from which the probability factor $P_3 = A_3/z_3 = 3 \times 10^{-3}$ was obtained. This probability factor is of the same order of magnitude as those found for the reactions $CF_2Cl\dot{C}Cl_2 + Cl_2$ [1] and $CHCl_2\dot{C}Cl_2 + Cl_2$ [16]. The value $z_4 = 9.4 \times 10^{10}$ l mol^{-1} s^{-1} was also calculated and the probability factor $P_4 = A_4/z_4 = 0.87 \times 10^{-2}$ was obtained. This is similar to the one found for the recombination of the $CF_2Cl\dot{C}Cl_2$ radicals [1].

TABLE 3

Comparison of kinetic data for CCl_2CF_2 and CFClCFCl

	k ($l\ mol^{-1}\ s^{-1}$)	k_3 ($l\ mol^{-1}\ s^{-1}$)	E_3 ($kcal\ mol^{-1}$)	P_3	k_4 ($l\ mol^{-1}\ s^{-1}$)	P_4
CCl_2CF_2[a]	1.12	3.36×10^4	5.1	1.0×10^{-3}	9.95×10^8	1.03×10^{-2}
CFClCFCl[b]	5.63	16.1×10^4	4.81	3.0×10^{-3}	8.2×10^8	0.87×10^{-2}

[a] From ref. 1.

[b] This work.

These values compare well with those recently obtained by direct measurements for the similar reactions $\dot{C}F_2Cl + Cl_2$ and $\dot{C}F_3 + Cl_2$ [17].

The value 8.91 ± 0.21 found for $\log_{10} k_4$ for the $CFCl_2\dot{C}FCl$ radical is similar to those found for the $CCl_3\dot{C}HCl$ [15], $CCl_3\dot{C}Cl_2$ [15] and $CF_2Cl\dot{C}Cl_2$ [1] radicals (9.3, 8.7 and 9.0 respectively) and somewhat less than that expected from the empirical relation proposed by Bertrand *et al.* [18].

Table 3 compares the values obtained in this work for CFClCFCl with the corresponding ones for CF_2CCl_2 [1]. It appears that the k_4 values as well as the activation energy E_3 are nearly the same for these two isomers. However, the chain propagating step constant k_3 and, consequently, the overall rate constant, is nearly five times higher for CFClCFCl. This difference results mainly from the difference between the corresponding probability factors and to a lesser extent from the small difference in the activation energies. It is concluded that there is less steric hindrance when the chlorine atom adds to the CFCl group of the $CFCl_2\dot{C}FCl$ radical than when it adds to the CCl_2 group of the $CF_2Cl\dot{C}Cl_2$ radical which already has two chlorine atoms.

References

1 C. Cobos and E. Castellano, *J. Photochem.*, *26* (1984) 9.
2 K. L. Müller and H. J. Schumacher, *Z. Phys. Chem.*, *Abt. B*, *35* (1937) 285.
3 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London*, *Ser. A*, *235* (1956) 518.
4 H. V. Halban and K. Siedentopf, *Z. Phys. Chem.*, *103* (1923) 71.
5 G. M. Burnett and H. W. Melville, in S. L. Friess, E. S. Lewis and A. Weissberger (eds.), *Techniques of Organic Chemistry*, Vol. 8, Part 2, Wiley-Interscience, New York, 2nd edn., 1963, pp. 1107 - 1137.
6 A. J. Arvia, S. L. Marchiano and J. J. Podestá, *Electrochim. Acta*, *12* (1967) 259.
7 N. C. Craig and D. A. Evans, *J. Am. Chem. Soc.*, *87* (1965) 4223.
8 H. Schmitz and H. J. Schumacher, *Z. Phys. Chem.*, *Abt. B*, *52* (1942) 72.
9 K. L. Müller and H. J. Schumacher, *Z. Phys. Chem.*, *Abt. B*, *35* (1937) 455.
10 C. Schott and H. J. Schumacher, *Z. Phys. Chem.*, *Abt. B*, *49* (1941) 107.
11 E. Castellano, N. Bergamin and H. J. Schumacher, *Z. Phys. Chem. N.F.*, *27* (1961) 112.
12 C. Vallana, E. Castellano and H. J. Schumacher, *Z. Phys. Chem. N. F.*, *46* (1965) 204.
13 M. C. Gonzalez and E. Castellano, *J. Photochem.*, *15* (1981) 303.
14 M. E. Roselli and H. J. Schumacher, *Z. Phys. Chem. N.F.*, *28* (1963) 326.
15 G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens and G. Verbeke, *Chem. Rev.*, *63* (1963) 355.
16 F. S. Dainton, D. A. Lomax and M. Weston, *Trans. Faraday Soc.*, *53* (1957) 460.
17 R. S. Timonen, J. J. Russell and D. Gutman, *Int. J. Chem. Kinet.*, *18* (10) (1986) 1193.
18 L. Bertrand, G. R. de Maré, G. Huybrechts, J. Olbregts and M. Toth, *Chem. Phys. Lett.*, *5* (1970) 183.