

THE KINETICS OF THE PHOTOCHEMICAL CHLORINATION OF 1,1-DICHLORO-2,2-DIFLUOROETHYLENE UNDER INTERMITTENT LIGHT

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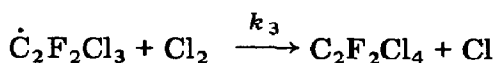
Summary

The gas phase photochlorination of 1,1-dichloro-2,2-difluoroethylene was studied in a static system at temperatures between 30 and 90 °C. The rate law was determined and was found to be in agreement with previous findings. C₂F₂Cl₄, the main product, is formed according to

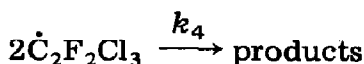
$$+ \frac{dp_{\text{C}_2\text{F}_2\text{Cl}_4}}{dt} = kp_{\text{Cl}_2} J_{\text{abs}}^{1/2}$$

where J is the amount of light absorbed.

The rate constants which were redetermined under continuous illumination are as follows: $k_{30^\circ\text{C}} = 1.12 \pm 0.04 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$; $k_{50^\circ\text{C}} = 1.81 \pm 0.08 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$; $k_{90^\circ\text{C}} = 4.56 \pm 0.2 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$. The rate constants for the elementary reactions



and



are

$$\log_{10} k_3 = 8.21 - \frac{5100 \pm 250}{4.57T}$$

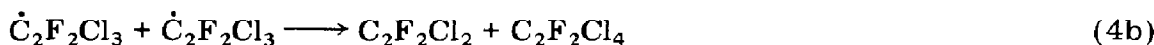
and

$$\log_{10} k_4 = 9.00 \pm 0.20$$

respectively, where k_3 and k_4 are in litres per mole per second. The second reaction is mainly an association between two radicals. The product of the association is 1,1,4,4-tetrafluorohexachlorobutane, suggesting the structure CF₂ClĊCl₂ for the radicals involved.

1. Introduction

The photochlorination of 1,1-dichloro-2,2-difluoroethylene under continuous illumination at temperatures ranging from 30 to 70 °C has been investigated by Schumacher and coworkers [1]. The reaction proceeded by a chain mechanism which is common to a series of photochlorination reactions of substituted ethylenes as follows:



From reactions (1) - (4) the rate law

$$+ \frac{dp_{\text{C}_2\text{F}_2\text{Cl}_4}}{dt} = kp_{\text{Cl}_2} J_{\text{abs}}^{1/2} \quad (5)$$

is obtained.

We repeated some of their experiments and found the same rate law. However, our numerical value for the rate constant differed somewhat.

As the rate depends on the square root of the amount of absorbed light, the rate constants included in the rate equation can be determined by using intermittent illumination provided by the rotating sector technique. Accordingly, the results of the gas phase photochlorination of 1,1-dichloro-2,2-difluoroethylene under intermittent light in the range from 30 to 90 °C are presented in this paper together with the redetermined values of the rate constant k .

2. Experimental details

Since the reaction occurs with a decrease in the total number of moles it 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 cm³ in volume with flat optical windows. The light source was an Osram HBO 200 high pressure mercury lamp fed by a stabilized a.c. power supply. A set of quartz lenses and stops was used to produce a parallel homogeneous light beam 4.5 cm in diameter. The 436 nm wavelength region was isolated with a system of optical filters (BG12 (4 mm) and GG15 (2 mm) (Schott and Gen, F.R.G.)). When necessary, the light intensity was reduced by means of neutral glasses or calibrated wire gauzes. In the experiments carried out under full illumination, the light intensity was measured with a Hatchard and Parker potassium ferrioxalate actinom-

eter [3] and the amount of absorbed light was calculated using the extinction coefficient of chlorine [4].

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 the light beam at its narrowest cross section, approximately 2 mm in diameter. An electronically controlled d.c. motor [6] was used to produce high sector speeds. A synchronous a.c. motor (Thamyr SA, Buenos Aires) at constant speed was used to produce low sector speeds. At the slowest sector speeds the penumbra error [7] was important. To ensure that this error was negligible the light beam was cut off sharply at the focal plane by an electromagnetically operated shutter. For this purpose and to maintain a 1:3 light-to-dark ratio, the same sector disk was used to cut a narrow IR radiation beam incident on an OPB 810 IR sensor which energized and de-energized the shutter coil by means of a suitable electric circuit.

All the runs were carried out in a darkened room. Whenever possible the components of the apparatus were blackened and those between the lamp housing and the reactor vessel were enclosed in a blackened cardboard box.

The $C_2F_2Cl_2$, supplied by Matheson Gas Products (U.S.A.), was purified by repeated low temperature trap-to-trap distillation. It was stored in a Pyrex trap cooled with liquid air. Cylinder chlorine was washed with water, dried over sulphuric acid, condensed, distilled at low temperature and finally stored in a trap cooled with liquid air. Both reactants were carefully degassed before use.

Since the quantum efficiency of the overall reaction is not sufficiently high, the nature of the products formed in the chain-terminating step cannot be ignored in calculating the rate of formation of $C_2F_2Cl_4$ and the chlorine concentration from pressure measurements. In an attempt to identify the products of reaction (4), a series of experiments was carried out in such conditions that the quantum efficiency was lower than 10 molecules quantum⁻¹. The reaction products from ten experiments were combined in a trap cooled in liquid air and distilled at -20 °C. The IR spectrum of the liquid residue showed bands at 1158, 1133, 1035, 1000, 921, 814, 772, 756, 696, 655, 622, 615 and 594 cm⁻¹ coincident with those reported in the literature [8] for 1,1,4,4-tetrafluorohexachlorobutane. Its vapour pressure measured in the range 20 - 95 °C could be represented by the equation $\log_{10} p_{\text{mm}} = -2486.4/T + 8.0882$, giving an extrapolated value of 204.5 °C for the boiling point. The calculated vapour pressures are in good agreement with the data reported for 1,1,4,4-tetrafluorohexachlorobutane [9, 10]. The mass spectra showed a base peak at $m/e = 109$ and strong peaks at 229, 85, 179, 163 and 31 consistent with the given structure. Therefore, it is concluded that at least an important fraction of reaction (4) is the association of two $\dot{C}_2F_2Cl_3$ radicals, as was assumed in previous work [1]:

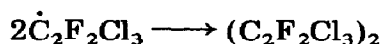
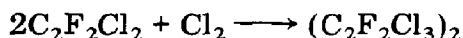


TABLE 1

$(p_{\text{Cl}_2})_i$	$(p_{\text{C}_2\text{F}_2\text{Cl}_2})_i$	$\Sigma\Delta p$	$(p_{\text{Cl}_2})_i - \Sigma\Delta p$	$(p_{\text{Cl}_2})_{\text{measd}}$	$(p_{\text{Cl}_2})_{\text{calc}}$
21.2	24.9	18.7	2.5	3.23	3.75
20.7	25.5	19.1	1.6	3.12	2.95
21.1	25.2	19.8	1.3	2.91	2.81

with a stoichiometric equation



For the dimer in the vapour phase, $\Delta n = -2$; if it remains condensed, $\Delta n = -3$.

At the temperatures used in this work, namely 30 °C, 50 °C and 90 °C, the dimer pressures are 0.76 Torr, 2.4 Torr and 17.3 Torr respectively. All the experiments were carried out in such a manner that the dimer always remained in the vapour phase. Then the following relations hold:

$$+ \frac{\Delta p_{\text{C}_2\text{F}_2\text{Cl}_2}}{\Delta t} = \frac{\phi}{\phi + 2} \frac{\Delta p}{\Delta t} \quad (6)$$

$$(p_{\text{Cl}_2})_t = (p_{\text{Cl}_2})_i - \frac{\phi + 1}{\phi + 2} \Delta p \quad (7)$$

$$\bar{p}_{\text{Cl}_2} = (p_{\text{Cl}_2})_i - \frac{1}{2} \frac{\phi + 1}{\phi + 2} \Delta p \quad (8)$$

in which $\phi (= \Delta p_{\text{C}_2\text{F}_2\text{Cl}_2} / J_{\text{abs}} \Delta t)$ is the mean quantum efficiency of the overall reaction during the time interval Δt , Δp is the pressure change, $(p_{\text{Cl}_2})_i$ and $(p_{\text{Cl}_2})_t$ are the chlorine pressures at the beginning and at the end of the time interval Δt respectively and \bar{p}_{Cl_2} is the mean chlorine pressure in the same time interval. These expressions must be used in connection with the rate equation (eqn. (5)) when the reaction is monitored manometrically. To check eqn. (7), some experiments were carried out at 90 °C to a high percentage of conversion after which the remaining chlorine was titrated iodometrically.

The experimental values together with those calculated using eqn. (7) are given in Table 1. The small differences between $(p_{\text{Cl}_2})_{\text{measd}}$ and $(p_{\text{Cl}_2})_{\text{calc}}$ are well within the experimental errors.

In all the subsequent calculations eqn. (5) was used together with relations (6) and (8).

2.1. Experiments under continuous illumination

A series of experiments was carried out in which the variables involved were systematically varied over a wide range. The experimental results,

which are not given here, confirmed the rate law found in previous work [1], but the numerical values for the rate constant of the overall reaction were slightly different. To obtain a more reliable value for the rate constant a series of experiments was carried out under continuous illumination at 30, 50 and 90 °C to a low percentage of conversion with a chlorine pressure of 100 Torr, a $C_2F_2Cl_2$ pressure of 50 Torr and a light intensity $J_0 \approx 8 \times 10^{17}$ quanta min^{-1} . In these conditions the initial quantum efficiency of the overall reaction was of the order of 40 molecules quantum $^{-1}$, 60 molecules quantum $^{-1}$ and 150 molecules quantum $^{-1}$ for 30 °C, 50 °C and 90 °C respectively.

In calculating the values of the rate constant with eqn. (5), the rate of formation of $C_2F_2Cl_4$ given by eqn. (6) and the mean chlorine pressure given by eqn. (8) were substituted into eqn. (5). Since ϕ is not known in advance these calculations were performed by an iterative method initially taking

$$+ \frac{\Delta p_{C_2F_2Cl_4}}{\Delta t} = \frac{\Delta p}{\Delta t}$$

and

$$(p_{Cl_2})_t = (p_{Cl_2})_i - \Delta p$$

The following values for k ($l^{1/2} mol^{-1/2} s^{-1/2}$) were obtained as an average of ten experiments carried out at each temperature: $k_{30^\circ C} = 1.12 \pm 0.04$; $k_{50^\circ C} = 1.81 \pm 0.08$; $k_{90^\circ C} = 4.56 \pm 0.2$. (From previous work $k_{50^\circ C} = 1.44 l^{1/2} mol^{-1/2} s^{-1/2}$.)

The activation energy E of the overall reaction calculated from these data was 5.1 ± 0.25 kcal mol^{-1} in close agreement with the value 5.3 ± 0.3 kcal mol^{-1} found in previous work [1].

2.2. Experiments with intermittent illumination

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 speeds was measured. This sequence was repeated once more. In this way the light intensity could be calculated and at the same time the constancy of the lamp output could be checked.

Since the chain propagation step is first order with respect to the concentration of radicals and the chain termination step is second order, the termination step is affected more than the propagation step by a change in the concentration of radicals. Under intermittent illumination the mean concentration of radicals in a complete light-to-dark period is lower than that under full illumination:

$$\frac{[\dot{R}]_{\text{sector}}}{[R]_{\text{ss}}} = \frac{V_{\text{sector}}}{V_{\text{cont}}} = \frac{\rho}{2}$$

Accordingly the quantum efficiency ϕ_s in a complete light-to-dark period is

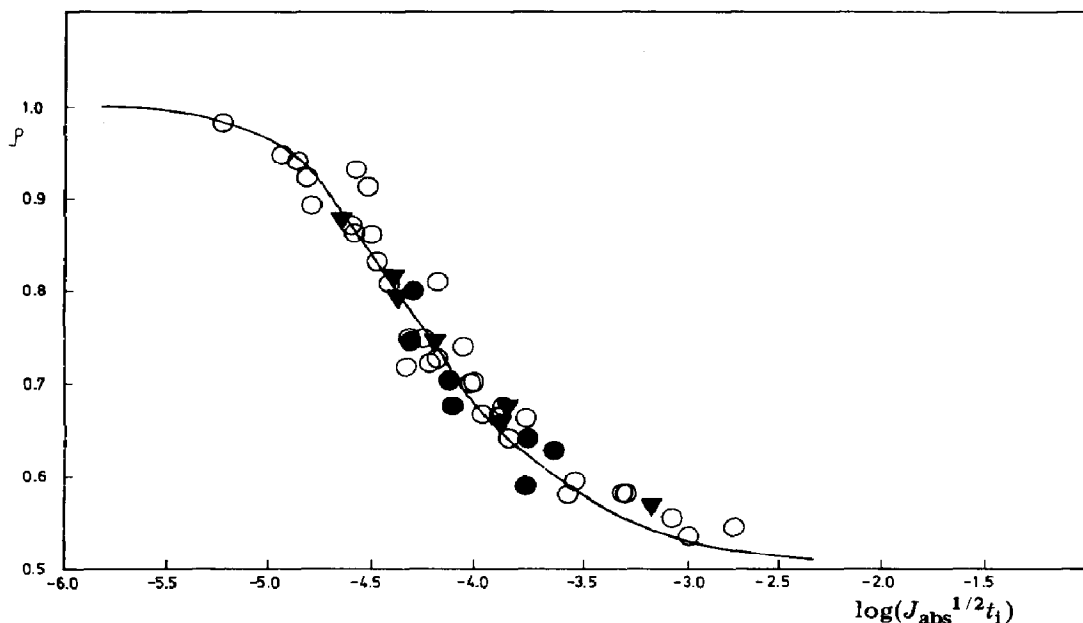


Fig. 1. Rotating sector curve ρ vs. $\log_{10}(J_{\text{abs}}^{1/2} t_i)$: —, theoretical curve (best fit to the experimental points with a chlorine pressure of 100 Torr and a $\text{C}_2\text{F}_2\text{Cl}_2$ pressure of 50 Torr); ●, $T = 30^\circ\text{C}$; ○, $T = 50^\circ\text{C}$; ▼, $T = 90^\circ\text{C}$.

higher than the quantum efficiency under continuous illumination:

$$\phi_s \approx \frac{2\phi}{\rho}$$

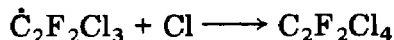
Substituting ϕ_s for ϕ in relations (6) or (7) the rate of formation of $\text{C}_2\text{F}_2\text{Cl}_4$ and the chlorine pressure could be calculated. In most of the experiments carried out under intermittent illumination these corrections were found to be unimportant.

The criterion $\rho_\infty = 1.00 \pm 0.01$, where ρ is equal to twice the rate obtained with the sector divided by the rate under continuous illumination of the same intensity, was applied. ρ_∞ refers to conditions of limiting fast sector speeds; $\rho_\infty = 1$ for a 90° sector when the rate is proportional to $J_{\text{abs}}^{1/2}$. When this value for ρ_∞ was not found, the results of the experiment were discarded and the reactants were subjected to further purification.

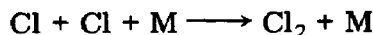
A typical plot of ρ versus $\log_{10}(J_{\text{abs}}^{1/2} t_i)$ where t_i (s) is the flash period is shown in Fig. 1. These points were compared with the theoretical curve of ρ versus $\log_{10} m$, where $m (= 2J_{\text{abs}}^{1/2} k_4^{1/2} t_i)$ is a dimensionless parameter which includes the lifetime $\tau (= (1/2)(J_{\text{abs}} k_4)^{-1/2})$ of the chain centres. At the position of the best fit of the theoretical curve to the experimental points (the maximum deviation was about 5%) the value of $\log_{10}(J_{\text{abs}}^{1/2} t_i)$ corresponding to the point at which $\log_{10} m = 0$, i.e. $m = 1$ and $t_i = \tau$, was read. It was found that $\tau = 0.11$ s for $J_{\text{abs}} = 1.27 \times 10^{13}$ quanta $\text{cm}^{-3} \text{s}^{-1}$.

3. Discussion

The reaction mechanism has been discussed elsewhere [1]. The results of the present work show that this mechanism is still valid even at a $\text{C}_2\text{F}_2\text{Cl}_2$ pressure of about 2 Torr, *i.e.* reactions (2) and (3) are not significantly reversible. For the same reason reactions such as



and



(M \equiv third body) are unlikely to occur.

In the stationary state, the lifetime of the chain is given by $\tau = (1/2) \times (J_{\text{abs}}k_4)^{-1/2}$ from which $k_4 = 9.95 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ is obtained. Within the experimental error this value does not depend on the temperature. Therefore E_4 must be close to zero as is usual for the recombination of radicals in photochlorination processes [11]. According to the mechanism $E = E_3 - E_4/2$. Taking $E_4 = 0$, E_3 is calculated to be $5.1 \pm 0.25 \text{ kcal mol}^{-1}$.

From the numerical value determined for k_4 and the corresponding rate constant for the overall reaction we obtain $k_3 = 5.7 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ at 50°C and hence

$$\log_{10} k_3 = 8.21 - \frac{5100 \pm 250}{4.57T}$$

Using 6 Å for the collision diameter of the $\dot{\text{C}}_2\text{F}_2\text{Cl}_3$ radical and 3.6 Å for that of chlorine, the calculated values for the probability factors P_3 and P_4 are

$$P_3 = \frac{A_3}{Z_3} = 1.0 \times 10^{-3}$$

for reaction (3) and

$$P_4 = \frac{A_4}{Z_4} = 1.03 \times 10^{-2}$$

for reaction (4).

The value of 9.00 ± 0.2 found for $\log_{10} k_4$ for the $\dot{\text{C}}_2\text{F}_2\text{Cl}_3$ radical recombination is of the same order of magnitude as those found for the recombinations of $\text{CCl}_3\dot{\text{C}}\text{HCl}$ and $\text{CCl}_3\dot{\text{C}}\text{Cl}_2$ radicals (9.3 and 8.7 respectively) [11] and somewhat less than that expected from the empirical relation proposed by Bertrand *et al.* [12].

With regard to the structure of the dimer $(\text{C}_2\text{F}_2\text{Cl}_3)_2$ formed in reaction (4), the experimental evidence agrees with the few data that we found in the literature for 1,1,4,4-tetrafluorohexachlorobutane. The structure assumed for the dimer suggests that the radical formed in reaction (2) is $\text{CF}_2\text{Cl}\dot{\text{C}}\text{Cl}_2$, as was expected from the fact that there is less steric hindrance when the chlorine atom adds to the CF_2 group of CF_2CCl_2 . This is consistent

with the results obtained with other substituted olefins, particularly with CFClCCl_2 , CF_2CHCl and CHFCCl_2 , giving rise to the radicals $\text{CFCl}_2\dot{\text{C}}\text{Cl}_2$, $\text{CF}_2\text{Cl}\dot{\text{C}}\text{HCl}$ and $\text{CHFCl}\dot{\text{C}}\text{Cl}_2$ respectively [13].

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