THE KINETICS OF THE PHOTOCHLORINATION OF PERFLUORO-2-BUTENE UNDER INTERMITTENT LIGHT

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Summary

The gas phase photochlorination of perfluoro-2-butene (C_4F_8) was studied under intermittent light in a static system at temperatures between 30 and 80 °C. It was shown in previous work that $C_4F_8Cl_2$, the only final product, is formed according to the equation

$$+ \frac{d[C_4F_8Cl_2]}{dt} = k[Cl_2]J_{abs}^{1/2}$$

where J_{abs} is the amount of light absorbed. The rate constants of the reactions

$$C_4F_8Cl + Cl_2 \rightarrow C_4F_8Cl_2 + Cl$$

and

$$2C_4F_8Cl \rightarrow \text{products}$$
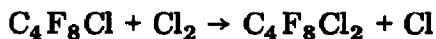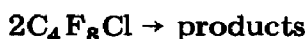
are

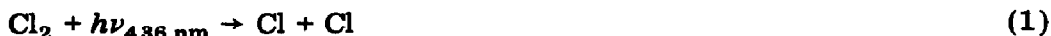$$\log k_3 = 8.48 - \frac{5770 \pm 300}{4.57T}$$

and

$$\log k_4 = 7.34 \pm 0.21$$

respectively where k_3 and k_4 are in litres per mole per second. A quantum efficiency ϕ of 505 molecules quantum^{-1} was obtained at 30 °C with a chlorine pressure of 100 Torr and $J_{abs} = 1.37 \times 10^{12}$ quanta cm^{-3} s^{-1}.

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1. Introduction

Roselli and Schumacher [1] studied the photochlorination of perfluoro-2-butene (C_4F_8) under continuous illumination some years ago. They established the rate law and the reaction stoichiometry, and they proposed

a mechanism common to a series of photochlorinations of substituted ethylenes:

$$C_4F_8 + Cl_2 \rightarrow C_4F_8Cl_2 \qquad \Delta n = -1$$

$$Cl_2 + h\nu_{436\,nm} \rightarrow Cl + Cl \tag{1}$$

$$Cl + C_4F_8 \rightarrow C_4F_8Cl \tag{2}$$

$$C_4F_8Cl + Cl_2 \rightarrow C_4F_8Cl_2 + Cl \tag{3}$$

$$C_4F_8Cl + C_4F_8Cl \rightarrow products \tag{4}$$

$$-\frac{d[C_4F_8]}{dt} = +\frac{d[C_4F_8Cl_2]}{dt} = \frac{\Delta p}{\Delta t} = \frac{k_3}{k_4^{1/2}}[Cl_2]J_{abs}^{1/2}$$

$$= k[Cl_2]J_{abs}^{1/2} \tag{5}$$

We repeated some of the experiments of Roselli and Schumacher under continuous illumination and within the limits of experimental error our results agreed with those obtained by them. As the rate depends on the square root of the absorbed light this reaction is suitable for an investigation using intermittent illumination.

We used the rotating sector method, which enabled us to calculate the absolute rate constants included in the rate equation, to investigate the gas phase photochlorination of C_4F_8 at temperatures of 30 and 80 °C under intermittent illumination. Since the reaction results in a decrease in the total mole number, a manometric method was used at constant volume and temperature to follow its progress.

2. Experimental details

The apparatus for continuous and intermittent illumination has been described elsewhere [2] and was used with minor modifications. The reactor vessel was a quartz cylinder 5 cm long, 5 cm in diameter and 98.1 cm^3 in volume with flat optical windows. The light source was a 200 W Osram HBO superpressure mercury lamp supplied by a stabilized a.c. circuit. A set of quartz lenses and stops was used to produce a parallel homogeneous light beam 45 mm in diameter. The 436 nm wavelength region was isolated with a system of optical filters (Schott and Gen BG12 (4 mm) and GG15 (2 mm)). When necessary the light intensity was reduced by means of neutral glasses or calibrated wire gauzes. The light intensity was measured with a Hatchard and Parker ferrioxalate actinometer [3] and the absorbed light was calculated using the extinction coefficient [4] of chlorine. The experiments with intermittent illumination were carried out according to the procedure suggested by Burnett and Melville [5].

A 90° blackened aluminium sector of diameter 30 cm was used to cut the light beam off at its narrowest cross section. An electronically controlled low voltage d.c. motor [6] was used to produce high sector speeds and a set

of synchronous a.c. motors (Thamyr S.A., Buenos Aires) at constant velocity was used to produce slow sector speeds. As the penumbra error [7] was of some importance at the slowest sector speeds the light beam was cut off sharply at the focal plane by an electromagnetically operated shutter. In order to maintain the light-to-dark ratio of 1:3 the same sector disc was used to cut a narrow IR radiation beam incident on an OPB 810 IR sensor which by means of a suitable electrical circuit energized and de-energized the shutter coil.

All the runs were carried out in a darkened room in order to prevent stray light from entering the reaction cell. Whenever possible the components of the system were blackened and those between the lamp housing and the reactor vessel were enclosed in a blackened cardboard box.

At the beginning of each experiment performed with the sector the light intensity was measured with the ferrioxalate actinometer. Since the rate equation is well established the measurements under continuous and intermittent illumination were carried out alternately on the same reaction mixture. In this way the constancy of the lamp output could be checked throughout the experiment.

The C_4F_8 was supplied by Matheson Gas Products (U.S.A.). It was purified by repeated low temperature trap-to-trap distillation and only the middle fraction was collected. It was stored in a Pyrex trap cooled with liquid air. Cylinder chlorine was washed with water, dried over H_2SO_4, condensed, distilled at low temperature and finally stored in a trap cooled with liquid air. Cylinder oxygen was circulated through a trap maintained at -130 °C and stored in a 2 l Pyrex flask. The chlorine and the C_4F_8 were carefully degassed before use.

3. Results

3.1. Experiments with continuous illumination

No thermal reaction or induction period was observed under the experimental conditions used. The experiments showed very good reproducibility. A series of experiments was carried out at 30 °C with the initial pressure of chlorine between 15 and 120 Torr and that of C_4F_8 between 10 and 90 Torr. As the conversion was about 80% the lowest C_4F_8 pressure investigated was about 2 Torr. The light intensity was varied from 0.5×10^{17} to 13×10^{17} quanta min^{-1}. Some experiments were also carried out at 80 °C to establish the temperature dependence of k.

A quantum efficiency ϕ of 505 molecules quantum^{-1} was obtained at 30 °C with a chlorine pressure of 100 Torr and a light absorption J_{abs} of 1.37×10^{12} quanta cm^{-3} s^{-1}. The rate law was identical with that previously obtained by Roselli and Schumacher [1]. Some of the results obtained are summarized in Table 1. The value of k in each experiment was calculated using eqn. (5). The mean values of k obtained at 30 and 80 °C were $k_{30.8 °C} = 4.56 \times 10^{-2}$ l$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$ and $k_{80.5 °C} = 17.5 \times 10^{-2}$ l$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$

TABLE 1

Experi-ment	T (°C)	Cl₂ (Torr)	C₄F₈ (Torr)	I_0 ($\times 10^{17}$ quanta min^{-1})	$\bar{k}$ (l$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$)
23	30.8	14.4	26.9	13.3	4.78
18		40.5	24.4	12.6	4.55
36		59.1	35.8	13.0	4.68
31		76.8	38.6	13.0	4.73
10		121.4	44.8	0.77	4.50
21		52.9	10.5	12.8	4.5
22		52	13.5	13.3	4.6
26		30.3	86.1	12.5	4.5
12		88	25.9	0.5	4.4
8		82.6	43.8	0.97	4.4
11		82.6	41.1	0.51	4.39
31		76.8	38.6	13.0	4.73
42	80.5	61.8	40.4	11.4	17.5
43		36.0	33.8	11.6	17.35

respectively. The activation energy E_0 of the overall reaction calculated from these data was 5.77 ± 0.3 kcal, similar to the value of 5.95 ± 0.45 found by Roselli and Schumacher [1].

Oxygen inhibits the reaction and promotes a sensitized oxidation of C_4F_8.

3.2. Experiments with intermittent illumination

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

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

was determined. The criterion ρ_∞ = 1 ± 0.01 was applied where ρ_∞ is the value of ρ at the upper limit of the rotational velocity of the sector. ρ_∞ must be equal to unity for a 90° sector if the rate is proportional to $J_{abs}^{1/2}$. If this condition for ρ_∞ was not fulfilled the results of the experiments were discarded and the reactants were subjected to further purification.

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

The chain lifetime τ was calculated by a standard method. It was found that τ = 0.57 s for J_{abs} = 2.1 × 10^{13} quanta cm^{-3} s^{-1}.

4. Discussion

The reaction mechanism has already been discussed by Roselli and Schumacher [1]. The results of the present work show that this mechanism
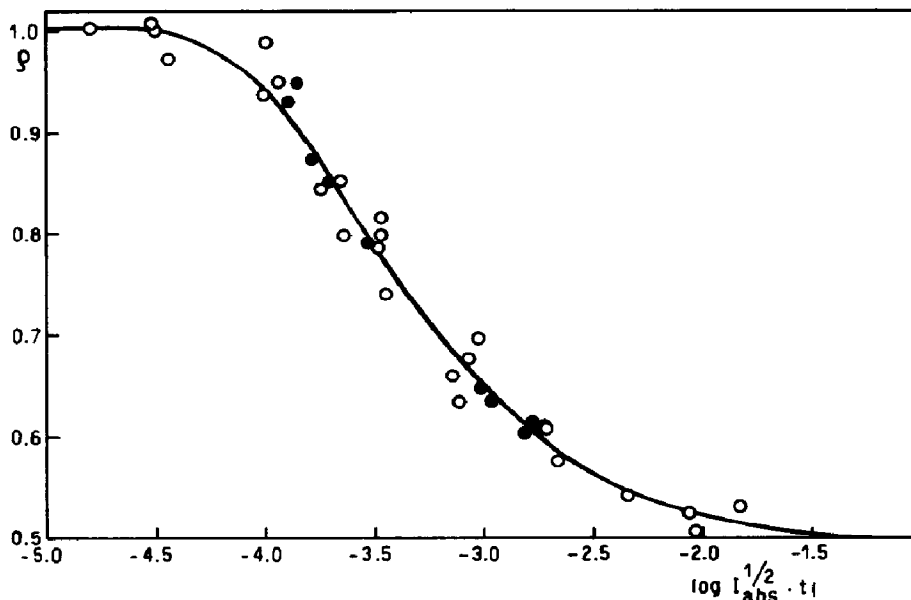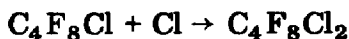
Fig. 1. Curve of ρ vs. $\log_{10}(J_{abs}{}^{1/2}t_1)$ (chlorine pressure, 50 Torr; C_4F_8 pressure, 50 Torr): ——, best fit to the experimental points; $\bigcirc$, $T = 30\ °C$; $\bullet$, $T = 80\ °C$.

is still valid even at C_4F_8 pressures of about 2 Torr, *i.e.* reactions (2) and (3) are not significantly reversible. For the same reason reactions such as

$$C_4F_8Cl + Cl \rightarrow C_4F_8Cl_2$$

and

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

are unlikely. The rather high quantum yield of reaction (4) makes chemical determination of the nature of the products impossible.

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

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

from which a value of 2.2×10^7 l mol^{-1} s^{-1} was obtained for k_4. This value is independent of temperature within the limits of experimental error.

According to the mechanism proposed by Roselli and Schumacher [1] the energy of activation of the overall reaction is $E_o = E_3 - \tfrac{1}{2}E_4$, and since k_4 is independent of temperature E_4 must be near zero which is the usual value for the recombination of radicals in photochlorination processes [8]. For $E_4 = 0$, E_3 is calculated to be 5.77 ± 0.3 kcal mol^{-1}. From the numerical value determined for k_4 we obtain

$$k_3 = 2.14 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$$

and hence

$$\log k_3 = 8.48 - \frac{5770 \pm 300}{4.57T}$$

If collision diameters of 6.5 Å and 3.6 Å are assumed for the collision diameters of C_4F_8Cl and chlorine respectively, the collision frequency Z_3 is found to be 1.7×10^{11} l mol^{-1} s^{-1} from which a probability factor

$$\alpha_3 = A_3/Z_3 = 1.77 \times 10^{-3}$$

can be calculated. This value is of the same order as those found for the reactions between C_3F_6Cl and chlorine [2] and between C_2HCl_4 and chlorine [9]. A probability factor $\alpha_4 = A_4/Z_4 = 2.4 \times 10^{-4}$ is obtained from the value of 9.3×10^{10} l mol^{-1} s^{-1} calculated for Z_4.

The value of 7.34 ± 0.21 found for $\log_{10} k_4$ for the C_4F_8Cl radical is considerably less than the values obtained for the C_3F_6Cl radical [2] and for the chloroethylene series [8] and other alkyl radicals [10 - 13]. It is also less than the value expected from the empirical relation proposed by Bertrand *et al.* [12]. However, it is comparable with the value of 7.27 reported for the C_5F_8Cl radical [14].

The appreciable hindrance of the recombination of C_4F_8Cl radicals accounts for the high quantum yield of the photochlorination despite the relatively high (5.77 kcal) activation energy of step (3).

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