

THE KINETICS AND MECHANISM OF THE FORMATION OF CHLORINE MONOFLUORIDE IN THE PHOTOCHEMICAL REACTION BETWEEN CHLORINE AND FLUORINE AT 365 nm

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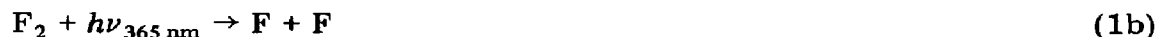
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Summary

The formation of ClF in the photochemical reaction between Cl₂ and F₂ at 365 nm has been investigated at temperatures between 30 and 50 °C. The reaction is a chain of short length. In the presence of less than 40 Torr of ClF, ClF is the only final product. The quantum efficiency Φ_{ClF} of its formation is directly proportional to the F₂ pressure. At ClF pressures above approximately 15 Torr, Φ_{ClF} is independent of the light intensity whereas the ClF pressure has a strong decreasing effect. At ClF pressures above 40 Torr the simultaneous formation of ClF₃ becomes observable.

The experimental results can be explained by the following mechanism:



or



The efficiency factor of ClF as the third body in reaction (5) is about 35 times larger than those of the other gases present, indicating that chemical forces are involved in its action. A value of $2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for the rate constant k_2 of reaction (2) at 30 °C.

1. Introduction

In an earlier investigation [1] of the photochemical reaction between fluorine and ClF at 365 nm we found that in the presence of excess fluorine the only detectable product is ClF₃ which is formed with unit quantum efficiency, whereas for $p_{F_2}/p_{ClF} < 0.5$ molecular chlorine begins to appear among the products. Results obtained in experiments performed in the presence of larger amounts of chlorine indicated that several short-lived polyatomic intermediates were probably formed.

The photochemical reaction between F₂ and Cl₂ has also been investigated by Axworthy [2] who obtained some qualitative results. Furthermore, several investigations of the thermal reaction have been reported [3 - 5]. However, the data reported in the literature, some of which are contradictory, are insufficient to interpret the results satisfactorily.

The present work was undertaken in order to obtain further information about this system and to enable us to develop a mechanism which could explain the experimental data.

2. Experimental details

2.1. Apparatus

The experimental arrangement was the same as that described previously [1]. The reactor was an optical quartz cell 10 cm long with plane windows and a diameter of 5 cm. It was located in a thermostat in which the temperature could be held constant to within ± 0.1 °C. A small U-tube in which the condensable part of the reaction mixture could be frozen out and distilled at a later time was inserted in the capillary between the reactor and the valve connecting the reaction system to the vacuum line.

The light source was a high pressure mercury lamp (type HBO500). A system of quartz lenses and a filter combination (Schott, Mainz) was used to obtain an almost homogeneous parallel light beam of wavelength 365 nm. The light intensity was determined by actinometry using the photochemical decomposition of F₂O. The intensity of the light entering the reactor was about 10^{19} photons min⁻¹.

The pressure was measured using a mercury manometer isolated from the system by a quartz spiral manometer which was used as a zeroing instrument. Since ClF is formed without any change in the molar concentration, the formation of ClF₃ can easily be detected by the corresponding pressure decrease. The reaction products were identified using IR spectroscopy.

The reaction mixture was analysed by pumping it slowly through the U-tube which was cooled to -195 °C. In this way the volatile components (F₂ and gaseous additives such as O₂ and N₂) were removed. The condensed phase (Cl₂ and ClF) was then re-evaporated in the reactor. The procedure was repeated until the pressure of the condensable components remained constant. This method of separating the gases was shown by distilling mix-

tures of known composition to be quantitative. The amount of fluorine which had been consumed during the reaction, and consequently the amount of ClF formed, was calculated from the pressure of the volatile component and the initial fluorine pressure. Since every pressure reading was subject to an error of ± 0.1 Torr and three readings (four if ClF is initially present) were made in order to determine the amount of the reacted fluorine, the mean error in the determination of p_{ClF} was ± 0.3 Torr (or ± 0.4 Torr if ClF was added to the reaction mixture).

2.2. Preparation and purification of the gases

ClF, F₂, Cl₂, N₂ and O₂ were prepared and/or purified as previously described [1]. Their purity was tested by IR spectroscopy.

3. Experiments and results

Most of the experiments were performed at 30 °C although some were carried out at 50 °C. The Cl₂ pressure was varied between 20 and 600 Torr, the F₂ pressure between 10 and 450 Torr and the ClF pressure between 0 and 50 Torr. Some experiments were performed in the presence of N₂ or O₂, and in others the light intensity was reduced to one-third by inserting a blackened mesh into the light path. To ensure reliable results the walls of the reactor were passivated prior to the experiments by exposing them to ClF and ClF₃ for several hours. Under these conditions no dark reaction was detected. The reproducibility of the results was generally quite good except at very low ClF pressures where, owing to the relatively large errors in the determination of ClF, a rather large dispersion of the experimental data was observed. Therefore the results of experiments performed at ClF pressures below 2 Torr were disregarded.

No pressure change was observed during the reaction for ClF pressures up to about 40 Torr, *i.e.* no measurable quantities of ClF₃ were formed. However, at higher ClF pressures a pressure decrease was observed and ClF₃ was detected in the products. In order not to complicate the system further we limited our studies to experiments with ClF pressures up to 40 Torr.

It was found that in the presence of only a few torrs of ClF the reaction rate was proportional to the fluorine pressure, whereas the light intensity appeared in the rate equation with an exponent that was rather less than unity. The total pressure had a negative effect. Among the various gases added to the system O₂ showed the greatest effect.

At higher ClF pressures ($p_{\text{ClF}} > 15$ Torr) the total pressure effect was dominated by the very strong inhibiting influence of ClF. Under these conditions the quantum efficiency of ClF formation was proportional to the F₂ pressure, independent of the light intensity and very strongly decreased by the ClF pressure. Φ_{ClF} was always very small and under our experimental conditions never exceeded a value of 2. This result, however, does not represent a limiting value.

TABLE 1

Experiments at 30 °C with ClF pressures between 2 and 40 Torr

Run	$(p_{\text{Cl}_2})_0$ (Torr)	$(p_{\text{F}_2})_0$ (Torr)	$(p_{\text{ClF}})_0$ (Torr)	p_{N_2} (Torr)	I (Torr min ⁻¹)	Δt (min)	\bar{p}_{ClF} (Torr)	Φ_{ClF}	$\Phi_{\text{ClF}}^{\text{calc}}$
87	200.6	24.0			2.09	6.0	2.1	0.33 ± 0.05	0.30
91	201.3	24.7			2.09	6.0	2.2	0.35 ± 0.05	0.31
92	200.7	24.9			2.09	9.0	2.9	0.31 ± 0.03	0.30
93	201.0	24.9			2.09	9.0	2.9	0.31 ± 0.03	0.30
83	201.3	50.4			2.09	3.0	2.0	0.64 ± 0.10	0.63
88	201.3	50.2			2.09	6.0	3.5	0.56 ± 0.05	0.58
112	202.7	52.9		244.5	1.96	7.8	3.4	0.44 ± 0.04	0.51
113	201.3	51.5		247.4	1.96	7.8	3.8	0.50 ± 0.04	0.48
69	199.9	49.8			2.09	10.0	5.3	0.51 ± 0.03	0.53
70	199.7	49.2			2.09	10.0	5.2	0.50 ± 0.03	0.52
74	200.3	49.8			2.09	10.0	5.7	0.55 ± 0.03	0.51
76	200.1	49.9			2.09	10.0	5.6	0.54 ± 0.03	0.52
108	200.7	49.0		198.6	2.09	10.0	4.3	0.41 ± 0.03	0.45
109	200.7	49.8		197.9	2.09	10.0	4.0	0.38 ± 0.03	0.47
114	201.4	51.2	5.0	242.7	1.96	8.8	6.8	0.39 ± 0.03	0.36
115	201.2	51.5	5.1	242.0	1.96	8.8	7.0	0.41 ± 0.03	0.36
71	200.4	50.5	5.0		2.09	10.0	9.4	0.42 ± 0.03	0.42
79	200.1	50.2	5.0		2.09	10.0	9.0	0.38 ± 0.03	0.43
72	201.0	50.4	10.0		2.09	10.0	13.3	0.32 ± 0.03	0.32
78	200.1	50.1	10.1		2.09	10.0	13.5	0.33 ± 0.03	0.32
116	201.2	51.6	12.2	235.3	1.96	11.0	14.9	0.25 ± 0.03	0.24
73	200.1	49.8	14.3		2.09	10.0	17.1	0.27 ± 0.03	0.24
77	200.0	49.8	14.0		2.09	10.0	16.5	0.24 ± 0.03	0.26
80	200.4	50.2	20.3		2.09	10.0	22.4	0.20 ± 0.03	0.18
117	201.5	51.7	22.1	224.6	1.96	21.8	25.0	0.14 ± 0.01	0.13
81	200.5	50.2	30.1		2.09	10.0	31.2	0.11 ± 0.03	0.11
123	201.2	51.7	37.2	209.4	1.96	46.3	40.3	0.07 ± 0.03	0.07
124	201.3	51.6		246.5	0.65	23.4	4.6	0.60 ± 0.04	0.67
122	202.4	52.9	5.4	239.1	0.65	26.4	8.8	0.40 ± 0.03	0.46
119	201.4	51.6	12.3	234.5	0.65	25.0	14.6	0.28 ± 0.04	0.27
130	201.1	51.7	22.2	224.3	0.65	60.0	24.8	0.13 ± 0.02	0.14
100	199.6	100.5			2.09	1.5	1.7	1.10 ± 0.20	1.22
84	199.9	100.7			2.09	3.0	3.5	1.12 ± 0.10	1.13
118	201.4	101.5		196.7	1.96	3.4	3.3	0.99 ± 0.09	1.00
86	201.4	197.8			2.09	3.0	5.1	1.63 ± 0.10	1.88
126	201.5	201.3	22.1	74.9	1.96	5.7	24.9	0.50 ± 0.05	0.52
105	398.3	49.7			2.09	10.0	3.5	0.33 ± 0.03	0.41
106	398.4	49.3			2.09	10.0	3.8	0.36 ± 0.03	0.40
151 ^a	196.0	50.5	35.3		—	30.0	37.2	(0.13 ± 0.02) ^a	—
150 ^a	395.4	51.5	35.3		—	30.0	37.1	(0.12 ± 0.02) ^a	—

^a I_0 unknown; the quoted values are reaction rates in torrs of ClF min⁻¹.

The experimental results are summarized in Tables 1 and 2 where $(p_{\text{F}_2})_0$, $(p_{\text{Cl}_2})_0$ and $(p_{\text{ClF}})_0$ represent the pressures of the gases at the beginning of the reaction, p_{N_2} and p_{O_2} represent the pressures of the gases added to the system, I (Torr min⁻¹) is the intensity of the absorbed light, Δt (min)

TABLE 2
Experiments under miscellaneous conditions

Run	$(p_{\text{Cl}_2})_0$ (Torr)	$(p_{\text{F}_2})_0$ (Torr)	$(p_{\text{ClF}})_0$ (Torr)	p_{O_2} (Torr)	I (Torr min ⁻¹)	Δt (min)	\bar{p}_{ClF} (Torr)	Φ_{ClF}
<i>At 30 °C with added O₂</i>								
110	201.1	49.9		208.0	2.09	10.0	1.9	0.18 ± 0.03
111	201.1	49.4		206.8	2.09	10.0	2.2	0.21 ± 0.03
<i>At 30 °C with more than 40 Torr of ClF</i>								
138 ^a	201.7	51.8	47.3		1.45	100.0	51.7	0.073 ± 0.006
141	199.6	451.9	46.9		1.45	6.0	49.4	0.57 ± 0.07
<i>At 50 °C</i>								
101	200.2	49.9			2.23	10.0	8.2	0.74 ± 0.03
102	199.7	49.7			2.23	10.0	8.3	0.74 ± 0.03

^a ClF₃ formation is observed; $\Phi_{\text{ClF}_3} = 0.004 \pm 0.001$.

is the reaction time, \bar{p}_{ClF} is the mean pressure of ClF during Δt , Φ_{ClF} is the experimental quantum efficiency and $\Phi_{\text{ClF}}^{\text{calc}}$ is the calculated quantum efficiency (see Section 4). The error in Φ_{ClF} is essentially based on the error in the determination of p_{ClF} which is, as stated above, ± 0.3 or ± 0.4 Torr. Because of the high extinction coefficient of Cl₂ at 365 nm the absorbed light intensity I is almost identical with the intensity of the incident light. Some experiments performed at 50 °C are included in Table 2. They indicate clearly that temperature has a positive effect on the formation of ClF.

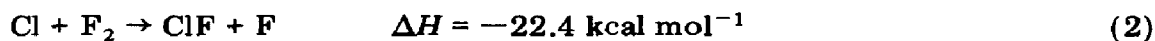
4. Discussion of the results

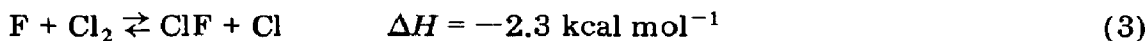
The first steps of the reaction after light absorption will be the dissociation of Cl₂, F₂ and ClF, followed by the reactions of the chlorine and fluorine atoms formed in these processes.

Consideration of the absorption coefficients of Cl₂ [6], F₂ [7] and ClF [1] shows that under the working conditions used here almost all the incident light is absorbed and that in all cases

$$I_{\text{Cl}_2} \gg I_{\text{F}_2} > I_{\text{ClF}}$$

Therefore the initial steps of the reaction are





Because of its high activation energy the back reaction (2) was not included in the scheme.

Only an estimated value of k_2 is reported in the literature [8]: $k_2 < 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C. This value is very low for this type of reaction. However, it agrees well with the reaction constant of the analogous reaction involving bromine atoms: $\text{Br} + \text{F}_2 \rightarrow \text{BrF} + \text{F}$ ($\Delta H = -(22 \pm 2) \text{ kcal mol}^{-1}$ and $k = 6.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C [9]). In contrast, reaction (3) is very fast [10, 11]: $k_3 = 5.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C. The equilibrium constant K_3 was estimated to be about 40 at 25 °C [12]. With these data the rate constant for the back reaction (3) can be readily calculated: $k_{-3} = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C. These results show that equilibrium (3) will not be disturbed by reaction (2) and consequently the ratio $p_{\text{Cl}}/p_{\text{F}}$ can be calculated. Under the present experimental conditions ($p_{\text{Cl}_2} \approx 200 \text{ Torr}$ and $p_{\text{ClF}} = 2 - 40 \text{ Torr}$) this ratio has values between 4000 and 200.

The low estimated value reported for k_2 , together with the low quantum efficiencies of ClF formation (see Tables 1 and 2), indicate that reaction (2) must be very slow and is probably the rate-determining step. Additionally, if equilibrium is established between the forward and back reactions (3) it can be concluded that the chlorine and not the fluorine atoms are responsible for the chain termination. One of the termination steps must be the homogeneous recombination of chlorine atoms:



However, because of the large inhibiting effect of ClF reaction (4) will only be dominant at very low ClF concentrations.

In order to explain this effect some additional reactions must be included in the above reaction scheme. The existence of at least one short-lived polyatomic intermediate, in the formation of which both chlorine atoms and ClF participate, has to be assumed. The simplest compound satisfying these conditions is Cl_2F . We therefore propose the following additional reactions:



or



where reactions (6) and (6') represent two alternative ways of consuming Cl_2F . It is not possible to determine experimentally which of these two reactions takes part in the process. Calculations using either reaction (6) or reaction (6') lead to almost identical equations.

The mechanism consisting of reactions (1) - (6) (or (6')) explains all experimental data in a quantitative way. For the stationary state we obtain

$$2I = 2k_4 p_{\text{Cl}}^2 p_{\text{M}} + k_5 p_{\text{Cl}} p_{\text{ClF}} p_{\text{M}'} + k_6 p_{\text{Cl}} p_{\text{Cl}_2\text{F}} \quad (7)$$

and

$$k_5 p_{\text{Cl}} p_{\text{ClF}} p_{\text{M}'} = k_6 p_{\text{Cl}} p_{\text{Cl}_2\text{F}} + 2k_6' p_{\text{Cl}_2\text{F}}^2 \quad (8)$$

With respect to the consumption of Cl_2F two limiting cases can be considered: $v_6 \gg v_6'$ which leads to

$$I = k_4 p_{\text{Cl}}^2 p_{\text{M}} + k_5 p_{\text{Cl}} p_{\text{ClF}} p_{\text{M}'} \quad (9a)$$

and $v_6' \gg v_6$ which leads to

$$I = k_4 p_{\text{Cl}}^2 p_{\text{M}} + \frac{k_5}{2} p_{\text{Cl}} p_{\text{ClF}} p_{\text{M}'} \quad (9b)$$

The quantum efficiency of ClF formation is expressed by

$$\Phi_{\text{ClF}} = \frac{1}{I} \frac{dp_{\text{ClF}}}{dt} = -\frac{2}{I} \frac{dp_{\text{F}_2}}{dt} = \frac{2I_{\text{F}_2}}{I} + \frac{2k_2 p_{\text{F}_2} p_{\text{Cl}}}{I} \quad (10)$$

where I is the total amount of light absorbed and I_{F_2} is the amount of light absorbed by molecular fluorine. Under these conditions, as was mentioned earlier, I is always nearly equal to I_0 and I_{F_2} is very small compared with the total absorbed light intensity. Elimination of p_{Cl} from either (9a) or (9b) and (10) gives finally

$$\Phi_{\text{ClF}} = \frac{2I_{\text{F}_2}}{I} + p_{\text{F}_2} \left[\left\{ \frac{A}{Ip_{\text{M}}} + \left(\frac{p_{\text{ClF}} p_{\text{M}'}}{2Ip_{\text{M}}} \frac{A}{B} \right)^2 \right\}^{1/2} - \frac{p_{\text{ClF}} p_{\text{M}'}}{2Ip_{\text{M}}} \frac{A}{B} \right] \quad (11)$$

where $A = 4k_2^2/k_4$ and $B = 2k_2/k_5$ (termination via (6)) or $B = 4k_2/k_5$ (termination via (6')). Equation (11) can be rewritten as

$$\frac{\chi^2 Ip_{\text{M}}}{A} + \frac{\chi p_{\text{ClF}} p_{\text{M}'}}{B} = 1 \quad (12)$$

where

$$\chi = \frac{1}{p_{\text{F}_2}} \left(\Phi_{\text{ClF}} - \frac{2I_{\text{F}_2}}{I} \right)$$

The relative weights of the first and second terms on the left-hand side of eqn. (12) represent the importance of reactions (4) and (5) respectively in the consumption of chlorine atoms. There are two limiting cases: (a) for high ClF pressures

$$\chi p_{\text{ClF}} p_{\text{M}'} = B \quad (13)$$

and (b) for low ClF pressures

$$\chi^2 Ip_{\text{M}} = A \quad (14)$$

Case (b), where reaction (4) is the only chain-terminating step, could never be realized. The experiments demonstrate that with decreasing p_{ClF} an effect of I on Φ_{ClF} begins to appear. However, the limit where Φ_{ClF} is proportional to $I^{-1/2}$ could not be reached because, as was mentioned earlier, it is not possible to obtain reliable results at ClF pressures below 2 Torr and at higher

ClF pressures reaction (5) is already dominant. In contrast, case (a), as will be demonstrated, is easily realizable. At high ClF pressures eqn. (13) holds. If the "effective" total pressure $p_{M'}$ in reaction (5) is represented in terms of the partial pressures of the gases present and their efficiency factors γ' , we obtain

$$p_{M'} = \gamma'_{\text{ClF}} p_{\text{ClF}} + \gamma'_{\text{Cl}_2} p_{\text{Cl}_2} + \gamma'_{\text{F}_2} p_{\text{F}_2} + \gamma'_{\text{N}_2} p_{\text{N}_2}$$

The γ' values are not known. However, the experiments show that γ'_{ClF} is much larger than γ'_{Cl_2} , γ'_{F_2} and γ'_{N_2} which do not differ much from each other. This indicates that ClF in reaction (5) probably does not act as a simple third body. If we set $\gamma'_{\text{Cl}_2} = \gamma'_{\text{F}_2} = \gamma'_{\text{N}_2} = 1$ we obtain

$$p_{M'} = p_{\text{Cl}_2} + p_{\text{F}_2} + p_{\text{N}_2} + \gamma'_{\text{ClF}} p_{\text{ClF}} = p_{\text{ClF}} (\gamma'_{\text{ClF}} - 1) + P \quad (15)$$

where P is the total pressure of the system. Substituting for $p_{M'}$ in eqn. (13) we obtain after rearrangement

$$\frac{1}{\chi p_{\text{ClF}}^2} = \frac{\gamma'_{\text{ClF}} - 1}{B} + \frac{P}{p_{\text{ClF}} B} \quad (16)$$

Figure 1 (which includes values from experiments with ClF pressures above 14 Torr only) shows the plot of $1/\chi p_{\text{ClF}}^2$ against P/p_{ClF} . A straight line is obtained which proves that under the conditions of these experiments reaction (5) consumes by far the largest number of chlorine atoms. Equations (13) and (16) can therefore be employed to a very good degree of approximation. γ'_{ClF} can be calculated from the ratio of the intercept to the slope, and B can be determined from the slope. The results are

$$\gamma'_{\text{ClF}} = 33 \pm 6 \quad B = 70 \pm 10 \text{ Torr}$$

The parameter B can also be obtained from the general equation (12) which also includes reaction (4). In order to apply this equation the γ factors

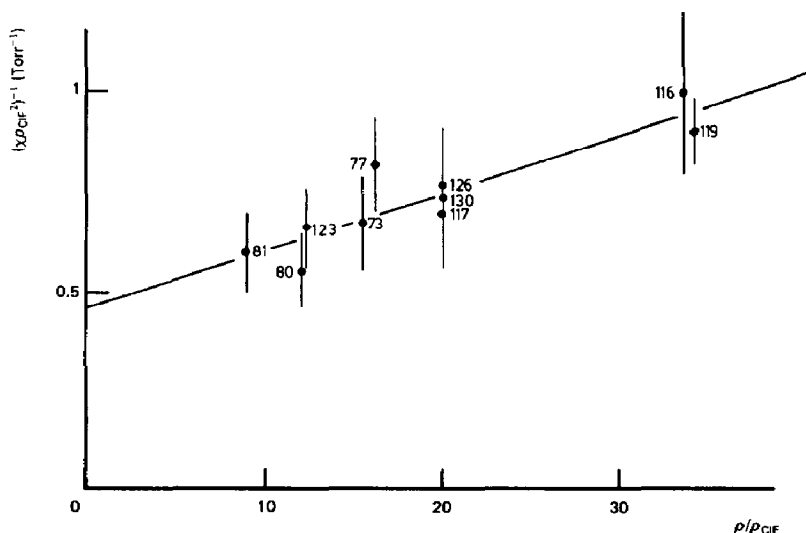


Fig. 1. Experiments with $p_{\text{ClF}} > 14$ Torr.

of the different gases participating in reaction (4) must be known. From the data reported in the literature it can be deduced that $\gamma_{\text{Cl}_2} = 2.5$ [13, 14] taking as a reference $\gamma_{\text{N}_2} = 1$. The γ values for F_2 and ClF are not known. However, it can be assumed that they will not be very different from that of nitrogen. We therefore define

$$p_{\text{M}} = \gamma_{\text{Cl}_2} p_{\text{Cl}_2} + p_{\text{F}_2} + p_{\text{ClF}} + p_{\text{N}_2} = (\gamma_{\text{Cl}_2} - 1)p_{\text{Cl}_2} + P \quad (17)$$

(Experiments with added O_2 are not taken into account.)

According to eqn. (12) a plot of $\chi^2 I p_{\text{M}}$ against $\chi p_{\text{ClF}} p_{\text{M}'}$ should be a straight line with the intercept with the ordinate equal to A and the intercept with the abscissa equal to B . If we take $\gamma_{\text{Cl}_2} = 2.5$ and $\gamma'_{\text{ClF}} = 33$ and calculate p_{M} and $p_{\text{M}'}$ using eqns. (17) and (15) respectively we obtain the following values:

$$A = 0.19 \text{ min}^{-1} \quad B = 73 \text{ Torr}$$

According to the experimental errors the uncertainty in these values is $\pm 15\%$.

Figure 2 enables the region where reaction (5) dominates to be defined. In this figure $1/\chi$ is plotted against $p_{\text{ClF}} p_{\text{M}'}$ with $p_{\text{M}'}$ obtained from eqn. (15). According to eqn. (13) this plot should be linear provided that reaction (4) can be neglected. It can be seen that a systematic deviation appears at low ClF pressures beginning at about 15 Torr and increasing as the zero point is approached. This indicates that the consumption of chlorine atoms via reaction (4) cannot be neglected at pressures below about 15 Torr.

The quantum efficiencies Φ_{ClF} for all the experiments were calculated from eqn. (11) using the given values of A and B . The results reported in Table 1 demonstrate the close agreement between the experimental and

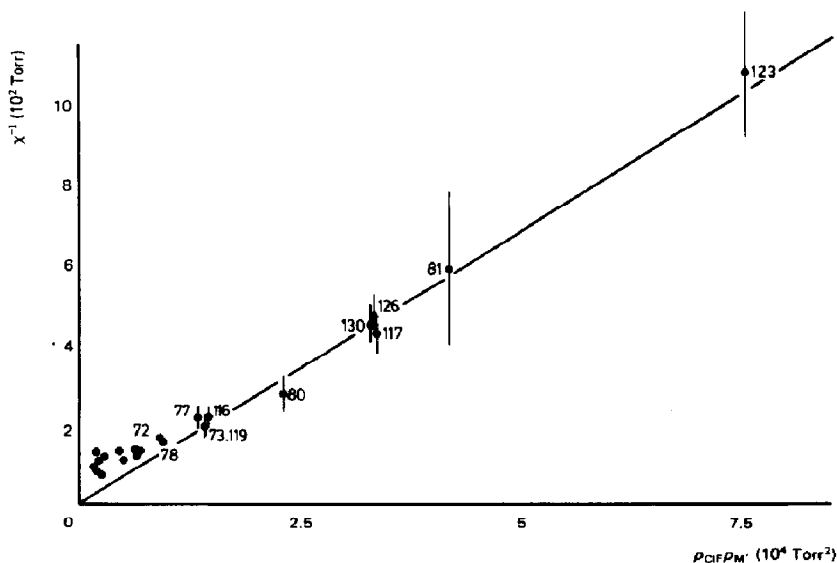


Fig. 2. Experiments with $p_{\text{ClF}} > 4$ Torr: $p_{\text{M}'} = p_{\text{ClF}}(\gamma'_{\text{ClF}} - 1) + P$; $\gamma'_{\text{ClF}} = 33$.

calculated values. It should be noted that if γ_{Cl_2} is assigned a different value, e.g. $\gamma_{\text{Cl}_2} = 1$, the agreement is equally good.

In summary, the proposed mechanism agrees quite well with the experimental data. The Cl_2F molecule, which plays a very important role in the proposed mechanism, is doubtless a very unstable intermediate and it has not so far been possible to identify it at room temperature. However, there are reasons to believe that it is formed in the low temperature photolysis of mixtures of Cl_2 and F_2 in matrixes [15]. It should be emphasized that Cl_2F cannot be formed if ClF is not present in the reaction mixture. This explains why this molecule was not found earlier in investigations of the reaction between fluorine atoms and Cl_2 [10].

The unusually high γ' factor for ClF in reaction (5) indicates, as stated earlier, that chemical forces are involved in its action, possibly producing a Cl_3F_2 molecule that is very short lived.

It is possible to calculate the rate constant k_2 of the rate-controlling step of the reaction from the numerical value of A and the recombination constant k_4 . If A is taken as 0.19 min^{-1} ($3.2 \times 10^{-3} \text{ s}^{-1}$) and the value of k_4 given in the literature for N_2 as the third body ($k_{4,\text{N}_2} = 8.1 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$ [14]), we obtain $k_2 = 2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 30°C . This is an extremely low value, being about a factor of 25 less than that of the analogous reaction with bromine atoms [9].

A rather good approximation can be made for the heat of activation of reaction (2). Comparison of the quantum efficiencies obtained at 50°C with those calculated at 30°C under similar conditions using eqn. (11), taking into account that the activation energy is essentially determined by k_2 throughout the p_{ClF} range, gives a value of $5 \pm 2 \text{ kcal mol}^{-1}$ for E_2 .

For $B = 73 \text{ Torr} = 3.9 \times 10^{-3} \text{ M}$, $k_5/k_2 \approx 750 \text{ M}^{-1}$. With the given value of k_2 we obtain $k_{5,\text{N}_2} \approx 2 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$. This is again a very low value, about a factor of 10^4 less than the rate constant for the recombination of chlorine atoms with N_2 as the third body. It indicates that the formation of Cl_2F has a very small probability factor.

It should finally be mentioned that there is no indication of heterogeneous reactions, e.g. wall recombination of chlorine atoms, taking part in the reaction. Calculations performed for our experimental conditions and the dimensions of the reactor confirm that wall reactions can be neglected.

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