

## RELATIVE REACTIVITY OF CHLORINE ATOMS WITH NO, NO<sub>2</sub> AND HCCl<sub>2</sub>F AT ROOM TEMPERATURE AND ATMOSPHERIC PRESSURE

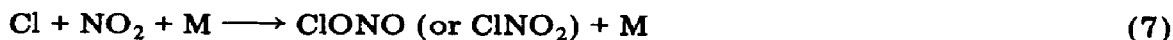
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### Summary

The reactions of chlorine atoms with NO, NO<sub>2</sub> and HCCl<sub>2</sub>F have been studied at 294 K and 1 atm total pressure. The experiments involved steady-state photolysis of Cl<sub>2</sub>-HCCl<sub>2</sub>F-O<sub>2</sub>-NO-NO<sub>2</sub>-N<sub>2</sub> mixtures. Two sets of experiments were done, one in which NO removal was monitored by its chemiluminescent reaction with O<sub>3</sub>, and one in which CClFO was monitored by *in situ* IR spectroscopy. The reactions studied were



From the chemiluminescence experiments  $k_6/k_1$  was found to be  $(1.0 \pm 0.2) \times 10^{-17} \text{ cm}^3$  with N<sub>2</sub> as a chaperone which leads to a value of  $k_1 = 1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  based on the literature value for  $k_6$  of  $1.7 \times 10^{-32} \times \exp(+530/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  (where  $T$  is in kelvins). Also  $k_7/k_6$  was found to be  $2.5 \pm 1.0$  which gives  $k_7 = 2.5 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ , which is considerably lower than the literature values of  $(7.2 - 16) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ . Part or all of the discrepancy may reflect the possibility that  $k_7$  is in its pressure fall-off region under our conditions of 1 atm pressure.

### 1. Introduction

We have initiated a series of experiments in our laboratory to study the reactions of CX<sub>2</sub>ClO<sub>2</sub> with NO and NO<sub>2</sub> (X ≡ H, F or Cl). We generate the CX<sub>2</sub>ClO<sub>2</sub> species by photolyzing Cl<sub>2</sub> in the presence of HCX<sub>2</sub>Cl and O<sub>2</sub>. Consequently, the reactions of chlorine atoms with HCX<sub>2</sub>Cl, NO and NO<sub>2</sub> must be known to interpret our data. During the course of our investigations,

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carried out at 1 atm pressure and 294 K, it became clear that the low pressure literature values for chlorine atom reactions with NO and NO<sub>2</sub> gave a relative rate coefficient inconsistent with our data. Thus we have remeasured this relative rate under our conditions and report the results here together with our results for the relative rate of chlorine atoms and NO with HCCl<sub>2</sub>F, for which no other measurement exists.

Chlorine atoms are known to add readily to both NO and NO<sub>2</sub>, the respective rate coefficients being  $1.7 \times 10^{-32} \exp(+530/T)$  (where  $T$  is in kelvins) and  $7.2 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  (at 298 K) with N<sub>2</sub> as a chaperone [1]. The reaction with NO was studied by Clark *et al.* [2] over the temperature range 270 - 620 K and their Arrhenius expression gives a value of  $5.2 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  at 471 K which is somewhat higher than the value of  $(2.1 \pm 0.6) \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  found earlier by Ashmore and Spencer [3] at this temperature. Ravishankara *et al.* [4] reported a value of  $1.63 \times 10^{-33} \exp(+1186/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for helium as a chaperone between 240 and 350 K. This gives a value at 298 K of  $8.8 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  which compares with a value of  $1.0 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  at 298 K for N<sub>2</sub> as a chaperone computed from the Arrhenius expression of Clark *et al.* [2].

The value of the rate coefficient for the addition of chlorine atoms to NO<sub>2</sub> was given as  $7.2 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  with N<sub>2</sub> as a chaperone at 298 K by Clyne and White [5] as a provisional value. Zahniser *et al.* [6] obtained a value of  $8 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  at 300 K with helium as a chaperone. This value was confirmed by Ravishankara *et al.* [4] who obtained  $1.45 \times 10^{-31} \exp(+529/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  and  $3.42 \times 10^{-31} \exp(+460/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  for helium and N<sub>2</sub> as chaperones respectively. These values lead to respective values at 298 K of  $8.55 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  and  $1.6 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ . These values are even higher than that of Clyne and White [5]. All of these values are low pressure values where the reaction is termolecular. There is no measurement at atmospheric pressure where the reaction could be in the pressure fall-off region and the rate constant would be reduced. Therefore we have measured this rate coefficient relative to that for addition of chlorine atoms to NO at 1 atm pressure.

## 2. Experimental details

Mixtures of Cl<sub>2</sub>, CHCl<sub>2</sub>F, O<sub>2</sub> and NO<sub>2</sub> with and without NO were irradiated at 366 nm in a cylindrical Pyrex cell of length 10 cm and diameter 3.7 cm which was equipped with NaF windows, and placed in the sample beam of a double-beam Beckman Acculab 9 IR spectrometer. A conventional mercury-free high vacuum line utilizing Teflon stopcocks with Viton O-rings was used. The radiation was from an Oriel high pressure 150 W mercury arc lamp and passed through a Corning filter CS 7-37 before entering the reaction cell. The strong CClFO peak at  $1832 \text{ cm}^{-1}$  was monitored continuously during irradiation using an external recorder.

In separate experiments, NO disappearance was monitored continuously both during irradiation and in the dark after irradiation had been terminated using the chemiluminescent reaction between NO and O<sub>3</sub> in the system described in a previous paper [7]. The initial rates of NO removal during irradiation were corrected for the time constant of the measurement system. The measurement time constant was 0.42 s<sup>-1</sup> leading to a maximum correction of 30%.

Absorbed IR light intensities  $I_a$  were determined by the photolysis of optically equivalent amounts of NO<sub>2</sub> taking  $-\Phi(\text{NO}_2) = 2.0$ . For the chemiluminescence runs azomethane was photolyzed in the presence of NO and O<sub>2</sub>, the quantum yield for NO removal for this system being 4.0.

The chlorine (Matheson high purity Research grade) was purified by distillation from 143 to 113 K. NO (Matheson) was purified by distillation from 87 to 77 K; the white color of the solid NO indicated that it was free of NO<sub>2</sub>. The NO<sub>2</sub> (Matheson) for the IR experiments was mixed with oxygen and cooled to 77 K and allowed to warm up to room temperature several times before use. It was stored in oxygen. For the chemiluminescence study NO<sub>2</sub> was used directly from the cylinder and corrected for the 5.0% NO content as determined by chemiluminescence analysis. O<sub>2</sub> and N<sub>2</sub> were slowly passed through two traps maintained at 77 K. Chromatographic analysis showed [CH<sub>4</sub>] ≤ 2.5 ppm in N<sub>2</sub> and [CH<sub>4</sub>] ≈ 20 ppm in O<sub>2</sub> with no detectable levels of other hydrocarbon impurities. The HCCl<sub>2</sub>F was purified by distillation from 156 to 143 K. Mass spectroscopy showed it to be free of impurities.

### 3. Results

With IR analysis, several runs were done in which Cl<sub>2</sub> was photolyzed in the presence of HCCl<sub>2</sub>F, O<sub>2</sub> and NO<sub>2</sub>, but in the absence of NO. CClFO formation was monitored. No CClFO was produced until all the NO<sub>2</sub> was consumed, but then CClFO was produced in high yields. With NO also present initially, CClFO formation was immediate and to begin with was proportional to the irradiation time. Then it levelled off before it rose sharply after a time corresponding to total NO<sub>x</sub> consumption. Presumably the levelling off corresponds to the exhaustion of NO, which occurs before the exhaustion of NO<sub>2</sub>. Besides the CClFO peaks, no other IR peaks could be positively identified, though product bands did occur at 940 cm<sup>-1</sup> and a doublet at 1720 cm<sup>-1</sup>.

For experiments with both NO and NO<sub>2</sub> present initially, the initial quantum yields  $\Phi_1(\text{CClFO})$  of CClFO formation are listed in Table 1. These runs were done at a constant [NO<sub>2</sub>]/[NO] value of 0.211 ± 0.025 but with a tenfold variation of both [NO] and [NO<sub>2</sub>]. As the concentration of these species increases by a factor of 10,  $\Phi_1(\text{CClFO})$  drops by a factor of about 4 - 6.

From the chemiluminescence experiments, initial quantum yields  $-\Phi_1(\text{NO})$  of NO disappearance were obtained from the irradiated mixtures

TABLE 1

CClFO quantum yields of formation from the photolysis of  $\text{Cl}_2$  at 366 nm in the presence of  $\text{HCCl}_2\text{F}-\text{O}_2-\text{NO}-\text{NO}_2$  mixtures<sup>a</sup>

[NO] (Torr)	[NO <sub>2</sub> ] (Torr)	[HCCl <sub>2</sub> F] (Torr)	[O <sub>2</sub> ] (Torr)	$\Phi_1(\text{CClFO})$
0.057	0.011	405	49.0	6.40
0.089	0.019	672	34.9	8.26
0.093	0.018	414	34.7	6.53
0.097	0.023	430	34.4	6.85
0.140	0.026	690	28.0	6.12
0.290	0.050	479	56.7	3.28
0.393	0.081	690	47.3	3.05
0.472	0.100	700	43.9	2.29
0.560	0.110	473	57.3	1.49
0.588	0.127	668	49.1	1.71

<sup>a</sup>[NO<sub>2</sub>]/[NO] = 0.211 ± 0.025; [Cl<sub>2</sub>] = 9.3 ± 1.0 Torr;  $I_a = 1.00 \pm 0.11$  mTorr s<sup>-1</sup>; T = 296 K.

TABLE 2

NO quantum yields of disappearance from the photolysis of  $\text{Cl}_2$  at 366 nm in the presence of  $\text{HCCl}_2\text{F}-\text{O}_2-\text{NO}-\text{NO}_2-\text{N}_2$  mixtures<sup>a</sup>

$10^4 \times [\text{NO}]/[\text{HCCl}_2\text{F}]$	[NO] (mTorr)	[NO <sub>2</sub> ] (mTorr)	[HCCl <sub>2</sub> F] (Torr)	$-\Phi_1(\text{NO})$
[NO <sub>2</sub> ]/[NO] ≈ 3.8				
2.25	6.49	21.5	28.9	1.06
3.41	5.60	21.5	16.4	0.622
7.49	5.71	22.4	7.62	0.378
16.6	7.87	30.1	4.75	0.264
[NO <sub>2</sub> ]/[NO] ≈ 0.85				
0.77	12.0	9.01	155	5.40
2.25	8.2	8.95	36.5	3.07
5.37	11.0	7.96	20.5	3.15 <sup>b</sup>
5.59	11.4	7.93	20.4	2.05
8.89	19.3	17.6	21.7	1.73
12.9	10.3	8.7	8.01	1.54 <sup>b</sup>
23.3	9.25	10.9	3.97	0.61
25.7	10.6	8.85	4.12	1.01

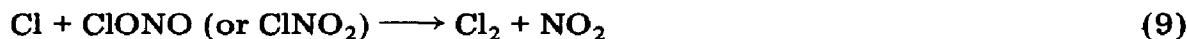
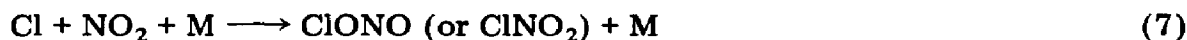
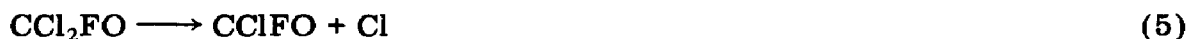
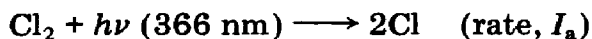
<sup>a</sup>[Cl<sub>2</sub>] ≈ 1 Torr; [O<sub>2</sub>] ≈ 30 - 50 Torr; mixture brought to 1 atm total pressure with N<sub>2</sub>;  $I_a = 0.27 \pm 0.3$  mTorr s<sup>-1</sup>; T = 294 K.

<sup>b</sup> $I_a = 0.41 \pm 0.01$  mTorr s<sup>-1</sup>.

initially containing both NO and NO<sub>2</sub>. These values are listed in Table 2;  $-\Phi_1(\text{NO})$  drops as [NO<sub>x</sub>]/[HCCl<sub>2</sub>F] increases, the inhibition being greater at the higher [NO<sub>2</sub>]/[NO] value, indicating the inhibiting effect of NO<sub>2</sub> on the system.

#### 4. Discussion

The results of the oxidation of  $\text{CCl}_2\text{F}$  can be explained by the mechanism



The mechanism of the  $\text{CX}_3$  radical oxidation has been discussed previously [8 - 11]. The only significant reaction with  $\text{O}_2$  is reaction (2). We propose reactions (3) and (4) for the fate of  $\text{CCl}_2\text{FO}_2$  by analogy with the reactions of  $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2$  and  $\text{CCl}_3\text{O}_2$ . Reaction (3) accounts for the conversion of  $\text{NO}$  to  $\text{NO}_2$  and reaction (4) accounts for the unstable intermediate  $\text{CCl}_2\text{FO}_2\text{NO}_2$  which can decompose thermally to act as a source of free radicals after the radiation is terminated. The  $\text{CCl}_2\text{FO}$  radical is thermodynamically unstable and decomposes via reaction (5) [9]. Reactions (6) - (9) are well known [1].

During the initial stages of the photolysis, the back process in reaction (4) and reactions (8) and (9) are unimportant and the rest of the mechanism leads to the steady-state rate law for  $\text{NO}$  removal

$$\frac{2\beta}{-\Phi(\text{NO})} = R + \frac{(1 + R)(1 + \alpha)k_6[\text{NO}][\text{M}]}{k_1[\text{HCCl}_2\text{F}]} \quad (I)$$

where

$$\alpha = \frac{k_7[\text{NO}_2]}{k_6[\text{NO}]}$$

$$R = \frac{k_4[\text{NO}_2]}{k_3[\text{NO}]}$$

$$\beta = \frac{1 + (1 + R)k_6[\text{NO}][\text{M}]}{k_1[\text{HCCl}_2\text{F}]}$$

Under the conditions of our experiments  $\beta \approx 1$ . Also for a fixed value of  $[\text{NO}_2]/[\text{NO}]$  both  $\alpha$  and  $R$  are constants. Thus a plot of  $-\Phi(\text{NO})^{-1}$  versus  $[\text{NO}]/[\text{HCCl}_2\text{F}]$  should give a straight line with intercept  $R$  and slope  $(1 + R)(1 + \alpha)k_6[\text{M}]/k_1$ . From the slopes at the two different  $[\text{NO}_2]/[\text{NO}]$  values both  $k_6/k_1$  and  $k_7/k_6$  can be determined. Using these,  $\beta$  can be computed and a new plot made to obtain better values of  $k_6/k_1$  and  $k_7/k_6$ . By successive iterations we find that  $k_6/k_1 = (1.0 \pm 0.2) \times 10^{-17} \text{ cm}^3$  for  $\text{M} \equiv \text{N}_2$  and  $k_7/k_6 = 2.5 \pm 1.0$ . Both plots also give  $k_4/k_3 = 0.50 \pm 0.10$ . By rearranging eqn. (I) slightly, all of the data can be placed on a common plot. The rearrangement gives

$$\frac{2\beta}{-\Phi(\text{NO})R} = 1 + \frac{(1 + R^{-1})(1 + \alpha)k_6[\text{NO}][\text{M}]}{k_1[\text{HCCl}_2\text{F}]} \quad (\text{II})$$

Figure 1 shows a plot of the left-hand side of eqn. (II) versus  $(1 + R^{-1})(1 + \alpha)[\text{NO}]/[\text{HCCl}_2\text{F}]$ . The data are fitted by a straight line in which the least accurate points at high  $[\text{NO}]/[\text{HCCl}_2\text{F}]$  have been neglected. The line gives an intercept of 1.0 and a slope of 240 which corresponds to  $k_6[\text{M}]/k_1$  and gives the value for  $k_6/k_1$  of  $1.0 \times 10^{-17} \text{ cm}^3$ . With the literature value for  $k_6$ ,  $k_1$  becomes  $1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is reasonable.

The value of  $2.5 \pm 1.0$  found for  $k_7/k_6$  is considerably lower than the literature values of 7 - 16. At our pressure of 1 atm,  $k_7$  may be in the pressure fall-off region, and this could account for the lower  $k_7/k_6$  obtained by us. In fact, data on the thermal decomposition of  $\text{ClNO}_2$  at 150 K indicate that at 1 atm  $\text{N}_2$ , the fall-off in rate constant is about a factor of 4 [12], about the same as obtained here.

For the experiments in which  $\Phi(\text{CClFO})$  was analyzed by IR spectroscopy, the rate law is

$$\Phi_1(\text{CClFO})^{-1} = \frac{k_4[\text{NO}_2]}{2k_3[\text{NO}]} + \left( \frac{1}{2} + \frac{k_4[\text{NO}_2]}{2k_3[\text{NO}]} \right) \left( \frac{k_6[\text{NO}][\text{M}] + k_7[\text{NO}_2][\text{M}]}{k_1[\text{HCCl}_2\text{F}]} \right) \quad (\text{III})$$

Substituting 0.211 for  $[\text{NO}_2]/[\text{NO}]$  as seen in Table 1 and taking  $[\text{M}] \approx [\text{HCCl}_2\text{F}]$  we obtain

$$\Phi_1(\text{CClFO})^{-1} = \frac{0.106k_4}{k_3} + \left( \frac{1}{2} + \frac{0.106k_4}{k_3} \right) \left( \frac{k_6 + 0.211k_7}{k_1} \right) [\text{NO}] \quad (\text{IV})$$

Figure 2 is a plot of  $\Phi_1(\text{CClFO})^{-1}$  versus  $[\text{NO}]$  for the data from Table 1. The plot is fitted by the best straight line which gives a slope of  $0.91 \pm 0.10 \text{ Torr}^{-1}$  and an intercept of  $0.050 \pm 0.015$ . From the intercept,  $k_4/k_3$  is deduced to be  $0.47 \pm 0.15$  in good agreement with the results from the chemiluminescence experiments and in reasonable agreement with the value of 0.68 found for the analogous reactions with the  $\text{CCl}_3\text{O}_2$  radical [13]. With this value and the value  $k_7/k_6 = 2.5$  found above, the slope of the plot in

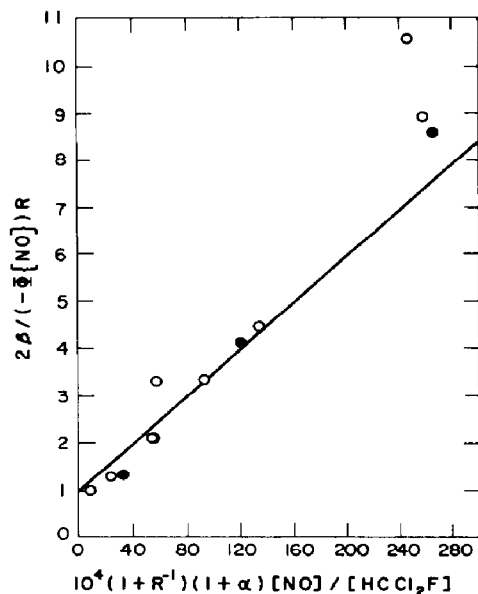


Fig. 1. Plot of  $2\beta/[-\Phi(\text{NO})R]$  vs.  $(1 + R^{-1})(1 + \alpha)[\text{NO}]/[\text{HCCl}_2\text{F}]$  at 294 K: ●,  $[\text{NO}_2]/[\text{NO}] = 3.8$ ; ○,  $[\text{NO}_2]/[\text{NO}] = 0.85$ .

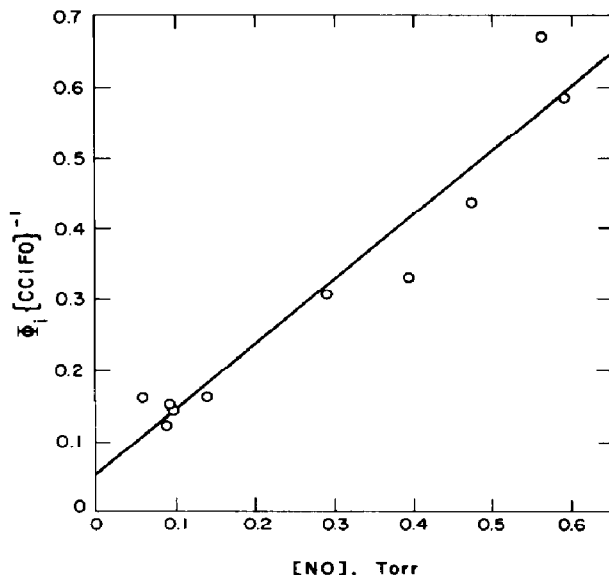


Fig. 2. Plot of  $\Phi_1(\text{CClFO})^{-1}$  vs.  $[\text{NO}]$  for runs with  $[\text{NO}_2]/[\text{NO}] = 0.211 \pm 0.020$  at 296 K.

Fig. 2 can be used to give  $k_6/k_1 = 3.3 \times 10^{-17} \text{ cm}^3$  with  $\text{HCCl}_2\text{F}$  as a chaperone. Thus  $\text{HCCl}_2\text{F}$  is 3.3 times as efficient as  $\text{N}_2$  as a chaperone in reaction (6).

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