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THE CHLORINE ATOM SENSITIZED OXIDATION OF $HCCl_3$, HCF_2Cl AND HCF_3

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Summary

The chlorine atom sensitized oxidations of $HCCl_3$, HCF_2Cl and HCF_3 were studied at 30 °C. The $HCCl_3$ and HCF_2Cl oxidized in a long chain process in which the only oxidation products were CCl_2O and CF_2O, respectively. The quantum yields depend on the $[HCX_3]/(I_a[M])^{1/2}$ values, with upper limits of 195 for $\varphi\{CCl_2O\}$ and 110 for $\varphi\{CF_2O\}$. In the HCF_3 system there is no chain reaction and the products are CF_2O and SiF_4 in a 4:1 ratio. Both products are simultaneously produced in the heterogeneous decomposition of the CF_3O radical at the wall of the cell. Depending on the experimental conditions $\varphi\{CF_2O\}$ ranges from 0.023 to 0.11. In the three halomethanes there is competition between the following reactions:

$$Cl + HCX_3 \longrightarrow CX_3 + HCl$$

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

with $k_2/k_6^{1/2}$ equal to 100, 0.34 and 1.6×10^{-3} $s^{-1/2}$ for $HCCl_3$, HCF_2Cl and HCF_3 respectively, where k_2 and k_6 are the k values for the first and second reactions respectively. Complete reaction mechanisms are proposed.

Introduction

There is now serious concern that some of the commonly used halocarbons may adversely affect the ozone concentration in the stratospheric layer surrounding our planet [1], and therefore the knowledge of the oxidation processes of these compounds is of great importance.

The oxidation of the haloethylenes has been extensively studied and reviewed [2]. The oxidation of the perhalomethanes has also been recently studied [3]. The only work on the oxidation mechanism of hydrogen-containing halomethanes reported to date is that of Sanhueza and Heicklen [4] who studied the oxidation of CCl_2H_2 and $CClH_3$. However, at the present time the oxidation mechanisms of chloroform ($HCCl_3$), fluoroform (HCF_3) and halocarbon 22 (HCF_2Cl), all widely used compounds, have not been reported.

This paper presents results on the oxidation of $HCCl_3$, HCF_2Cl and HCF_3 initiated by the chlorine atom.

Experimental

The experimental procedure used was similar to that described previously [4, 5].

The $HCCl_3$ (Baker Analyzed Reagent), HCF_2Cl, HCF_3 (Peninsular Research Laboratory) and SiF_4 (Matheson) were redistilled under vacuum before use. Their infrared spectra showed no impurity peaks.

The halomethanes and the reaction products were monitored by *in situ* infrared spectroscopy. The bands shown in Table 1 with the listed peak extinction coefficients (to base 10) were monitored.

In the three systems studied the HCl was detected by its characteristic band at 3030 - 2800 cm^{-1}, but no quantitative estimates were made.

TABLE 1

Compound	Band (cm^{-1})	Peak extinction coefficient ($Torr^{-1}$ cm^{-1})
$HCCl_3$	1238	6.23×10^{-3}
HCF_2Cl	1340	5.0×10^{-3}
HCF_3	1395	7.19×10^{-3}
CCl_2O	1860	15.8×10^{-3}
CF_2O	1985	13.8×10^{-3}
SiF_4	1040	85.0×10^{-3}

Results

$HCCl_3$

When mixtures of Cl_2, O_2 and $HCCl_3$ were irradiated at 3655 Å, the reaction products were CCl_2O and HCl. The CCl_2O was produced in a long chain reaction and the quantum yields ranged between 100 and 215 under our experimental conditions; $-\varphi\{HCCl_3\}$ was equal to $\varphi\{CCl_2O\}$ within the range of experimental error. Complete time histories of representative data are displayed in Fig. 1 where the loss of $HCCl_3$ and the production of CCl_2O are plotted against the irradiation time.

The $[HCCl_3]$ was varied by a factor of 16, $[O_2]$ by a factor of 19, I_a by a factor of 5 and [M] by a factor of 15. The results are summarized in Table 2. The quantum yields for the consumption of $HCCl_3$ and for the production of CCl_2O increased with the $HCCl_3$ pressure, approaching an upper limiting value of 200, and decreased with either the increase of the light intensity or the increase of the total pressure. The values of the quantum yields were independent of the oxygen pressure.

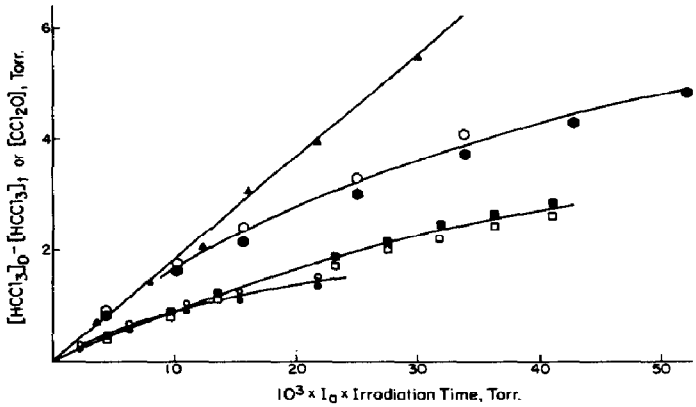

Fig. 1. Plot of $HCCl_3$ consumption and CCl_2O production *vs.* extent of reaction in the chlorine atom sensitized oxidation of $HCCl_3$. The symbol key is given in Table 2.

TABLE 2

The chlorine atom sensitized oxidation of $HCCl_3$ and HCF_2Cl at 30 ± 2 °C

Symbol[a] for Figs. 1, 2, 5, 6	HCX_3 (Torr)	O_2 (Torr)	Cl_2 (Torr)	I_a[b] (10^3 Torr s^{-1})	$-\varphi\{HCX_3\}$[c]	$\varphi\{CX_2O\}$[c]
$HCCl_3$						
● ○[d]	1.60	4.0	4.0	0.44	120	115
▲ ▲	2.60	6.0	1.76	0.19	100	105
◐ ◑	2.90	6.1	8.31	0.91	100	110
□ ■	3.94	77.0	8.31	0.91	97	102
◇ ◆	5.18	4.3	3.84	0.42	210	215
◧ ◨	5.60	8.1	1.80	0.20	190	200
⬢ ⬡	8.80	19.9	8.23	0.91	183	197
— ▲	26.0	6.2	1.76	0.19		185
HCF_2Cl						
● ○	1.79	7.61	1.33	0.15	16.0	15.0
▲ ▲	2.50	4.00	1.33	0.15	21.0	20.0
◐ ◑	3.40	4.10	1.50	0.21	10.0	10.0
◐ ◑	3.48	5.61	8.31	0.91	17.0	19.0
▲ △	3.60	97.0	1.50	0.21	15.0	14.0
◧ ◨	5.06	5.45	6.47	0.71	20.0	20.0
■ □	9.00	4.32	1.33	0.15	51.0	48.0
— ⬡	28.0	3.46	1.25	0.14	100	100

[a]Symbols for the consumption of methane and for the production of CX_2O respectively.
[b]Assuming quantum yield of C_2Cl_4 oxidation to be 300 at high O_2 pressure [5].
[c]Based on initial rates.
[d]In the presence of 30 Torr of N_2.
[e]In the presence of 90 Torr of N_2.

HCF_2Cl

The results obtained with the HCF_2Cl were similar to those already discussed for the $HCCl_3$ system. With this halomethane CF_2O was the only oxida-

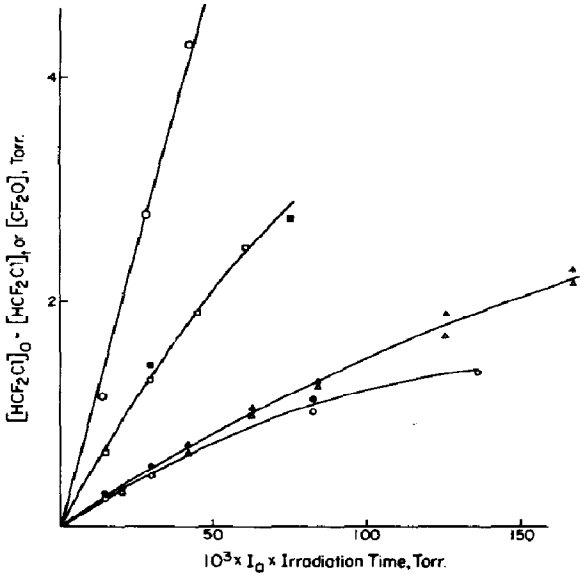

Fig. 2. Plot of HCF_2Cl consumption and CF_2O production *vs.* extent of reaction in the chlorine atom sensitized oxidation of HCF_2Cl. The symbol key is given in Table 2.

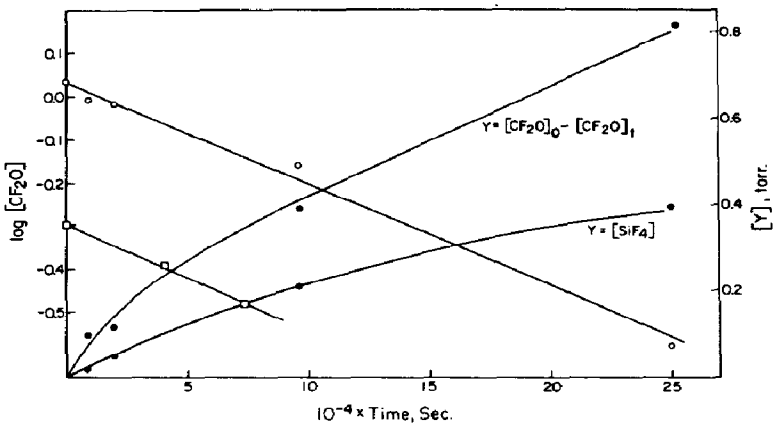

Fig. 3. Plot of CF_2O first order decay: □ $[CF_2O]_0$ = 0.5 Torr; ○ $[CF_2O]_0$ = 1.02 Torr. Plot of CF_2O consumption and SiF_4 production *vs.* time.

tion product and was produced with quantum yields which ranged between 10 and 100 depending on the experimental conditions.

Figure 2 shows the irradiation time history for four runs, and the quantum yields obtained in the consumption of the HCF_2Cl and in the production of CF_2O are summarized in Table 2.

HCF_3

When mixtures of Cl_2, O_2 and HCF_3 are photolysed with radiation principally at 3600 Å, the products of the reaction are CF_2O, SiF_4 and HCl. Since it is well known [6] that the CF_2O decomposes heterogeneously with glass,

$$2CF_2O + \text{wall} \longrightarrow SiF_4 + 2CO_2$$

and since in our system long irradiation time experiments were performed, the CF_2O decomposition was studied separately.

Figure 3 is a plot of the CF_2O disappearance and SiF_4 production as a function of time. The decomposition was done in the presence of 5 Torr of HCF_3 and 5 Torr of O_2. The data (log $[CF_2O]$ *versus* time) give straight lines showing a first order decay:

$$-\frac{d[CF_2O]}{dt} = 2\frac{d[SiF_4]}{dt} = k_{het}[CF_2O]$$

with $k_{het} = 5.3 \times 10^{-6}\ s^{-1}$. The reaction cell was conditioned before performing the experiments in order to obtain reproducible results.

In the oxidation experiments CF_2O and SiF_4 were produced. Figure 4 is the time history for one experiment. The values for $\varphi\{CF_2O\}$ and $\varphi\{SiF_4\}$ were calculated from

$$\varphi\{CF_2O\} \approx R(CF_2O)/I_a + k_{het}[CF_2O]_{av}/I_a \quad \text{(I)}$$

$$\varphi\{SiF_4\} \approx R(SiF_4)/I_a - k_{het}[CF_2O]_{av}/2I_a \quad \text{(II)}$$

where $[CF_2O]_{av} \approx ([CF_2O]_0 + [CF_2O]_t)/2$.

The correction due to the term $k_{het}[CF_2O]_{av}/I_a$ was always around 20% (or less). The ratio $\varphi\{CF_2O\}/\varphi\{SiF_4\}$ was 4 (in the experiments where the cell was previously conditioned), independent of the condition. The quantum yield increased with the fluoroform partial pressure and decreased with I_a and with the total pressure. The results are summarized in Table 3.

Discussion

$HCCl_3$ and HCF_2Cl systems

In the $HCCl_3$ and the HCF_2Cl systems the results could be explained through the following chain reaction mechanism.

$$Cl_2 + h\nu \longrightarrow 2Cl \quad (1)$$

$$HCX_2Cl + Cl \longrightarrow CX_2Cl + HCl \quad (2)$$

$$CX_2Cl + O_2 \longrightarrow CX_2ClO_2 \quad (3)$$

$$2CX_2ClO_2 \longrightarrow 2CX_2ClO + O_2 \quad (4a)$$

$$\longrightarrow (CX_2ClO)_2 + O_2 \quad (4b)$$

$$CX_2ClO \longrightarrow CX_2O + Cl \quad (5)$$

$$Cl + Cl + M \longrightarrow Cl_2 + M \quad (6)$$

This mechanism predicts that, if termination is exclusively by reaction (4b),

$$-\varphi\{HCX_2Cl\} = \varphi\{CX_2O\} = 2k_4/k_{4b} \quad \text{(III)}$$

However, if termination is exclusively by reaction (6), then

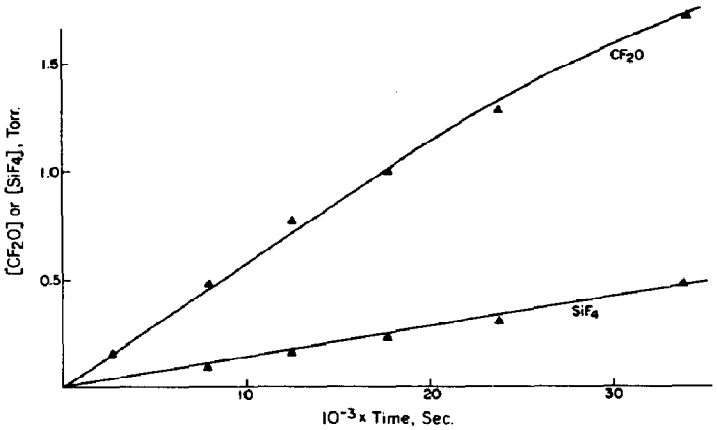

Fig. 4. Production of CF_2O and SiF_4 in the chlorine atom sensitized oxidation of HCF_3. The pressure data were modified to eliminate the effects of the heterogeneous decomposition of CF_2O. The symbol key is given in Table 3.

TABLE 3

The chlorine atom sensitized oxidation of HCF_3 at 30 ± 2 °C

Symbol[a] for Figs. 4 and 7	HCF_3 (Torr)	O_2 (Torr)	Cl_2 (Torr)	I_a[b] (10^3 Torr s^{-1})	$\varphi\{HCF_3\}$ × 10^2	$\varphi\{CF_2O\}$ × 10^2 [c]	$\varphi\{SiF_4\}$ × 10^2 [c]
○ ●	2.55	124.4	3.68	0.45	2.5	2.5	0.4
— ◐	3.70	3.21	3.90	0.48		6.0	
— ◆	4.70	29.2	3.76	0.46		6.1	(0.38)[d]
◧ ◨	8.34	123.0	3.76	0.46	5.1	5.2	(0.46)[d]
□ ■	9.50	127.0	3.61	0.44	6.8	5.7	1.3
— ▲	9.80	25.0	3.65	0.45		9.5	
○ ●	11.4	113.6	1.53	0.19	13.0	11.0	2.54
△ ▲	12.5	117.5	8.27	1.02	5.4	5.7	1.35
— ◑	21.0	123.0	3.76	0.46		11.7	(1.48)[d]

[a]Symbols for the consumption of HCF_3 and the production of CF_2O and SiF_4 respectively.
[b]Assuming quantum yield of C_2Cl_4 oxidation to be 300 at high O_2 pressure [5].
[c]Calculated from eqns. (I) and (II) respectively.
[d]The cell was not conditioned.

$$-\varphi\{HCX_2Cl\} = \varphi\{CX_2O\} = \frac{k_2}{k_6^{1/2}} \frac{[HCX_2Cl]}{(I_a[M])^{1/2}} \qquad \text{(IV)}$$

Equation (III) applies at high values of $[HCX_2Cl]/(I_a[M])^{1/2}$, whereas eqn. (IV) applies at low values of that parameter. Figures 5 and 6 are plots of $-\varphi\{HCX_2Cl\}$ or $\varphi\{CX_2O\}$ *versus* $[HCX_2Cl]/(I_a[M])^{1/2}$. The plots behave as predicted. At high $[HCX_2Cl]/(I_a[M])^{1/2}$ the quantum yields are constant, giving k_4/k_{4b} equal to 195 and 110 for $HCCl_3$ and HCF_2Cl respectively. At low $[HCX_2Cl]/(I_a[M])^{1/2}$ the quantum yields decrease as this parameter decreases. Since at intermediate values both termination reactions must operate simultaneously, the ratios $k_2/k_6^{1/2}$ were obtained at very low values of $[HCX_3]/(I_a[M])^{1/2}$. The ratios

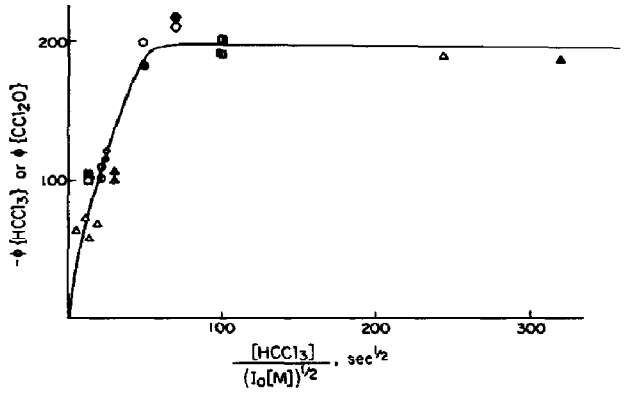

Fig. 5. Plot of $-\varphi\{HCCl_3\}$ or $\varphi\{CCl_2O\}$ *vs.* $[HCCl_3]/(I_a[M])^{1/2}$ for the $HCCl_3$ reaction. The symbol key is given in Table 2: △, points obtained at high conversion from the plots shown in Fig. 1 (or similar plots).

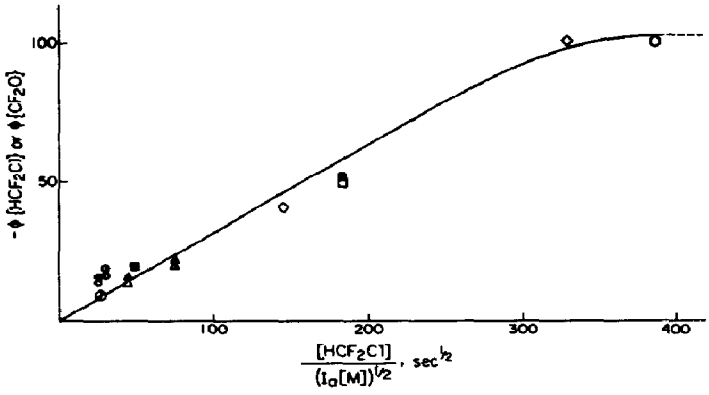

Fig. 6. Plot of $-\varphi\{HCF_2Cl\}$ or $\varphi\{CF_2O\}$ *vs.* $[HCF_2Cl]/(I_a[M])^{1/2}$ for the HCF_2Cl reaction. The symbol key is given in Table 2: ◇, points obtained at high conversion from the plots show in Fig. 2 (or similar plots).

obtained for $k_2/k_6^{1/2}$ were 100 $s^{-1/2}$ for $HCCl_3$ and 0.34 $s^{-1/2}$ for HCF_2Cl. These values are reasonable, and those corresponding to the $HCCl_3$ system agree perfectly with early values [9].

Assuming that in both systems we have similar conditions, especially the third body, and using the value of $k_2(HCCl_3) = 2.9 \times 10^{10}$ mol^{-1} cm^3 s^{-1} at 30 °C [9], we have

$$\frac{k_2(HCCl_3)}{k_2(HCF_2Cl)} = 294 \text{ and } k_2(HCF_2Cl) = 9.55 \times 10^7 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

The results and the rate coefficient ratios obtained in this study are summarized and compared with those for similar reactions in Table 4.

It is interesting to point out that the replacement of two hydrogen atoms in the HCH_2Cl molecule by two fluorine or two chlorine atoms (to produce HCF_2Cl or $HCCl_3$ molecules) involves the occurrence of a long chain in the oxidation process. Since long chains are related to the exothermicity of

TABLE 4

The chlorine atom sensitized oxidation of HCX_3 (X = Cl, F or H)

Methane	CX_3O	Oxidation products	$\varphi\{OX\}$ [a]	k_4/k_{4b}	$k_2/k_6^{1/2}$ ($s^{-1/2}$)	Ref.	log k_2 (mol^{-1} cm^3 s^{-1})
HCF_3	$F-CF_2O$	CF_2O and SiF_4	$\sim 10^{-1}$		1.6×10^{-3}	This work	6.23 [9]
	$H-CH_2O$ [b]	CH_3OH, CH_2O, CH_3COOH and CH_3OOCH_3	($\lesssim 1$) [b]			[10 - 12]	10.66 [9]
HCH_2Cl	$Cl-CH_2O$	CHClO [c]	2			[4]	11.16 [9]
$HCHCl_2$	Cl—CHClO	CHClO [c], CF_2O and CO	56	(5.9) [d]		[4]	11.28 [9]
HCF_2Cl	$Cl-CF_2O$	CF_2O	100	50	0.34	This work	7.98
$HCCl_3$	$Cl-CCl_2O$	CCl_2O	200	98	100	This work	10.46 [9]
	Cl—CFClO [e]	CFClO	f			[8]	

[a] $\varphi\{OX\} = -\varphi\{HCX_3\}$.
[b] The CH_3 radical was produced from the photolysis of the azomethane [10, 12] or ICH_3 [11].
[c] The CHClO is unstable and rapidly decomposes to CO and HCl.
[d] In this system the reaction k_{4b} does not exclusively lead to termination [4].
[e] The $CFCl_2$ radical was produced by the photolysis of $CFCl_3$. Each ClCFClO radical produces one CFClO molecule.
[f] The $HCCl_2F$ must oxidize in a long chain (see text).

halomethoxy radical dissociation [2, 7], the presence of the halogen atoms must produce a weakening in the Cl—CX_2O bond. From the values in Table 4 we can conclude that long chain oxidation occurs in the HCX_2Cl molecules when one of the X is a Cl or a F atom. Then it is possible to predict that $HCCl_2F$ must be oxidized in a long chain reaction having CFClO as the exclusive oxidation product [8].

HCF_3 system

The oxidation of the CF_3 radical has been studied by several authors [13, 14]. The CF_3 was obtained from the photolysis of CF_3Cl, CF_3Br or CF_3I. In all cases CF_2O, CO_2 and SiF_4 were found as products. However, the SiF_4 production was not computed quantitatively in any of these studies.

The simplest mechanism that can explain the result on the oxidation of the HCF_3 molecule (Table 3) is

$$Cl + HCF_3 \longrightarrow CF_3 + HCl \qquad (2')$$

$$CF_3 + O_2 \longrightarrow CF_3O_2 \qquad (3')$$

$$2CF_3O_2 \longrightarrow 2CF_3O + O_2 \qquad (4')$$

$$CF_3O + \text{wall} \longrightarrow CF_2O + \frac{1}{4}SiF_4 \qquad (7)$$

with reactions (1) and (6) as the initiation and the termination steps respectively. Since the quantum yields are low, reaction (2′) is much less important than reaction (6). The mechanism predicts that

$$[Cl] \approx (I_a/k_6[M])^{1/2}$$

and

$$-\varphi\{HCF_3\} \approx \varphi\{CF_2O\} \approx 4\varphi\{SiF_4\} \approx \frac{k_2}{k_6^{1/2}} \frac{[HCF_3]}{(I_a[M])^{1/2}}$$

Plots of the quantum yields (HCF_3, CF_2O or SiF_4) *versus* $[HCF_3]/(I_a[M])^{1/2}$ are shown in Fig. 7. The plots behave as predicted, and good straight lines

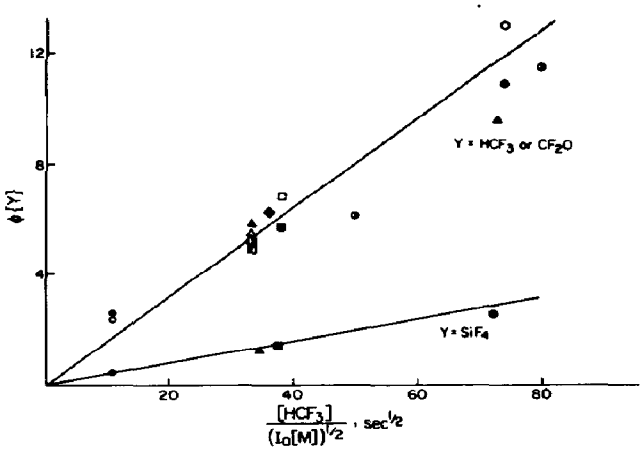

Fig. 7. Plot of $-\varphi\{HCF_3\}$ or $\varphi\{CF_2O\}$ or $\varphi\{SiF_4\}$ *vs.* $[HCF_3]/(I_a[M])^{1/2}$ for the HCF_3 reaction. The symbol key is given in Table 3.

are observed with $k_2/k_6^{1/2} = 1.6 \times 10^3\ s^{-1/2}$. Assuming that M is the same in the $HCCl_3$ and HCF_3 systems we have that, at 30 °C,

$$k_2(HCCl_3)/k_2(HCF_3) = 6 \times 10^4$$

This is in reasonable agreement with values obtained from the bibliography (2×10^4) [9].

There are two alternative schemes which also explain the previously mentioned experimental result that $\varphi\{CF_2O\}/\varphi\{SiF_4\}$ attains a value of 4 under varying conditions. These are

$$CF_3 + O_2 \longrightarrow CF_2O + FO$$

$$FO + \text{wall} \longrightarrow \tfrac{1}{4}\, SiF_4$$

and

$$CF_3O + Cl_2 \longrightarrow CF_2O + ClF + Cl$$

$$FCl + \text{wall} \longrightarrow \tfrac{1}{2}\, Cl_2 + \tfrac{1}{4}\, SiF_4$$

However, these two schemes are unlikely since both the FO radical and the ClF molecule are highly reactive, and possibly they could react with the other components of the gas mixture (*i.e.* HCF_3), and therefore could not yield a ratio of precisely 4:1 as is observed. However, little is known about reactions involving FO or ClF, and hence we cannot rule out these possibilities.

Acknowledgment

The author wishes to thank Dr. J. Heicklen for his useful comments.

References

1 M. J. Molina and F. S. Rowland, Nature (London), 249 (1974) 810.
2 E. Sanhueza, I. C. Hisatsune and J. Heicklen, The Oxidation of Haloethylenes, Center for Air Environment Studies, Pennsylvania State Univ. Rep. No. 387 - 75, 1975; Chem. Rev., 76 (1976) 801.
3 R. K. M. Jayanty, R. Simonaitis and J. Heicklen, J. Photochem., 4 (1975) 381.
4 E. Sanhueza and J. Heicklen, J. Phys. Chem., 79 (1975) 7.
5 E. Mathias, E. Sanhueza, I. C. Hisatsune and J. Heicklen, Can. J. Chem., 52 (1974) 3852.
6 J. Heicklen, Adv. Photochem., 7 (1969) 57.
7 L. Bertrand, L. Exsteen, J. A. Franklin, G. Huybrechts and J. Olbregts, Int. J. Chem. Kinet., 3 (1971) 89.
8 D. Marsh and J. Heicklen, J. Phys. Chem., 69 (1965) 4410.
9 V. N. Kondratiev, Rate Constants of Gas Phase Reaction, Office of Standard Reference Data, National Bureau of Standards (U.S.A.), 1972.
10 D. F. Dever and J. G. Calvert, J. Am. Chem. Soc., 84 (1962) 1362.
11 J. Heicklen and H. S. Johnston, J. Am. Chem. Soc., 84 (1962) 4030.
12 R. Shortridge and J. Heicklen, Can. J. Chem., 51 (1973) 2251.
13 W. C. Francis and R. N. Haszeldine, J. Chem. Soc., (1955) 2151.
14 J. Heicklen, J. Phys. Chem., 70 (1966) 112.