

**THE KINETICS OF THE PHOTOCHEMICAL REACTION BETWEEN TRIFLUOROMETHYLHYPOCHLORITE (CF<sub>3</sub>OCl) AND 1,1-DICHLORO-2,2-DIFLUOROETHYLENE (CF<sub>2</sub>CCl<sub>2</sub>)**

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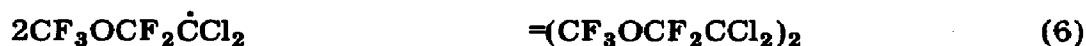
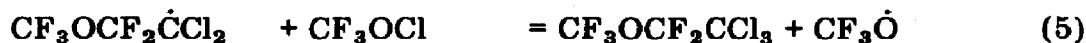
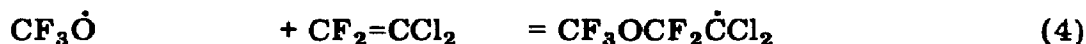
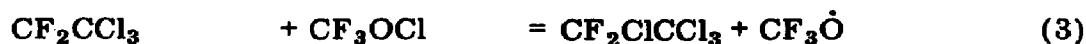
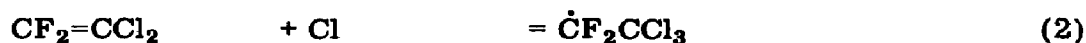
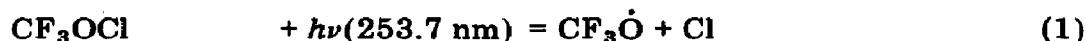
(Received April 6, 1978; in revised form October 16, 1978)

**Summary**

The photochemical reaction between CF<sub>3</sub>OCl and CF<sub>2</sub>CCl<sub>2</sub> has been investigated with light of wavelength 253.7 nm between 15 and 30 °C. The main product is CF<sub>3</sub>OCF<sub>2</sub>CCl<sub>3</sub>. Very small amounts of CF<sub>2</sub>ClCCl<sub>3</sub> and (CF<sub>3</sub>OCF<sub>2</sub>CCl<sub>2</sub>)<sub>2</sub> are also formed.

The reaction is a chain reaction. Its rate is proportional to the square root of the absorbed light and proportional to the CF<sub>3</sub>OCl pressure. Above a limiting pressure CF<sub>2</sub>CCl<sub>2</sub> and the total pressure have no influence.

The experimental results can be explained using the following mechanism:



$$\frac{dp}{dt} = -\frac{d[\text{CF}_3\text{OCl}]}{dt} = 2I_{\text{abs}} + k_5(2/k_6)^{1/2} I_{\text{abs}}^{1/2} [\text{CF}_3\text{OCl}]$$

The temperature coefficient of the rate constant  $k = k_5(2/k_6)^{1/2}$  is  $1.32 \pm 0.10$  for each 10 °C.  $E = E_5 - 1/2E_6$ , where  $E_6 \approx 0$  and  $E_5 = 5.0 \pm 1.5$  kcal.

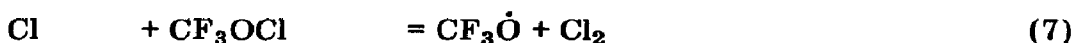
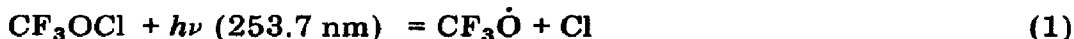
$$\Phi(-\text{CF}_3\text{OCl}) = 2 + k_5(2/k_6)^{1/2} [\text{CF}_3\text{OCl}] I_{\text{abs}}^{-1/2}$$

At 30 °C with 100 Torr CF<sub>3</sub>OCl and  $I_{\text{abs}} = 0.040$  Torr min<sup>-1</sup>

$$\Phi(-\text{CF}_3\text{OCl}) = 73 \text{ molecules photon}^{-1}$$

## 1. Introduction

From earlier research [1, 2] it is known that  $\text{CF}_3\text{OCl}$  absorbs light at 253.7 nm and dissociates into a  $\text{CF}_3\dot{\text{O}}$  radical and a Cl atom. If there are no other molecules present which can react with these species, then the peroxide  $\text{CF}_3\text{OOCF}_3$  and  $\text{Cl}_2$  are the only products. They are both formed with a quantum yield  $\Phi$  of 1.0 molecule photon<sup>-1</sup>:



In this paper the photochemical reaction between  $\text{CF}_3\text{OCl}$  and  $\text{CF}_2\text{CCl}_2$  at 253.7 nm will be treated. At this wavelength  $\text{CF}_2\text{CCl}_2$  does not absorb.

## 2. Experimental

### 2.1. Apparatus

Preliminary experiments showed that the reaction is accompanied by a decrease in pressure. It was therefore decided to follow the course of the reaction by pressure measurements at constant volume.

The apparatus used was of a conventional type as described previously [1]. A quartz cell with plane windows, 5 cm long by 5 cm diameter and a volume of 98.1 ml, served as a reaction vessel. A sensitive quartz spiral manometer was utilized as the zeroing instrument. Special metal valves were used instead of greased stopcocks. In order to be able to separate the reaction products by distillation a small U-tube was placed between the reaction cell and the valve which connected it to the pumping system. A Lauda thermostat maintained a constant temperature within  $\pm 0.05$  °C.

The light source was a low pressure mercury lamp model Hannovia 735 A-7. An optical system combined with a chlorine filter produced a well-defined homogeneous and approximately parallel light beam at 253.7 nm. The intensity  $I_0$  of the incident light was measured periodically with a potassium ferrioxalate actinometer [3] and the absorbed light was calculated using the value  $\epsilon = 40.74 \text{ l mol}^{-1} \text{ cm}^{-1}$  for the absorption coefficient of  $\text{CF}_3\text{OCl}$  [1].

### 2.2. Preparation and purification of the reactants

$\text{CF}_3\text{OCl}$  was prepared according to the method of Gould [4] by the reaction of FCl with  $\text{COF}_2$  in the presence of CsF as catalyst. It was purified through a low temperature distillation and the only traces of impurity to be found were of  $\text{COF}_2$ . It was then stored in a trap cooled with liquid air.

$\text{CF}_4$  and  $\text{O}_2$  were commercial products and were purified according to conventional methods and held in 3 l bulbs.

### 3. Results

In all experiments  $\text{CF}_3\text{OCl}$  was admitted first in the reaction cell followed by  $\text{CF}_2\text{CCl}_2$  and the inert gases. The reaction was monitored at frequent intervals until the end. If  $\text{CF}_3\text{OCl}$  was in excess then the total pressure decrease at the end of the reaction was equal to the initial ethylene pressure. The amount of  $\text{CF}_3\text{OCl}$  consumed, which was determined by pumping it off from the condensed products, was only slightly less than the amount of ethylene consumed. Apparently a small part of the ethylene (of the order of 1%) polymerized during the course of the reaction.

If the ethylene was in excess then for the same reason the total pressure decrease at the end of the reaction was somewhat higher (about 1%) than the initial pressure of the  $\text{CF}_3\text{OCl}$ .

$\text{CF}_3\text{OCl}$  alone is thermally stable. However, when the  $\text{CF}_2\text{CCl}_2$  entered it was observed that a small thermal reaction always occurred connected with a pressure decrease. Its rate was greater at high ethylene pressures but in comparison with the rate of the photochemical reaction it was generally very slow. It also decreased rapidly with the progress of the light reaction. This was proved by interrupting the light reaction from time to time and measuring the dark reaction which consisted of a heterogeneous polymerization of the ethylene.

After performing a certain number of experiments the velocity of the dark reaction increased strongly. When this happened it was observed that the walls of the reaction cell were covered with a thin colourless film. In these cases the cell was cut off and thoroughly cleaned. After this procedure the reaction then continued to follow its normal course.

The reaction products were identified from their IR spectra using a Perkin-Elmer spectrometer type 325. They were taken after the  $\text{CF}_3\text{OCl}$  had been eliminated by distillation from the reaction mixture. The following bands could be observed. 1307 (s), 1249 (vs), 1238 (vs), 1182 (m), 1143 (s), 1032 (vw), 950 (vw), 870 (m), 860 (m), 797 (m) and  $659\text{ cm}^{-1}$  (w).

Most of these bands, especially those of higher intensity, correspond to the 2,2,2-trichloro-1,1-difluoroethyl trifluoromethyl ether ( $\text{Cl}_3\text{CCF}_2\text{OCF}_3$ ) which according to the literature [5] shows absorption bands at 1304 (s), 1243 (vs), 1238 (vs), 1225 (s), 1181 (m), 1144 (s), 870 (m), 860 (w) and  $664\text{ cm}^{-1}$  (w).

This substance is without doubt the main product. The very weak bands at 1032 and  $950\text{ cm}^{-1}$  belong most probably to traces of  $\text{CF}_3\text{OCl}$  which had been retained by the products.

The bands of the other two products,  $(\text{CF}_3\text{OCF}_2\text{CCl}_3)_2$  and  $\text{CF}_2\text{ClCCl}_3$ , which according to the reaction mechanism are formed in relatively small quantities, are mostly overlapped by the bands of the main product. Only two bands of  $\text{CF}_2\text{ClCCl}_3$  [6] (at 855 (s) and 787 (s)  $\text{cm}^{-1}$ ) could be clearly observed.

Numerous experiments were performed at 14.9 and 30.0 °C. In these experiments the initial pressures of  $\text{CF}_3\text{OCl}$  were varied between 15 and 85

Torr and those of  $\text{CF}_2\text{CCl}_2$  between 16 and 220 Torr. Furthermore some experiments were made in the presence of the reaction products and of  $\text{CF}_4$  up to 320 Torr. The light intensity  $I_0$  was changed by a factor of 3.

The reproducibility of the experiments with the clean cells was very good. The experiments showed clearly that the rate of reaction is proportional to the  $\text{CF}_3\text{OCl}$  pressure and to the square root of the light intensity. The pressure of  $\text{CF}_2\text{CCl}_2$  above a limiting value of the order of 1 Torr or less as well as the pressure of inert gases and the reaction products had no influence on the course of the reaction:

$$-\frac{dp}{dt} = -\frac{d[\text{CF}_2\text{CCl}_2]}{dt} = kI_{\text{abs}}^{1/2} [\text{CF}_3\text{OCl}] \quad (\text{I})$$

Added oxygen changed the course of the reaction completely. In the presence of  $\text{O}_2$  the reaction began with a strong pressure increase but after a short time it almost ceased. This reaction was not further studied.

The experimental results are summarized in Tables 1 - 3 [7]. Tables 2 and 3 give details of two complete experiments to demonstrate how the reaction proceeded.

In Table 1  $T$  represents the temperature in degrees Celsius and  $\text{CF}_3\text{OCl}_1$ ,  $\text{CF}_2\text{CCl}_2$  and  $X$  the initial pressures of the corresponding gases in torr;  $k$  is the mean value of the rate constant in  $\text{l}^{1/2} \text{mol}^{-1/2} \text{s}^{-1/2}$  calculated according

TABLE 1

Rate constants of the photochemical reaction between  $\text{CF}_3\text{OCl}$  and  $\text{CF}_2\text{CCl}_2$

Number	$T$ (°C)	$\text{CF}_3\text{OCl}_1$ (Torr)	$\text{C}_2\text{F}_2\text{Cl}_2$ (Torr)	$X$ (Torr)	$I_0$ (Torr min <sup>-1</sup> )	$I_{\text{abs}_j}$ (% $I_0$ )	$k$ ( $\text{l}^{1/2} \text{mol}^{-1/2} \text{s}^{-1/2}$ )
5	30.0	61.4	81.6	—	0.067	79.6	2.77
6	30.0	63.5	78.3	—	0.022	81.7	2.45
7	30.0	33.5	86.0	—	0.067	57.9	2.61
9	30.0	60.2	33.5	—	0.067	79.3	2.52
11	30.0	27.9	50.0	28.2	0.067	50.9	2.70
				R. prod.			
12	30.0	43.6	29.6	—	0.044	68.4	2.59
13	30.0	41.9	47.8	304.5 ( $\text{CF}_4$ )	0.044	66.8	2.56
16	14.9	70.1	86.8	—	0.042	83.6	1.81
22	14.9	27.8	41.0	206.1 ( $\text{CF}_4$ )	0.042	50.6	1.57
23	14.9	30.8	178.6	—	0.033	54.4	1.76
24	14.9	30.8	221.0	—	0.033	54.4	1.63
26	14.9	31.3	42.4	—	0.031	55.2	1.91
27	14.9	32.6	44.0	—	0.031	56.5	1.61
28	14.9	33.4	40.5	—	0.010	57.5	1.73
29	14.9	85.8	88.6	—	0.031	89.0	1.68
30	14.9	15.6	16.7	—	0.031	33.6	1.71
31	14.9	90.7	39.2	—	0.031	90.5	1.71

$$k_{(14.9^\circ\text{C})} = 1.71 \pm 0.10 \text{ l}^{1/2} \text{mol}^{-1/2} \text{s}^{-1/2}; k_{(30^\circ\text{C})} = 2.61 \pm 0.15 \text{ l}^{1/2} \text{mol}^{-1/2} \text{s}^{-1/2}.$$

to eqn. (II);  $I_0$  is the intensity of the incident light expressed in Torr min<sup>-1</sup> and  $I_{abs}$  the absorbed light as a percentage of  $I_0$ .

TABLE 2

Details of run no. 12

$\Sigma\Delta t$ (min)	$\Sigma\Delta p$ (Torr)	CF <sub>3</sub> OCl (Torr)	C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub> (Torr)	$I_a$ (% $I_0$ )	$k$ (l <sup>1/2</sup> mol <sup>-1/2</sup> s <sup>-1/2</sup> )
0	0	43.6	29.6	Dark reaction	
20.0	2.5	41.1	27.1		
64.5	4.8	38.8	24.8		
0	4.8	38.8	24.8		
3.6	8.5	35.1	21.1	62.6	2.61
6.9	11.0	32.6	18.6	58.0	2.56
12.1	15.1	28.5	14.5	54.0	2.77
42.1	15.1	28.5	14.5	Dark reaction	
45.6	17.5	26.1	12.1	50.3	2.83
62.0	24.9	18.7	4.7	43.6	2.35
72.0	28.1	15.5	1.5	36.3	2.39

For conditions see Table 1.

$$\bar{k} = 2.59 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$$

TABLE 3

Details of run no. 22

$\Sigma\Delta t$ (min)	$\Sigma\Delta p$ Torr	CF <sub>3</sub> OCl Torr	C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub> Torr	$I_a$ (% $I_0$ )	$k$ (l <sup>1/2</sup> mol <sup>-1/2</sup> s <sup>-1/2</sup> )
0	0	27.8	41.0	Dark reaction	
33.0	1.0	26.8	40.0		
0	1.0	26.8	40.0		
5.5	3.2	24.6	37.8	48.0	1.71
12.5	5.4	22.4	35.6	45.0	1.47
19.5	7.5	20.3	33.5	42.5	1.59
27.5	9.6	18.2	31.4	39.2	1.63
36.5	11.8	16.0	29.2	36.3	1.71
62.5	11.8	16.0	29.2	Dark reaction	
73.5	14.0	13.8	27.0	34.0	1.67
85.5	15.8	12.0	25.2	30.0	1.56
103.5	18.0	9.8	23.0	25.6	1.54
159.3	22.3	5.5	18.7	18.0	1.65

For conditions see Table 1.

$$\bar{k} = 1.63 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$$

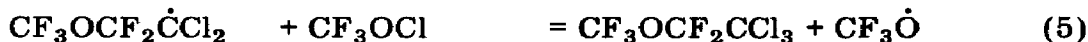
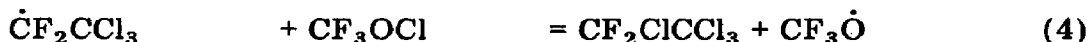
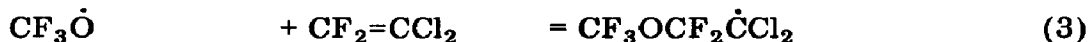
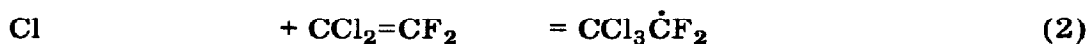
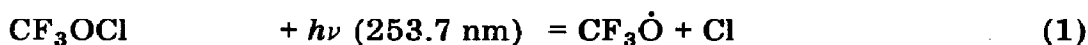
#### 4. Discussion

On the basis of the experimental rate equation and with the knowledge that in the primary process  $\text{CF}_3\text{O}$  radicals and Cl atoms are formed and that the final main product is  $\text{CF}_3\text{OCF}_2\text{CCl}_3$  it is easy to deduce the reaction mechanism.

The fact that the  $\text{CF}_2\text{CCl}_2$  pressure does not appear in the rate equation indicates that all primarily formed  $\text{CF}_3\text{O}$  radicals and Cl atoms will rapidly add to the olefin molecules forming the new radicals  $\text{CF}_2\text{Cl}\dot{\text{C}}\text{Cl}_2$  and  $\text{CF}_3\text{-OCF}_2\dot{\text{C}}\text{Cl}_2$  respectively. It has to be emphasized that the  $\text{CF}_3\text{O}$  radical adds only to the carbon atom of the olefin which is bound to the two F atoms.

The radicals then react with  $\text{CF}_3\text{OCl}$  molecules producing the stable molecules  $\text{CF}_2\text{ClCCl}_3$  and  $\text{CF}_3\text{OCF}_2\text{CCl}_3$  and at the same time regenerating  $\text{CF}_3\text{O}$  radicals. Consequently  $\text{CF}_3\dot{\text{O}}$  and  $\text{CF}_3\text{OCF}_2\dot{\text{C}}\text{Cl}_2$  must be considered to be the chain carriers,  $\text{CF}_3\text{OCF}_2\text{CCl}_3$  being the main reaction product.

The following reaction mechanism is obtained:



This mechanism leads to the rate equation

$$-\frac{d[\text{CF}_3\text{OCl}]}{dt} = 2I_{\text{abs}} + k_5 \left( \frac{2}{k_6} \right)^{1/2} [\text{CF}_3\text{OCl}] I_{\text{abs}}^{1/2} \quad (\text{II})$$

For a long chain length and with  $k = k_5(2/k_6)^{1/2}$  eqn. (II) is identical to the experimentally found eqn. (I).

The quantum yield for the consumption of  $\text{CF}_3\text{OCl}$  is

$$\Phi(-\text{CF}_3\text{OCl}) = 2 + k_5 \left( \frac{2}{k_6} \right)^{1/2} I_{\text{abs}}^{-1/2} [\text{CF}_3\text{OCl}]$$

whereas that for the formation of  $\text{CF}_3\text{OCF}_2\text{CCl}_3$  is

$$\Phi(\text{CF}_3\text{OCF}_2\text{CCl}_3) = k_5 \left( \frac{2}{k_6} \right)^{1/2} I_{\text{abs}}^{-1/2} [\text{CF}_3\text{OCl}]$$

This expression is identical with the chain length of the reaction.

At 30 °C and for a  $\text{CF}_3\text{OF}$  pressure of 100 Torr and  $I_{\text{abs}} = 0.40 \text{ Torr min}^{-1}$  a quantum yield  $\Phi(\text{CF}_3\text{OCF}_2\text{CCl}_3) = 73$  molecules per photon is ob-

tained.  $\text{CF}_3\text{ClCCl}_3$  and  $\text{CF}_3\text{OCF}_2\text{CCl}_2$  are both formed with a quantum yield of 1:

$$\Phi(\text{CFCl}_2\text{CCl}_3) = \Phi(\text{CF}_3\text{OCF}_2\text{CCl}_2)_2 = 1.0 \text{ molecules photon}^{-1}$$

From the temperature coefficient of  $k$  the apparent heat of activation can be calculated:  $E = E_5 - \frac{1}{2}E_6 = 5 \pm 1.5 \text{ kcal}$ ;  $E_6$  can be considered to be zero and so  $E_5 = 5 \pm 1.5 \text{ kcal}$ . This is a common value for such a reaction.

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