Photodecomposition of Halogenated Ketones

Part 1.—The Gas Phase Photolysis of 1,3-Dichlorotetrafluoroacetone

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Upon irradiation with light in the near ultra-violet region of the spectrum, 1,3-dichlorotetrafluoroacetone has been shown to decompose into a molecule of carbon monoxide and two chlorodifluoromethyl radicals. 1,2-Dichlorotetrafluoroethane is formed by radical combination and dichlorodifluoromethane by chlorine abstraction from the ketone, the latter process having an energy of activation of 3·5 kcal mole^{-1}. The chlorodifluoromethyl radicals are believed to disproportionate and form CF_2 which reacts further to yield 1,3-dichlorohexafluoropropane. There is a marked change in the ratio of these products when the wavelength of the light is changed from 3130 Å to 2537 Å.

In the photolysis of simple ketones containing only three carbon atoms, three distinct modes of breakdown have been observed. For acetone, there are two alternative modes of breakdown. At room temperature upon irradiation with light of wavelength *ca.* 3000 Å, both modes of breakdown have been detected. A single C—C bond may be ruptured with the formation of an acetyl radical [1] and a methyl radical

$$CH_3COCH_3 \xrightarrow{h\nu} CH_3\dot{C}O + \dot{C}H_3$$

or two C—C bonds may have been broken with the formation of two methyl radicals and a molecule of carbon monoxide,

$$CH_3COCH_3 \xrightarrow{h\nu} 2\dot{C}H_3 + CO.$$

At higher temperatures and shorter wavelengths the latter process appears to predominate.

The primary act in the photolysis of hexafluoroacetone was the production of two trifluoromethyl radicals and a molecule of carbon monoxide,[2]

$$CF_3COCF_3 \xrightarrow{h\nu} 2\dot{C}F_3 + CO.$$

The observed mass balance and the absence from the reaction products of any compounds which could arise from the reactions of the trifluoroacetyl radical suggests that its lifetime is too short for it to take part in combination reactions. The possibility that this radical intervenes in the photodecomposition of 1,1,1-trifluoroacetone is not ruled out by the studies of Sieger and Calvert and the greater preponderance of reaction products containing the CH_3 radical favours such a mechanism.[3]

With chloroacetone, an entirely different primary step is encountered. The carbon-halogen bond is broken with the formation of the acetonyl radical and a chlorine atom,

$$ClCH_2COCH_3 \rightarrow \dot{C}l + \dot{C}H_2COCH_3.$$

There was almost no evidence of products arising from the CH_2Cl radical.[4]

In highly halogenated ketones there is the possibility of any of these modes of breakdown occurring as the primary step of photolysis. The pyrolysis of 1,3-dichlorotetrafluoroacetone was studied by Woolf[5] and later by Patrick and Derbyshire.[6] They showed that chlorodifluoromethyl radicals were formed which combined to form dichlorotetrafluoroethane. In a preliminary study[7] the gas phase photolysis of 1,3-dichlorotetrafluoroacetone was shown to be a more complex process involving a number of side reactions. A later qualitative study has confirmed the original identification of the reaction products, but since unfiltered polychromatic light was used and the photolysis took place partly in the liquid and partly in the gas phase, a detailed comparison of results is not justified.[8]

The purpose of the present paper is to examine the photolysis of 1,3-dichlorotetrafluoroacetone in greater detail and to elucidate the primary mode of decomposition.

EXPERIMENTAL

MATERIALS

1,3-DICHLOROTETRAFLUOROACETONE was obtained from L. Light & Co. Ltd. and also from Kodak Ltd. No impurities could be detected by gas chromatography, mass spectrometry or n.m.r. spectroscopy but it was possible that the sample contained up to 3 % of the asymmetrical isomeric ketone.

DICHLORODIFLUOROMETHANE was obtained from the Imperial Chemical Industries Ltd., Widnes. It was purified by bulb-to-bulb distillation *in vacuo* (b.p. −41°C) and its purity checked by mass spectrometry.

1,2-DICHLOROTETRAFLUOROETHANE was obtained from Imperial Smelters Ltd. It was purified by bulb-to-bulb distillation (b.p. 4°C) and its purity checked by mass spectrometry.

APPARATUS

A conventional vacuum system is used to exhaust the cylindrical silica reaction cell (volume 30 ml) which is held in a furnace. The light from a medium-pressure mercury-vapour lamp (Phillips, 125 W, type H.P.K.) is focused by a quartz optical system and allowed to pass through a filter system consisting of a Chance 0X7 filter, 1 cm of potassium chromate solution (0·2 g/l.), 4 cm of nickel sulphate solution (440 g/l., $NiSO_4 . 7H_2O$) and 1 cm of potassium biphthalate solution (4 g/l.) in order to isolate the 3130 Å line. After traversing the reaction cell, the light falls upon a photocell (Rank-Cintel Q.V.A. 39) whose output is indicated upon a sensitive galvanometer. After photolysis, the reaction products are frozen into a U-tube by cooling with liquid air and the carbon monoxide is pumped by means of a small mercury-diffusion pump into a bulb where its pressure may be measured by means of a McLeod gauge. The remaining reaction products are then swept directly into a gas-chromatography apparatus with a stream of nitrogen. The columns used were 4 mm wide, 12 ft long, and packed with 30/60 mesh Johns-Manville C22 fire-brick (acid-washed) coated with 10 % w/w dinonyl phthalate. Detection was by means of a katharometer. Samples could be trapped in U-tubes cooled in liquid air as they emerged from the base of the column and transferred directly to an A.E.I. M.S.2 mass spectrometer for positive identification.

QUANTUM INPUT

The quantum input to the cell was measured using a potassium ferrioxalate actinometer and the method developed by Parker and Hatchard[9] in which the photoreduction is followed colorimetrically using 1 : 10 phenanthroline as reagent. The average of four determinations of the amount of light falling upon the front face of the cell was $1{\cdot}67 \times 10^{15}$ quanta/sec. In a similar manner the light emerging from the empty cell was found to be $0{\cdot}81 \times 10^{15}$ quanta/sec showing that approximately half of the light was absorbed or scattered by the cell. It was considered, therefore, that the true quantum input was that emerging from the first window into the cell and this was taken to be the average of the two values or 1·24 × 10^{15} quanta/sec. The relationship between the photocell output and the quantum input was investigated by measuring the optical density of a filter of known density, using both the actinometer and the photocell. The results for a filter of 47 % transmission were 47·1 % using the photocell and 48·6 % using the actinometer. These results showed that it was permissible to calculate the quantum yields of products using the photocell to determine the quantum input. The light output of the lamp was kept steady by the use of a constant-voltage transformer.

CALIBRATION OF THE GAS-CHROMATOGRAPHY APPARATUS

The gas-chromatography apparatus was calibrated by admitting known pressures of the sample to a bulb of known volume and transferring the sample to the U-tube by freezing it in liquid air. The sample was then swept into the apparatus with nitrogen and the area under the peak drawn by the recorder measured. A graph of peak area against pressure was plotted. When determining the concentration of the sample in the reaction products it was necessary to refer to the calibrating graphs.

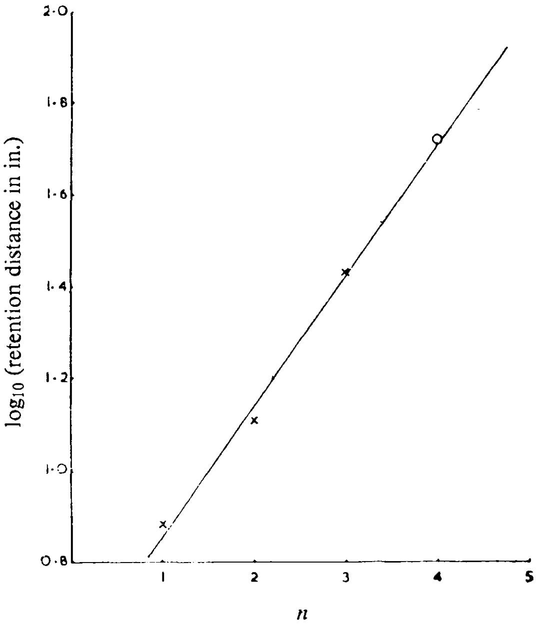

FIG. 1.—Retention volumes of halogenated alkanes.

× points for compounds of type $(CF_2)_nCl_2$,

○ unknown

ANALYSIS OF PRODUCTS

A sample of the ketone was photolyzed to a high conversion and the products separated upon the gas-chromatography apparatus. As each peak appeared on the recorder, the constituent emerging from the base of the gas-chromatography column was trapped in a U-tube cooled with liquid air and transferred to the mass spectrometer. Identification was made by comparison of the mass spectrum and retention volume of the constituent with those of authentic samples. A typical analysis is presented in table 1.

TABLE 1

constituent	yield × 10^{-6} moles
carbon monoxide	11·8
dichlorodifluoromethane	0·51
1,2-dichlorotetrafluoroethane	8·45
1,3-dichlorohexafluoropropane	0·34

An authentic sample of 1,3-dichlorohexafluoropropane was not available. The mass spectrum, however, suggested the formula $C_3F_6Cl_2$ and the logarithm of its retention volume fell upon a straight line made by plotting the retention volume of CF_2Cl_2 and $C_2F_4Cl_2$ against carbon number (fig. 1), a method of identification first suggested by Evans and Smith.[10] If the photolysis products were examined directly on the mass spectrometer, then in addition to mass peaks corresponding to the parent ketone and the three products already listed, there were small mass peaks suggesting the presence of 1, 4-dichloro-octafluorobutane and 1,4-dichlorohexafluoromethylethylketone.

CALCULATION OF QUANTUM YIELDS

Fig. 2 and 3 show the ultra-violet absorption spectrum and the variation of optical density with concentration. It can be seen that the ketone has a very high molar extinction coefficient but that Beer's law is obeyed over the range of concentrations studied. However, as a result of the high molar extinction coefficient, at 3130 Å the light was non-

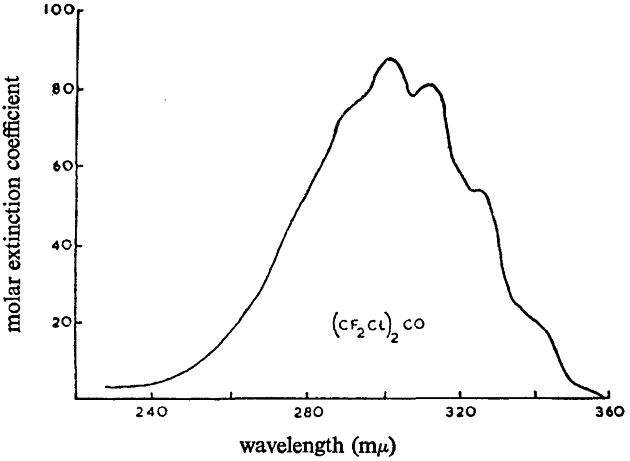

FIG. 2.—Absorption spectrum of 1,3-dichlorotetrafluoroacetone.

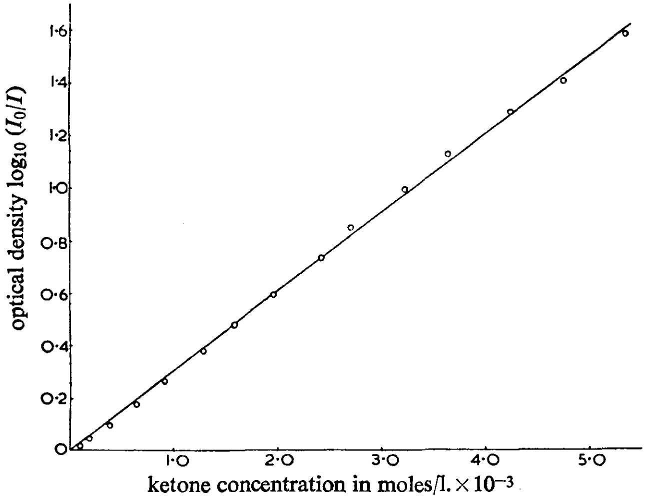

FIG. 3.—Variation in optical density with concentration of 1,3-dichlorotetrafluoroacetone.

uniformly absorbed along the length of the cell. Above 100 mm pressure of 1,3-dichlorotetrafluoroacetone, absorption was almost complete across the length of the cell. The treatment adopted to overcome this difficulty is due to Noyes.[11] If the light absorbed in an elementary layer of the ketone of thickness dl and distance l from the front face of the cell, is dI quanta/sec cm^2, then

$$\mathrm{d}I = I_0 a(c) \exp(-acl)\mathrm{d}l \text{ (assuming Beer's Law),}$$

where I_0 is the number of quanta/cm^2 sec leaving the inner front face of the cell.

Then the light absorbed in quanta/ml sec is

$$\mathrm{d}I/\mathrm{d}t = I' = I_0 a(c) \exp(-acl).$$

Integrating over the whole length L of the cell, the total mean number of quanta absorbed I_a is

$$I_a = \frac{1}{L}\int_0^L I'\mathrm{d}l = I_0[1-\exp(-acL)]/L \text{ quanta/ml sec.}$$

Considering the quantum yield Φ of a species X in an elementary section of the cell dl,

$$\Phi = \frac{\mathrm{d}X}{\mathrm{d}t}\frac{I}{I'},$$

where dX/dt is the local rate of appearance of X. This differs from the experimentally determined quantum yield which is

$$\Phi_{\text{expt.}} = \left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)_{\text{av}} \frac{I}{\int_0^L I'\mathrm{d}l}$$

$$\Phi_{\text{expt.}} = \frac{\text{net rate of formation of } X \text{ in molecules/ml sec}}{I_a \text{ in quanta/ml sec}},$$

where $I_a = I_0[1-\exp(-acL)]/L$.

This equation is used to calculate Φ in the experimental results described below.

RESULTS AND DISCUSSION

EFFECT OF IRRADIATION TIME ON QUANTUM YIELD AND MASS BALANCE

Fig. 4 shows the variation of product yield with irradiation time. It can be seen that the yield increases linearly with time and there is no perceptible decrease up to an irradiation time of 120 min corresponding to a conversion of 7 %. The quantum input was about $7{\cdot}0 \times 10^{13}$ quanta/ml sec and the slight variation in yield indicated at one point on the graph is due to a decrease in this input.

Tables 2 and 3 present the quantum yields of the products of reaction. The average quantum yield of CO is 0·8 and the average sum of the quantum yields of the other products (CF_2Cl_2, $C_2F_4Cl_2$, $C_3F_6Cl_2$) is 0·6 so that there is a difference of 25 % due to the formation of compounds too involatile to be studied with the present analytical procedure. The nature of the compounds responsible for the mass deficiency is undetermined. Although 1,4-dichlorooctafluorobutane and 1,4-dichlorohexafluoromethylethylketone have been detected in high-conversion photolysis, mass spectrometrically they were not present in sufficient concentration to explain the mass deficiency. Further, the retention volume of 1,4-dichlorooctafluorobutane can be predicted from the logarithm plot of the retention volume given in fig. 2. The calculated retention volume was sufficiently small to enable the presence of the butane to be detected with the analytical procedure described.

1,3-Dichlorotetrafluoroacetone was strongly adsorbed upon all varieties of firebrick used as the support for the stationary phase (acid-washed, acid- and alkali-washed and siliconized) so that it would be logical to assume that high-boiling oxygenated products would also be so adsorbed. However, the ratio of the carbon monoxide to CF_2Cl radicals in the product would have to be lower than in the original ketone in order to explain the apparent loss of CF_2Cl radicals. It has been suggested [3] that radicals can add to the C=O double bond in ketones and the combination products of such a reaction would have a composition in which the CO/CF_2Cl ratio was low, but at present there is no evidence for the existence of such products.

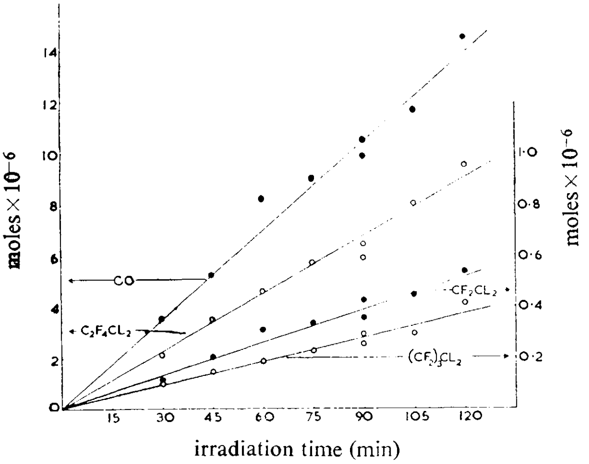

FIG. 4.—Variation in product yield with irradiation time.

TABLE 2.—VARIATION I_a AND KETONE CONCENTRATION AT ROOM TEMPERATURE (approx. 20°C)

run	irradn. time, min	I_a × 10^{13} quanta/ml sec	[ketone] × 10^{-3} mole/l.	CO		CF_2Cl_2		$C_2F_4Cl_2$		$(CF_2)_3Cl_2$		$\Sigma\Phi \frac{CF_2Cl}{2}$
				× 10^{-6} mole	Φ	× 10^{-7} mole	Φ	× 10^{-6} mole	Φ	× 10^{-7} mole	Φ	
1	120	4·84	5·56	11·62	0·86	4·54	0·034	7·24	0·53	3·18	0·024	0·58
2	120	3·44	5·48	8·34	0·87	3·31	0·034	5·19	0·54	2·10	0·022	0·59
3	120	2·90	5·43	6·34	0·78	2·24	0·028	3·84	0·47	1·55	0·019	0·51
4	120	2·40	5·42	5·75	0·86	2·12	0·032	3·30	0·49	1·56	0·023	0·54
5	60	5·11	9·73	6·02	0·84	2·06	0·029	3·83	0·54	1·37	0·019	0·57
6	60	5·09	7·65	6·10	0·86	1·73	0·024	3·46	0·49	1·16	0·016	0·53
7	60	5·56	5·50	6·06	0·78	2·20	0·028	3·96	0·51	1·38	0·018	0·55
8	120	5·42	4·36	11·80	0·78	5·12	0·034	8·45	0·56	3·42	0·023	0·61
9	60	5·32	4·43	6·15	0·83	2·77	0·027	3·98	0·53	2·06	0·028	0·58
10	60	4·80	3·27	5·65	0·84	2·03	0·030	3·56	0·53	1·20	0·018	0·57
11	60	3·56	2·14	4·08	0·82	1·33	0·027	2·74	0·55	0·94	0·019	0·59
12	60	1·22	0·93	1·43	0·84	0·54	0·032	0·91	0·53	0·24	0·014	0·57

TABLE 3.—VARIATION OF KETONE CONCENTRATION AT CONSTANT I_a

run	irradn. time, min	I_a × 10^{13} quanta/ml sec	[ketone] × 10^{-3} mole/l	CO		CF_2Cl_2		$C_2F_4Cl_2$		$(CF_2)_3Cl_2$		$\Sigma\Phi \frac{CF_2Cl}{2}$
				× 10^{-6} mole	Φ	× 10^{-7} mole	Φ	× 10^{-6} mole	Φ	× 10^{-7} mole	Φ	
2	120	3·44	5·48	8·34	0·87	3·31	0·034	5·19	0·54	2·10	0·022	0·59
11	60	3·56	2·14	4·08	0·82	1·33	0·027	2·74	0·55	0·94	0·019	0·59
13	50	3·98	1·92	3·44	0·74	2·00	0·043	3·21	0·69	1·06	0·024	0·75
14	50	3·91	1·86	4·00	0·88	2·26	0·049	2·98	0·65	1·58	0·035	0·73
15	75	3·90	9·59	5·41	0·79	3·36	0·049	4·50	0·66	2·61	0·038	0·74

Small quantities of volatile white solid collect in the U-trap after a number of runs have been carried out. This has also been observed in the pyrolysis [6] and flash photolysis [12] of 1,3-dichlorotetrafluoroacetone. It has not been positively identified but may be a polymer of CF_2 produced in a secondary reaction.

VARIATION OF QUANTUM YIELD WITH LIGHT INTENSITY

Table 2 presents the results of photolyses carried out at constant pressure and varying light intensity. It can be seen that the quantum yield is almost independent of light intensity and total yield of products increases linearly with increase in light intensity.

VARIATION OF QUANTUM YIELD WITH KETONE PRESSURE

Table 3 presents the results of photolyses carried out with varying ketone pressure and constant light intensity. There is no marked effect upon the quantum yield of CO with pressure but the quantum yield of radical products is increased.

VARIATION OF QUANTUM YIELD WITH TEMPERATURE

Table 4 presents the results of photolyses carried out at constant ketone pressure and I_a at varying temperatures up to 180°C. Fig. 5 gives a plot of the quantum yields of the photolysis products against temperature. While the quantum yields of CO and the 1,3-dichlorohexafluoropropane fall slightly with increase of temperature and the quantum yield of 1,2-dichlorotetrafluoroethane falls more rapidly, the quantum yield of the dichlorodifluoromethane rises. There appears to be no definite increase in mass balance-deficiency with rise in temperature as was noticed with acetone [13] and trifluoroacetone.[3]

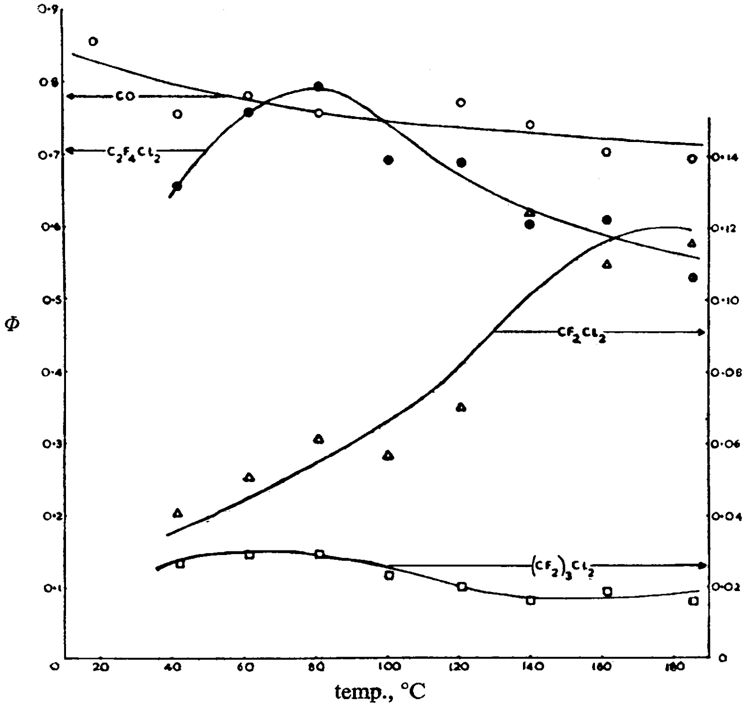

FIG. 5.—Variation in quantum yield with temperature.

TABLE 4.—TEMPERATURE VARIATION

run	temp., °C	I_a $\times 10^{13}$ quanta/ml sec	[ketone] $\times 10^{-3}$ mole/l.	CO		CF_2Cl_2		$C_2F_4Cl_2$		$(CF_2)_3Cl_2$		$\Sigma\Phi\ \frac{CF_2Cl}{2}$
				$\times 10^{-6}$ mole	Φ	$\times 10^{-7}$ mole	Φ	$\times 10^{-6}$ mole	Φ	$\times 10^{-7}$ mole	Φ	
16	41·9	4·58	6·65	4·85	0·76	2·62	0·041	4·21	0·66	1·73	0·027	0·72
17	61·4	4·45	5·75	4·85	0·78	3·12	0·050	4·72	0·76	1·80	0·029	0·83
18	81·0	4·71	5·40	4·99	0·76	4·04	0·061	5·23	0·79	1·92	0·029	0·86
19	100·4	4·66	7·54	—	—	3·70	0·057	4·52	0·69	1·52	0·023	—
20	120·6	4·51	5·56	4·88	0·77	4·42	0·070	4·35	0·69	1·27	0·020	0·75
21	140·0	4·34	5·10	4·51	0·74	7·50	0·124	3·66	0·60	1·00	0·017	0·69
22	161·4	4·41	6·03	3·79	0·71	5·86	0·110	3·28	0·61	1·01	0·019	0·69
23	185·4	4·12	5·62	4·09	0·70	6·78	0·116	3·12	0·53	0·94	0·016	0·61

Time of irradiation all runs = 60 min, except 22 (52 min) and 23 (61 min).

EFFECT OF WAVELENGTH AND OF SULPHUR HEXAFLUORIDE ADDITION

Table 5 summarizes the results obtained by varying the wavelength of the light and of adding sulphur hexafluoride. When the mercury lamp was replaced by a zinc resonance lamp (Osram Zn Spectral lamp), whose emission contained, in addition to the resonance line at 3070 Å, a group of three lines in the 3300 Å region, no marked difference was observed in the $CF_2Cl_2/C_2F_4Cl_2$ ratio. This is not unexpected in view of the small wavelength interval (60 Å) and so no quantum yields were measured. When, however, the medium-pressure mercury lamp was replaced by a low-pressure lamp emitting a strong resonance line at 2537 Å there was a large increase in the $CF_2Cl_2/C_2F_4Cl_2$ ratio while the yield of the 1,3-dichlorohexafluoropropane became vanishingly small. On adding an equal amount of sulphur hexafluoride the quantum yields of the radical products fell while the $CF_2Cl_2/C_2F_4Cl_2$ ratio rose slightly. This contrasts with the behaviour at a wavelength of 3130 Å when a four-fold excess of sulphur hexafluoride gave no change in the $CF_2Cl_2/C_2F_4Cl_2$ ratio or the quantum yields.

TABLE 5.—VARIATION OF WAVELENGTH

run	irradn. time, min	I_a $\times 10^{13}$ quanta/ml sec	[ketone] $\times 10^{-3}$ mole/l.	wave-length, Å	CO		CF_2Cl_2		$C_2F_4Cl_2$		$(CF_2)_3Cl_2$		$\Sigma\Phi\ \frac{CF_2Cl}{2}$
					$\times 10^{-6}$ mole	Φ	$\times 10^{-7}$ mole	Φ	$\times 10^{-6}$ mole	Φ	$\times 10^{-7}$ mole	Φ	
13	50	3·98	1·92	3130	3·44	0·74	2·00	0·043	3·21	0·69	1·06	0·024	0·75
*14	50	3·91	1·86	3130	4·00	0·88	2·26	0·049	2·98	0·65	1·58	0·035	0·73
25	180	0·91	5·5	2537	3·42	0·90	23·67	0·62	1·05	0·27	v. small	—	0·58
†26	180	0·975	5·5	2537	3·64	0·89	21·96	0·54	0·81	0·20	v. small	—	0·47

* contains 15·4 cm SF_6; † contains 9·0 cm SF_6.

THE PRIMARY STEP

If the possibility of molecular elimination of carbon monoxide is rejected, then the primary step in the photolysis of 1,3-dichlorotetrafluoroacetone may be expressed by any of the following equations:

$$ClCF_2COCF_2Cl \xrightarrow{h\nu} \dot{C}F_2Cl + \dot{C}OCF_2Cl, \tag{1}$$

$$ClCF_2COCF_2Cl \xrightarrow{h\nu} 2\dot{C}F_2Cl + CO, \tag{2}$$

$$ClCF_2COCF_2Cl \xrightarrow{h\nu} \dot{C}F_2COCF_2Cl + \dot{C}l. \tag{3}$$

With the present analytical system, no products which would arise by secondary reactions of the CF_2ClCO radical have been identified. The similarity between photolysis and electron impact has frequently been stressed and it may be significant that while the CH_3CO^+ ion is responsible for the most intense peak in the mass spectrum of acetone, the mass peak due to CF_2ClCO^+ in the mass spectrum of 1,3-dichlorotetrafluoroacetone is negligible. Further, the quantum yield of CO does not rise with temperature as with acetone where the acetyl radical initially formed decomposes at higher temperatures. The most probable primary step is therefore (2), since (3) does not give rise to CF_2Cl radicals and therefore cannot be responsible for the appearance of 1,2-dichlorotetrafluoroethane in the reaction products.

The quantum yield for CO is never unity and so it is probable that the photolysis involves the initial formation of an excited molecule with an appreciable lifetime and capable of collisional deactivation. No fluorescence studies have been made to confirm this possibility. On the other hand, no marked variation of CO quantum yield with ketone pressure was noted over the limited range of pressure studied. The CO quantum yields from 1,3-dichlorotetrafluoroacetone are much higher than those observed for hexafluoroacetone at the same pressure, so it must be assumed that any excited molecule has a correspondingly shorter lifetime.

The primary step in photolysis at 2537 Å (low-pressure mercury arc) may differ from that at 3130 Å for there is a big difference in the $\Phi\ CF_2Cl_2/\Phi\ C_2F_4Cl_2$ ratio. This is only 0·05 at 3130 Å but rises to 1·9 at 2537 Å. The interpretation of this unexpected difference in behaviour is difficult. If the primary step (2) is still the predominant mode of breakdown then the concentration of CF_2Cl must be reduced by some secondary process, either abstraction or disproportionation, which would lead to the formation of dichlorodifluoromethane. An alternative possibility is that the carbon-chlorine bond is broken preferentially at this wavelength as in process (3) with the secondary production of dichlorodifluoromethane by combination of the chlorine atoms with CF_2Cl radicals produced in process (2). Such a primary step might be assisted by mercury photosensitization.

$$^3P_1Hg + ClCF_2COCF_2Cl \rightarrow \dot{H}gCl + \dot{C}F_2COCF_2Cl, \qquad (4)$$

but a high $CF_2Cl_2/C_2F_4Cl_2$ ratio is observed in the flash photolysis of 1,3-dichlorotetrafluoroacetone and the presence of chlorine atoms may be demonstrated by the addition of oxygen when the characteristic absorption of ClO appears.[12]

SECONDARY REACTIONS

Secondary reactions of the radicals formed in the primary step lead to the formation of CF_2Cl_2, $C_2F_4Cl_2$, $C_3F_6Cl_2$, $C_4F_8Cl_2$ and possibly other involatile unidentified products. The 1,2-dichlorotetrafluoroethane must arise by the combination of two CF_2Cl radicals,

$$2\dot{C}F_2Cl \rightarrow CF_2ClCF_2Cl, \qquad k_3 \qquad (5)$$

and its rate of formation should be directly proportional to I_a. Fig. 6 shows a plot of the rate of formation of 1,2-dichlorotetrafluoroethane against I_a and it can be seen that a linear relationship exists. The figure also shows that the rate of formation of CO is also proportional to I_a. It can also be shown by plotting the logarithm of the rate of formation of these products against the logarithm of I_a that the intensity exponent for both CO and $C_2F_4Cl_2$ is unity (fig. 7). The dichlorodifluoromethane which appears in the products of photolysis may be formed in three ways. Two chlorodifluoromethyl radicals formed in the primary step may disproportionate with the formation of a diradical,

$$2CF_2Cl \rightarrow CF_2 + CF_2Cl_2. \qquad (6)$$

A chlorodifluoromethyl radical may abstract a chlorine atom from the parent ketone with the formation of a chlorotetrafluoroacetonyl radical,

$$\dot{C}F_2Cl + ClCF_2COCF_2Cl \rightarrow CF_2Cl_2 + \dot{C}F_2COCF_2Cl. \quad k_2 \qquad (7)$$

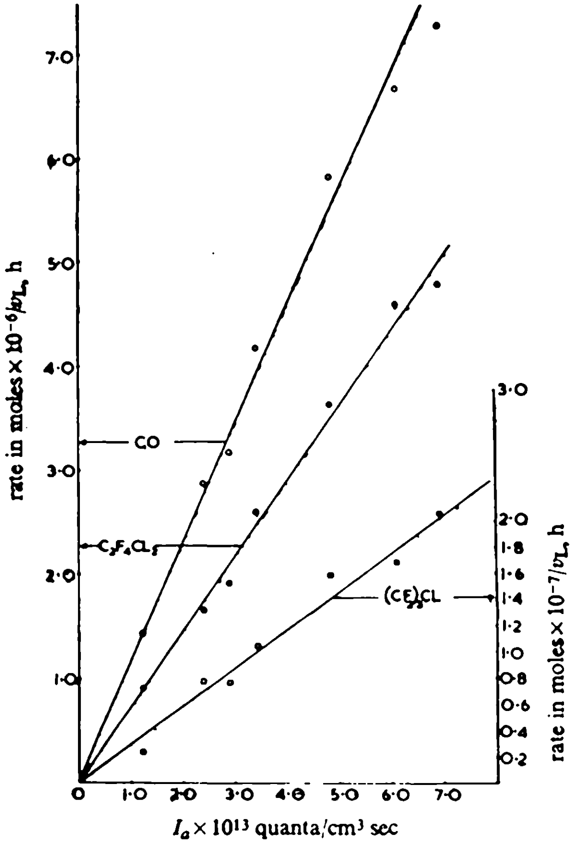

FIG. 6.—Variation in rate of formation of products with intensity of illumination.

The products of two competing primary steps may interact

$$CF_2ClCOCF_2Cl \begin{cases} \nearrow 2\dot{C}F_2Cl + CO \\ \searrow \dot{C}l + \dot{C}F_2COCF_2Cl \end{cases}$$

$$\dot{C}F_2Cl + \dot{C}l \rightarrow CF_2Cl_2. \qquad (8)$$

If there were uniform light absorption throughout the cell the $d[CF_2Cl]/dt$ would be proportional to I_a, $I_a^{\frac{1}{2}}$ and $I_a^{3/2}$ for the three cases. However, the non-uniform absorption makes it necessary to consider the rates of formation in the elementary sections and integration leads to expressions involving such terms as

$$\frac{2I_0}{La^{\frac{1}{2}}c^{\frac{1}{2}}}[1-\exp(-acL/2)].$$

Despite this complexity, the treatment used by Noyes [11] to demonstrate hydrogen abstraction in acetone photolysis may be applied. The ratio of the quantum yields

$$\frac{\Phi CF_2Cl_2}{\Phi C_2F_4Cl_2^{\frac{1}{2}}} = \frac{1}{I_a^{\frac{1}{2}}}\,\frac{[d[CF_2Cl_2]/dt]_{\text{average}}}{[d[C_2F_4Cl_2]/dt]^{\frac{1}{2}}_{\text{average}}}$$

but the absolute rate ratio,

$$\frac{d[CF_2Cl_2]/dt}{[d[C_2F_4Cl_2]/dt]^{\frac{1}{2}}} = \frac{k_2[\text{ketone}][CF_2Cl]}{k_3^{\frac{1}{2}}[CF_2Cl]} = \frac{k_2}{k_3^{\frac{1}{2}}}[\text{ketone}]$$

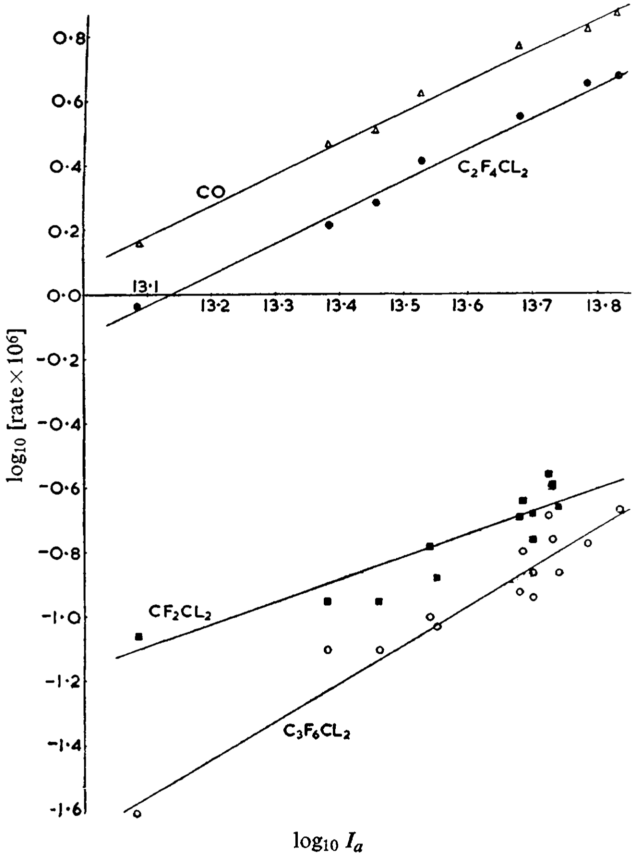

FIG. 7.—Intensity exponent for the products of photolysis of 1,3-dichlorotetrafluoroacetone.

is independent of both light intensity and radical concentration so that a plot of the quantum yield ratio $\Phi CF_2Cl_2/\Phi C_2F_4Cl_2^{\frac{1}{2}}$ against the function $[\text{ketone}]/I_a^{\frac{1}{2}}$ should be a straight line passing through the origin if the sole source of dichlorodifluoromethane is abstraction from 1,3-dichlorotetrafluoroacetone. Fig. 8 presents such a plot and demonstrates that no linear relationship exists between these quantities. However, the increase in the amount of dichlorodifluoromethane formed with rise in temperature suggests that some abstraction is taking place so that there are at least two processes by which the dichlorodifluoromethane is formed. For the two alternative mechanisms proposed, the net rate of formation of dichlorodifluoromethane will be independent of the ketone concentration and proportional to I_a.

Fig. 9 shows a plot of the net rate of formation of dichlorodifluoromethane against I_a with variation in both the ketone concentration and light intensity. The points indicate a linear relationship but do not provide any measure of distinguishing between the alternative mechanisms.

The disproportionation of methyl radicals has not been reported and it has been claimed that trifluoromethyl radicals definitely do not disproportionate to form CF_4. However, tetrafluoroethylene has been shown to occur in the mercury-photosensitized decomposition of dichlorodifluoromethane and this is assumed to be due to the dimerization of CF_2 radicals formed by disproportionation of CF_2Cl radicals.[14]

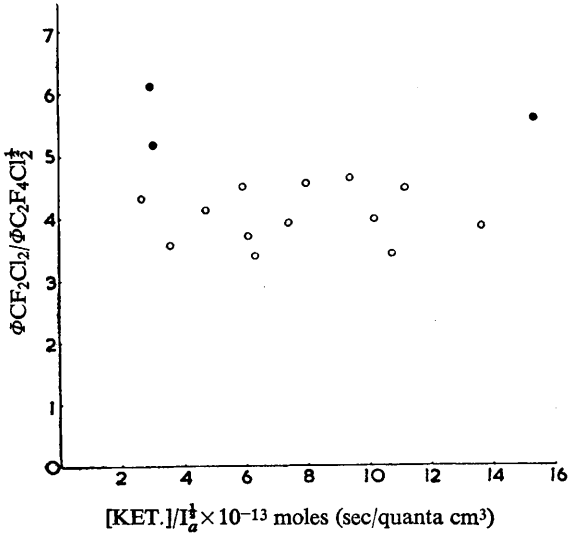

FIG. 8.—Quantum yield function against $[KET.]/I_a^{\frac{1}{2}}$ (room temperature).

At present the precise effect of wavelength upon the production of dichlorodifluoromethane has not been investigated in any detail but it would appear that the shorter wavelengths promote its formation. Under the conditions of flash photolysis the yield is increased and, upon irradiation with light of wavelength 2537 Å, it becomes the major product. Both abstraction and disproportionation would be favoured by the increased energy input at shorter wavelengths but the decomposition at 2537 Å may be mercury-photosensitized and involve an alternative primary step.

The rate of formation of dichlorodifluoromethane rises with increase in temperature and this suggests that it arises by a process involving an energy of activation such as abstraction. While the process of hydrogen abstraction has been studied extensively,[15] chlorine abstraction in the gas phase has only been observed for a few reactions such as the attack of methyl radicals on chloroacetone [4] or the attack of methylene upon carbon tetrachloride.[16]* In the liquid phase, chlorine abstraction by methyl radicals [17] and by the larger polymer radicals has been shown to take place. No energy of activation for this process has been suggested but by analogy with hydrogen abstraction, values within the range 3-10 kcal/mole could be anticipated.

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* Since this paper was submitted, Evans and Szwarc have published a detailed study of halogen abstraction by methyl radicals (*Trans. Faraday Soc.*, 1961, 57, 1915).

In fig. 10, log [rate CF_2Cl_2/([rate $C_2F_4Cl_2]^{\frac{1}{2}}[CF_2ClCOCF_2Cl]$)] is plotted against the reciprocal of the absolute temperature $1/T$. The shape of the best straight line which can be drawn through the points corresponds to a value of $E_2-\frac{1}{2}E_1 = 3$ kcal/mole, but as there are two processes involved in the formation of dichlorodifluoromethane it is more likely that the graph is curved and that only the points at the higher temperatures are acceptable. The straight line through the upper part of the graph gives a value of 5 kcal for the energy difference. Further studies at temperatures between 200° and 300°C are required before it is possible to make a more accurate estimate of $E_2-\frac{1}{2}E_1$.

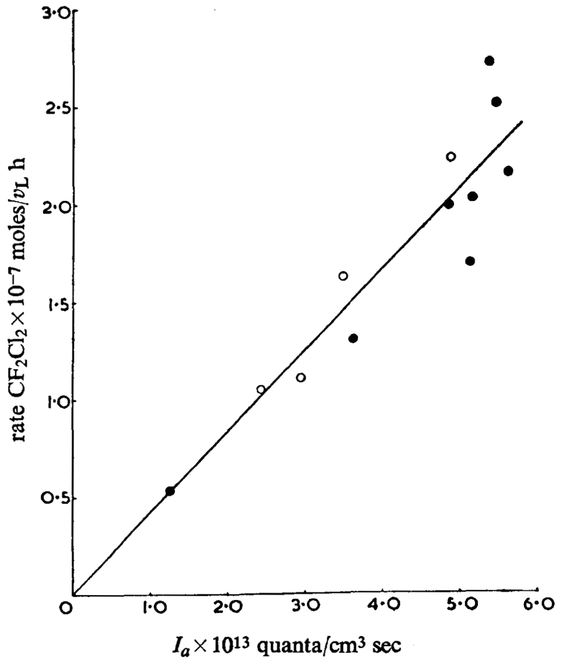

FIG. 9.—Variation in rate of formation of CF_2Cl_2 with intensity of illumination.
○ = runs I_a varied, [KET.] constant; ● = runs [KET.] varied

1,3-DICHLOROHEXAFLUOROPROPANE

In the original analytical study of the products of photolysis of 1,3-dichlorotetrafluoroacetone [7] it was suggested that the 1,3-dichlorohexafluoropropane could arise by the combination of chlorodifluoromethyl and chlorotetrafluoroethyl radicals formed by the following sequence of reactions:

$$\dot{C}F_2Cl + CF_2ClCOCF_2Cl \rightarrow CF_2Cl_2 + \dot{C}F_2COCF_2Cl$$

$$\dot{C}F_2Cl + CF_2COCF_2Cl \rightarrow CF_2ClCOCF_2CF_2Cl \qquad (9)$$

$$CF_2ClCOCF_2CF_2Cl \xrightarrow{h\nu} CF_2Cl + CO + \dot{C}F_2CF_2Cl \qquad (10)$$

$$\dot{C}F_2Cl + \dot{C}F_2CF_2Cl \rightarrow ClCF_2CF_2CF_2Cl. \qquad (11)$$

This suggestion was repeated by Haszeldine [4] but the present quantitative investigation reveals that it is most unlikely that a significant proportion of 1,3-dichlorohexafluoropropane is formed in this way. Even if it is assumed that the extinction coefficient of the 1,4-dichlorohexafluoromethylethylketone, which has been detected among the products of high conversion photolyses, is equal to or greater than that for 1,3-dichlorotetrafluoroacetone itself, the concentration of 1,3-dichlorohexafluoropropane could not rise until it was comparable with that of the dichlorodifluoromethane. This is in fact found to be the case. Secondly, the rate of production of 1,4-dichlorohexafluoropropane would increase steadily until the stationary state concentrations of 1,4-dichlorohexafluoromethylethylketone was reached. In fact, the rate of production of 1,3-dichlorohexafluoropropane appears to be constant (fig. 2) even at the shortest irradiation time. An alternative mechanism by which the 1,3-dichlorohexafluoropropane may be formed involves the addition of chlorodifluoromethyl radicals to the CF_2 formed by the disproportionation of the chlorodifluoromethyl radicals, thus:

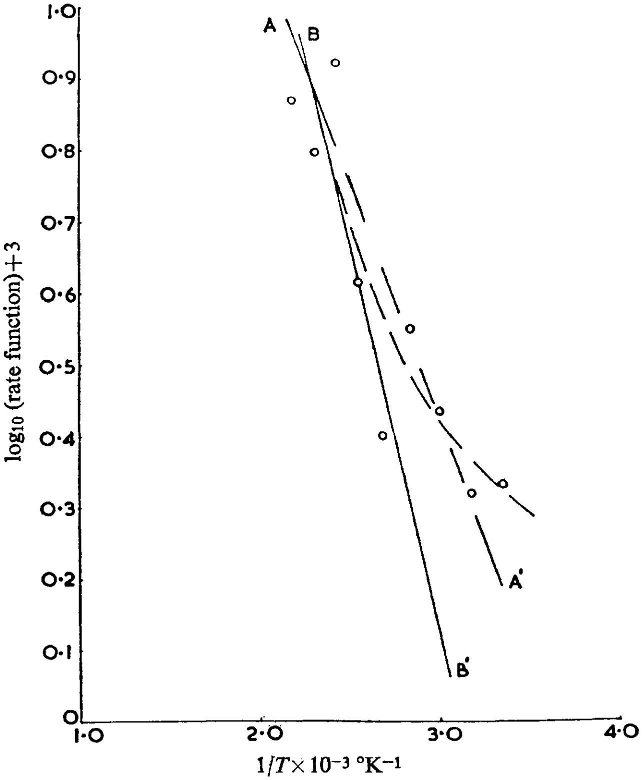

FIG. 10. Arrhenius plot of rate function $R_{CF_2Cl_2}/[R_{C_2F_4Cl_2}]^{\frac{1}{2}}[\text{KET.}]$ against $1/T$.

$$2\dot{C}F_2Cl \rightarrow CF_2Cl_2 + CF_2$$

$$CF_2 + \dot{C}F_2Cl \rightarrow \dot{C}F_2CF_2Cl \qquad (12)$$

$$\dot{C}F_2CF_2Cl + \dot{C}F_2Cl \rightarrow ClCF_2CF_2CF_2Cl$$

$$2\dot{C}F_2CF_2Cl \rightarrow ClCF_2CF_2CF_2CF_2Cl. \qquad (13)$$

This addition of radicals to CF_2 could occur either in the gas phase or on the walls of the vessel. It has been shown [18] that the CF_2 formed in the flash photolysis of 1,3-dichlorotetrafluoroacetone disappears by a zero-order process which probably involves diffusion to the walls of the vessel. There is at present no other direct evidence to show that CF_2 reacts with radicals and it has been shown to the contrary that CF_2 does not react with CO or olefines. However, Gunning[14] has observed 1,3-dichlorohexafluoropropane and 1,4-dichloro-octafluorobutane in the products of the mercury-sensitized decomposition of dichlorodifluoromethane and it is difficult to avoid the conclusion that those products are formed by a similar reaction sequence.

This assumption provides the basis for an estimate of the disproportionation-combination ratio for chlorodifluoromethyl radicals. If CF_2 is formed by disproportionation and disappears by reacting with chlorodifluoromethyl radicals only, then applying stationary state conditions,

$$\text{rate}_{\text{disp.}} = \text{rate}_{C_3F_6Cl_2} + \text{rate}_{C_4F_8C_2}.$$

$\text{Rate}_{C_4F_8Cl_2}$ is small and cannot be measured with any great accuracy but it can be calculated assuming statistical recombination of chlorodifluoromethyl and 2-chlorotetrafluoroethyl radicals, whence

$$\text{rate}_{C_4F_8Cl_2} = \text{rate}^2_{C_3F_6Cl_2}/4\ \text{rate}^2_{C_2F_4Cl_2},$$

$$\Delta = k_d/k_c = \text{rate}_{\text{disp.}}/\text{rate}_{C_2F_4Cl_2}$$

$$= \frac{\text{rate}_{C_3F_6Cl_2} + (\text{rate}^2_{C_3F_6Cl_2}/4\ \text{rate}_{C_2F_4Cl_2})}{\text{rate}_{C_2F_4Cl_2}}$$

$$= \frac{\text{rate}_{C_3F_6Cl_2}}{\text{rate}_{C_2F_4Cl_2}} + \frac{\text{rate}^2_{C_3F_6Cl_2}}{4\ \text{rate}^2_{C_2F_4Cl_2}}.$$

Table 6 lists a number of values of Δ calculated under varying conditions of pressure, intensity and temperature. It can be seen that the value is fairly constant whereas the value calculated from $\Delta = \text{rate}_{CF_2Cl_2}/\text{rate}_{C_2F_4Cl_2}$ varies widely, a further indication of the complexity of the reactions involved in the formation of the dichlorodifluoromethane.

TABLE 6

run	$\Delta = \frac{\text{rate}_{C_3F_6Cl_2}}{\text{rate}_{C_2F_4Cl_2}} + \frac{\text{rate}^2_{C_3F_6Cl_2}}{4\text{rate}^2_{C_2F_4Cl_2}}$	$\Delta = \frac{\text{rate}_{CF_2Cl_2}}{\text{rate}_{C_2F_4Cl_2}} + \frac{\text{rate}^2_{CF_2Cl_2}}{4\text{rate}^2_{C_2F_4Cl_2}}$
1	·045	·063
2	·040	·064
3	·040	·058
4	·047	·064
5	·036	·054
6	·034	·050
10	·034	·057
11	·034	·049
12	·026	·059
21	·027	·205
22	·031	·179
23	·030	·217

Finally, it is necessary to account for the greatly reduced 1,3-dichlorohexafluoropropane yield when the wavelength is changed to 2537 Å. As indicated in the previous section, the yield of dichlorodifluoromethane is greatly increased and it is possible that the formation of the methane by an abstraction process is much facilitated by the excess energy available, with subsequent reductions in the yields of both the ethane and the propane. However, no significant change is noted when the ketone is irradiated in the presence of an equal quantity of sulphur hexafluoride which should tend to remove energy from the radicals. Since there is the possibility of mercury photosensitization, a more detailed study of the effect of wavelength must be undertaken before any definite conclusions can be reached.

CONCLUSIONS

(1) 1,3-Dichlorotetrafluoroacetone decomposes upon irradiation with light of wavelength 3130 Å into two chlorodifluoromethyl radicals and a molecule of carbon monoxide. (2) 1,2-Dichlorotetrafluoroethane is formed by the combination of two chlorodifluoromethyl radicals. (3) Dichlorodifluoromethane is formed by at least two processes one of which is temperature sensitive. This process is tentatively proposed as chlorine abstraction from the 1,3-dichlorotetrafluoroacetone and has an energy of activation of 3-5 kcal/mole. (4) Chlorodifluoromethyl radicals may disproportionate to form CF_2 and dichlorodifluoromethane, the disproportionation-combination ratio being 0·04. (5) Chlorodifluoromethyl radicals may react with CF_2 to form chlorotetrafluoroethyl radicals which combine together and with chlorodifluoromethyl radicals to form 1,3-dichlorotetrafluoropropane and 1,4-dichloro-octafluorobutane. (6) 1,4-Dichlorohexafluoromethylethyl ketone is formed by the combination of chlorotetrafluoroacetonyl radicals and chlorodifluoromethyl radicals. (7) The wavelength of the light has a profound effect upon the proportions in which the radical products are formed.

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