The Photodecomposition of Halogenated Ketones

Part 2.—The Photolysis of 1,1,3-trichlorotrifluoroacetone

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Upon irradiation in the gas phase with light of wavelength 3130 Å 1, 1, 3-trichlorotrifluoroacetone decomposes into two halogenated methyl radicals and a molecule of carbon monoxide. Three halogenated ethanes are formed by the combination of the two dissimilar radicals, CF_2Cl and $CFCl_2$ and the relative amounts of the three ethanes are those which would be predicted by simple collision theory. CCl_3F and CF_2Cl_2 are formed by at least two processes one of which is temperature sensitive. This latter process is considered to be abstraction of chlorine atoms from the parent ketone and has an energy of activation of approximately 3 kcal/mole. At room temperature these products are mainly formed by disproportionation of the halogenated methyl radicals. The CF_2 formed in the disproportionation may react further with CF_2Cl radicals to form 1, 3-dichlorohexafluoropropane.

The photodecomposition of 1, 3-dichlorotetrafluoroacetone was discussed in a previous paper.[1] It was shown that the ketone behaved in a similar fashion to hexafluoroacetone in that two halogenated methyl radicals and a molecule of carbon monoxide constituted the products of the primary step. The photolysis of 1, 1, 3-trichlorotrifluoroacetone in the liquid phase has also been studied by the present authors,[2] and it has been shown to behave in a similar fashion, although the subsequent reactions are complicated by the presence of two dissimilar radicals. It is the purpose of the present paper to examine the gas phase photolysis of 1, 1, 3-trichlorotrifluoroacetone in detail and to attempt to elucidate the course of the secondary processes.

EXPERIMENTAL

1, 1, 3-trichlorotrifluoroacetone was obtained from L. Light and Co. Ltd. It was purified by conversion to the hydrate followed by fractional distillation through a packed column, the fraction boiling at 32·4°C/35 mm being collected. This was then dehydrated to the ketone with phosphorus pentoxide and the product redistilled. Dichlorodifluoromethane (Arcton 4), b.p. −41°C, and 1, 2, 2-trichloro-1, 2, 2-trifluoroethane (Arcton 63), b.p. 47°C, were obtained from Imperial Chemical Industries Ltd., Widnes, and were purified by bulb to bulb distillation under reduced pressure.

Trichlorofluoromethane (Isceon II) b.p. 24°C and 1, 2-dichlorotetrafluoroethane, b.p. 4°C were obtained from Imperial Smelters Ltd. and were purified in a similar manner.

1, 1, 2, 2-tetrachlorodifluoroethane b.p. 92·8°C and perfluoroethyl cyclohexane were supplied by Professor J. C. Tatlow of this department.

The apparatus has been fully described in a previous paper.[1] The photolysis products were transferred by a stream of nitrogen directly to the inlet system of a gas chromatography apparatus which was used in conjunction with a mass spectrometer (A.E.I. type M.S.2) to identify and estimate the products. The most difficult analytical problem was the assay of 1, 1, 2, 2-tetrachlorodifluoroethane in the presence of a large excess of 1, 1, 3-trichlorotrifluoroacetone. The stationary phase used was dinonyl phthalate and when this was supported upon untreated 30-60 mesh C 22 firebrick (Johns Manville Co. Ltd.) the ketone was very strongly adsorbed, appearing as a long shallow hump on the chromatogram upon which the peaks due to the photolysis products were superimposed. The use of acid and acid-alkali washed grades of the same firebrick improved the ketone peak shape but did not permit complete resolution of the ethane and the ketone peaks. A further marginal improvement was obtained by substituting firebrick which had been siliconised but the best results were obtained with a sample of siliconised Celite supplied by Messrs. Silicote Supports Ltd.

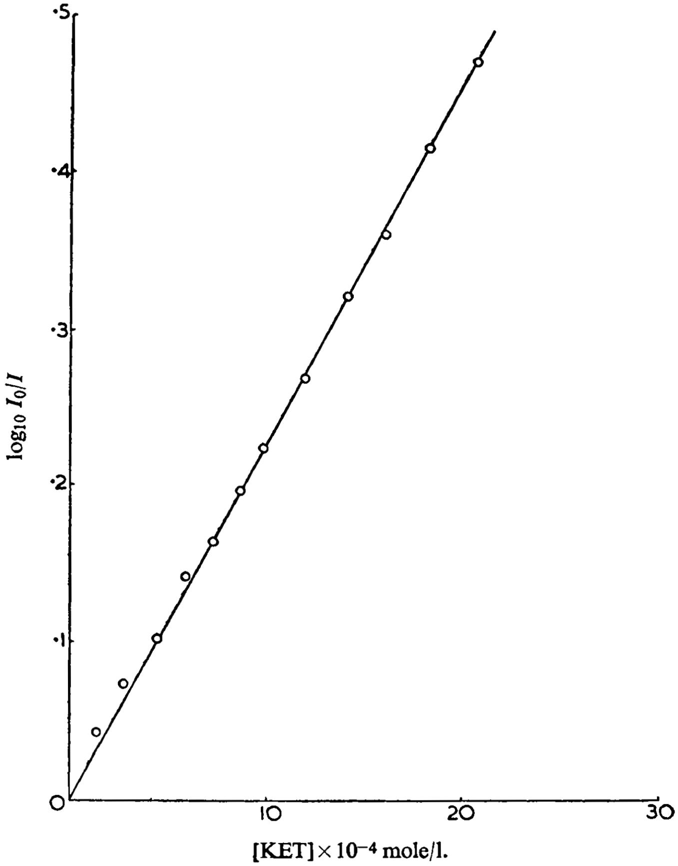

FIG. 1.—Absorption of 1, 1, 3-trichlorotrifluoroacetone at 3130 Å.

Despite the improvement in the resolution of the ketone and ethane obtained in this manner, the involatile nature of the ethane made its estimation much less certain than that of the other products. The retention volumes of the products are expressed in table 1 in a manner due to Smith[3] which permits data obtained on different columns to be compared by reference to the retention volume of a " theoretical nonane " determined by extrapolation.

The absorption spectrum in the near ultra violet of 1, 1, 3-trichlorotrifluoroacetone was similar to that of 1, 3-dichlorotetrafluoroacetone,[1] absorption occurring in the 2950 Å region,

TABLE 1

compound	retention time R_x, min	R_{x9}
CF_2Cl_2	1·14	$2{\cdot}28 \times 10^{-3}$
$C_2F_4Cl_2$	1·84	$3{\cdot}67 \times 10^{-3}$
$CFCl_3$	8·4	$1{\cdot}68 \times 10^{-2}$
$C_2F_3Cl_3$	11·92	$2{\cdot}38 \times 10^{-2}$
$C_2F_2Cl_4$	71·90	$1{\cdot}44 \times 10^{-1}$

Fig. 1 shows a plot of the optical density of the reaction cell, at a wavelength of 3130 Å, against the ketone concentration. It can be seen that Beers Law is obeyed over the range of pressures studied. From the slope of the graph the molar absorption and extinction coefficients can be calculated. The values obtained were $\alpha_{3130\text{Å}} = 130{\cdot}8$, $\varepsilon_{3130\text{ Å}} = 56{\cdot}7$ and $\varepsilon_{2537\text{Å}} = 9{\cdot}4$.

RESULTS AND DISCUSSION

The results of a number of photolyses are given in table 2. As in the case of the photolysis of 1, 3-dichlorotetrafluoroacetone described in a previous communication,[1] no products were detected which could arise from the reactions of a halogenated acetyl radical and it is therefore assumed that the predominant primary mode of breakdown is the formation of a molecule of carbon monoxide and two halogenated methyl radicals.

$$CFCl_2COCF_2Cl \xrightarrow{h\nu} CO + CFCl_2 + CF_2Cl. \tag{1}$$

The combination of the two different radicals can give rise to three different halogenated ethanes as in eqn. (2)-(4).

$$2CF_2Cl \rightarrow CF_2ClCF_2Cl \tag{2}$$

$$2CFCl_2 \rightarrow CFCl_2CFCl_2 \tag{3}$$

$$CF_2Cl + CFCl_2 \rightarrow CF_2ClCFCl_2. \tag{4}$$

The halogenated methanes could arise in two distinct ways, each involving two alternative reactions. Each radical could abstract a chlorine atom from either end of the ketone molecule as in eqn. (5)-(8):

$$CF_2Cl + ClCF_2COCFCl_2 \rightarrow CF_2Cl_2 + CF_2COCFCl_2 \tag{5}$$

$$CF_2Cl + CF_2ClCOCFCl_2 \rightarrow CF_2Cl_2 + CF_2ClCOCFCl \tag{6}$$

$$CFCl_2 + ClCF_2COCFCl_2 \rightarrow CFCl_3 + CF_2COCFCl_2 \tag{7}$$

$$CFCl_2 + CF_2ClCOCFCl_2 \rightarrow CFCl_3 + CF_2ClCOCFCl. \tag{8}$$

Disproportionation between like or unlike radicals could also occur with the formation of transient biradicals, eqn. (9)-(12).

$$2CF_2Cl \rightarrow CF_2 + CF_2Cl_2 \tag{9}$$

$$CF_2Cl + CFCl_2 \rightarrow CFCl + CF_2Cl_2 \tag{10}$$

$$CF_2Cl + CFCl_2 \rightarrow CF_2 + CFCl_3 \tag{11}$$

$$2CFCl_2 \rightarrow CFCl + CFCl_3. \tag{12}$$

Some support for the occurrence of reactions 9 and 11 is given by the identification of absorption bands due to CF_2 in the flash photolysis of 1, 1, 3-trichlorotrifluoroacetone.[4]

1, 3-dichlorohexafluoropropane has been observed in the products of photolysis of 1, 3-dichlorotetrafluoroacetone [11] and it was suggested that it was formed by the interaction of CF_2 and CF_2Cl radicals as in eqn. (13), (14).

$$CF_2 + CF_2Cl \rightarrow CF_2CF_2Cl \tag{13}$$

$$CF_2CF_2Cl + CF_2Cl \rightarrow ClCF_2CF_2CF_2Cl. \tag{14}$$

A similar mechanism may account for the presence of 1, 3-dichlorohexafluoropropane among the products of a high conversion photolysis of 1, 1, 3-trichlorotrifluoroacetone.

Table 2 summarizes the results of a number of runs carried out at various temperatures. It can be seen that the quantum yields of the products are not unity, the highest yield being that for carbon monoxide. This suggests that energy is being lost, possibly by fluorescence, and it has been shown [5] that the ketone fluoresces strongly in a glass at liquid nitrogen temperature, the fluorescence spectrum exhibiting fine structure in the blue and near ultra-violet region of the spectrum (max. *ca.* 3100 Å). These observations were confirmed by irradiating the ketone in the form of a thin film at liquid nitrogen temperature. No detectable breakdown occurred after irradiation times up to 2 h.

TABLE 2

temp. °C	irradn. time (min)	$I_a \times 10^{13}$ q/cm³ sec	[KET] $\times 10^{-3}$ moles/l	quantum yields						$\Sigma\Phi CF_2Cl$	$\Sigma\Phi CFCl_2$	$\frac{\Sigma\Phi R.P}{2\Phi CO}$	$\frac{[a]}{([b][c])}$
				CO	CF_2Cl_2	$C_2F_4Cl_2$	$CFCl_3$	$C_2F_3Cl_3$	$C_2F_2Cl_4$				
20·0	60	2·68	2·49	0·92	0·021	0·20	v. small	0·31	0·057	0·73	0·42	0·63	
39·7	90	3·22	2·23	0·63	0·020	0·13	0·012	0·22	0·080	0·50	0·39	0·71	2·1
83·3	120	3·37	2·49	0·55	0·034	0·092	0·035	0·16	0·050	0·38	0·29	0·61	2·4
99·0	120	3·12	2·16	0·50	0·039	0·077	0·054	0·15	0·040	0·34	0·28	0·63	2·7
121·9	90	2·92	2·00	0·46	0·033	0·071	0·048	0·15		0·32		0·60	
142·7	105	3·01	2·11	0·42	0·041	0·060	0·055	0·11	0·043	0·27	0·25	0·62	2·2
162·2	120	2·99	2·19	0·40	0·046	0·054	0·047	0·083		0·24		0·48	
184·1	120	2·87	1·92	0·32	0·049	0·034	0·057	0·054	0·018	0·17	0·15	0·50	2·2
†59	165	0·75	2·90	0·57	0·21	0	0·15	0·023	0·08	0·23	0·31	0·48	
59	150	1·28	2·36	0·68	0·023	0·12	0·026	0·21	0·11	0·47	0·46	0·68	1·9
59	150	1·32	2·89	0·69	0·024	0·14	0·024	0·23	0·11	0·53	0·47	0·73	1·9
59	135	2·11	2·96	0·65	0·025	0·13	0·024	0·24	0·074	0·52	0·41	0·72	2·4
59	92	2·51	1·65	0·59	0·025	0·11	0·015	0·20	0·052	0·44	0·32	0·65	2·6
59	120	2·62	2·82	0·66	0·027	0·13	0·020	0·22	0·070	0·51	0·38	0·67	2·3
59	90	3·19	2·30	0·62	0·016	0·11	0·019	0·19	0·067	0·43	0·34	0·62	2·2
59	120	3·34	2·56	0·59	0·023	0·11	0·017	0·19	0·058	0·43	0·32	0·64	2·4
59	95	4·52	2·88	0·64	0·022	0·12	0·027	0·22	0·087	0·48	0·42	0·71	2·2
59	60	1·46	0·89	0·61	0·032	0·11	0·038	0·19	0·054	0·44	0·34	0·64	2·5
•59	60	1·27	0·78	0·66	0	0·15	0	0·20	0·083	0·50	0·37	0·66	1·8

(*a*) $CF_2ClCFCl_2$. (*b*) CF_2ClCF_2Cl. (*c*) $CFCl_2CFCl_2$

• 1·8 cm ketone, 29 cm C_8F_{16} † 2537 Å.

There is also a striking mass balance deficiency, for the total amount of radical products which could be estimated was only about two-thirds of the amount of carbon monoxide. It must be assumed that the radicals also undergo reactions leading to the formation of involatile products which would not be detected with the present analytical technique, or an alternative primary step leading to the formation of involatile products may occur.

The variation in the product yield with change in experimental parameters is now considered in detail. A series of preliminary runs established the fact that as in the case of 1,3-dichlorotetrafluoroacetone, the amounts of the photolysis products listed above increased linearly with the duration of irradiation. As would be expected from the nature of these products no secondary photolysis took place.

Table 2 includes runs in which the ketone concentration was kept constant and the intensity of illumination varied. In order to determine the value of the intensity exponent the logarithm of the rate of formation of the photolysis products was plotted against the logarithm of I_a. I_a is defined by the equation

$$I_a = (1/L)I_0(1 - e^{-\alpha c L})$$

where I_0 is the incident intensity in quanta/cm² sec, L is the length of the cell, c is the ketone concentration and α the extinction coefficient.

Fig. 2 illustrates the results of such a plot for six of the photolysis products. It can be seen that the intensity exponent as determined from the slope is unity for carbon monoxide and two of the three halogenated ethanes. This is in accordance with the proposed mechanism (eqn. (1)-(4)). The scatter of points for 1, 1, 3, 3-tetrachlorodifluoroethane is due to experimental difficulties associated with the relatively low vapour pressure of this compound. The slope of the graph for dichloroaifluoromethane suggests an intensity exponent of close to unity and this

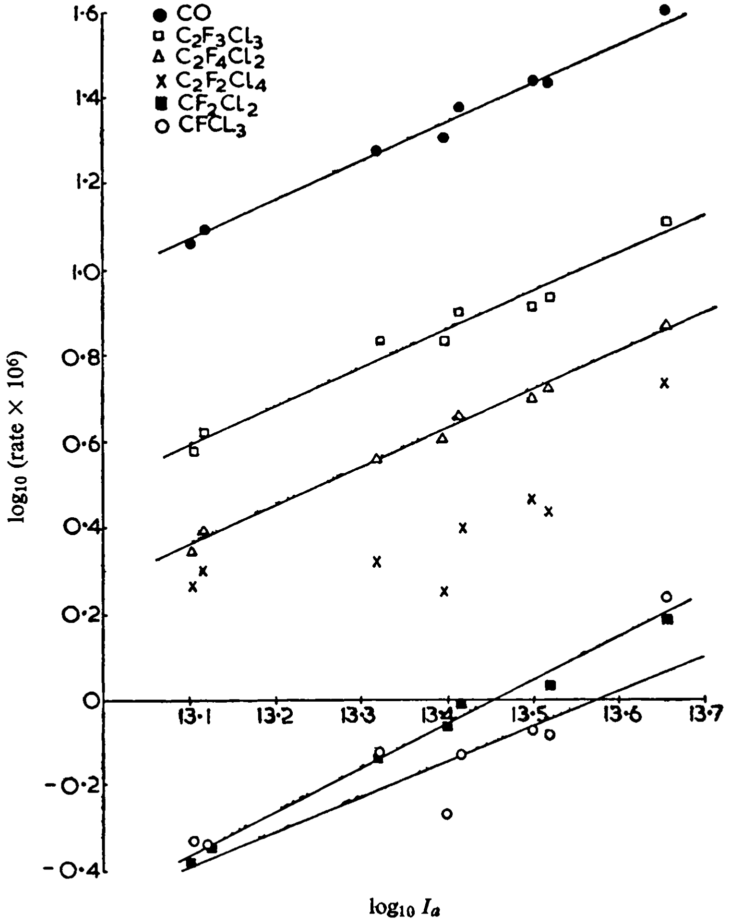

FIG. 2.—Intensity Exponent of photolysis products of 1, 1, 3-trichlorotrifluoroacetone.

would support a disproportionation (eqn. (9), (11)) rather than an abstraction mechanism for its formation. The intensity exponent for trichlorofluoromethane as determined by a least mean squares calculation is 0·85 but this is not sufficiently different from unity to suggest that abstraction plays a significant part in its formation.

In the study of the photolysis of 1, 3-dichlorotetrafluoroacetone [1] it was shown that, at room temperature, the bulk of the dichlorodifluoromethane was not formed by abstraction of chlorine from the ketone. No significant relationship between $[CF_2Cl_2]/[C_2F_4Cl_2]^{\frac{1}{2}}$ and $[CF_2ClCOCF_2Cl]/I_a^{\frac{1}{2}}$ could be demonstrated using the method suggested by Noyes. In fact, because of the non-uniform light absorption along the length of the cell, it would be more precise to plot $[CF_2Cl_2]/[C_2F_4Cl_2]^{\frac{1}{2}}$

against $[c]^{\frac{1}{2}}(1-e^{-\frac{1}{2}\alpha cL}/\alpha^{\frac{1}{2}}I^{\frac{1}{2}}(1-e^{-\alpha cL})$ but over the range of concentrations studied, the result is the same and this would be anticipated from the constancy of

$$[CF_2Cl_2]/[C_2F_4Cl_2].$$

A similar result is obtained in the photolysis of 1, 1, 3-trichlorotrifluoroacetone, and the test suggests that no significant amount of chlorine abstraction takes place at room temperature.

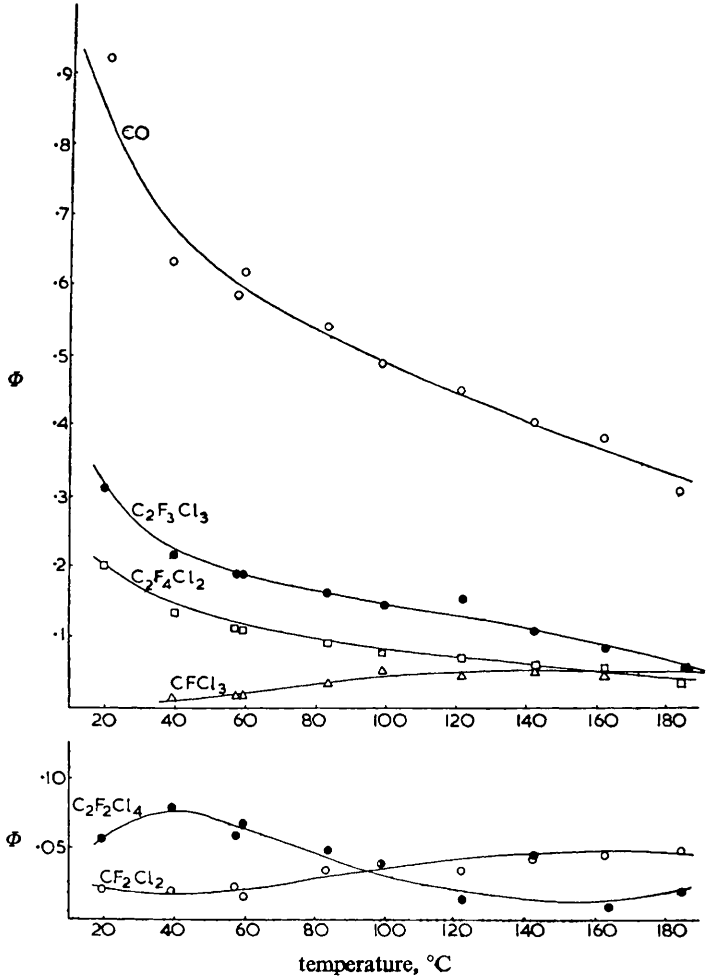

FIG. 3.—Variation in quantum yield with temperature.

EFFECT OF TEMPERATURE

Table 2 includes the results of a series of runs carried out at temperatures up to 184°C. The quantum yield of the photolysis products is plotted against temperature in fig. 3 and it can be seen that there is an unexpected decrease in the rate of formation of carbon monoxide and the three halogenated ethanes with rise of temperature. In contrast to this, the rate of formation of the halogenated methanes appears to rise with increasing temperature, suggesting a mode of formation involving an energy of activation. It would appear that at elevated temperatures some of the halogenated methane is formed by a route involving chlorine abstraction (eqn. (5)-(8)). An estimate of the value of the energy of activation may be made by making an Arrhenius plot of rate of formation of CF_2Cl/rate of formation of $C_2F_4Cl_2^{\frac{1}{2}}[CF_2ClCOCFCl_2]$ against $1/T$ (fig. 4) a value for the energy difference $E_5 - \frac{1}{2}E_2$ can be derived from the slope of the graph. If the value of E_2 is assumed to be close to zero then E_5 is 3 kcal/mole. This is in agreement with the value obtained in the photolysis of 1, 3-dichlorotetrafluoroacetone and is close to the value obtained by Szwarc [6] for bromine and iodine abstraction reactions. Nevertheless the complex nature of the reaction system makes this value uncertain.

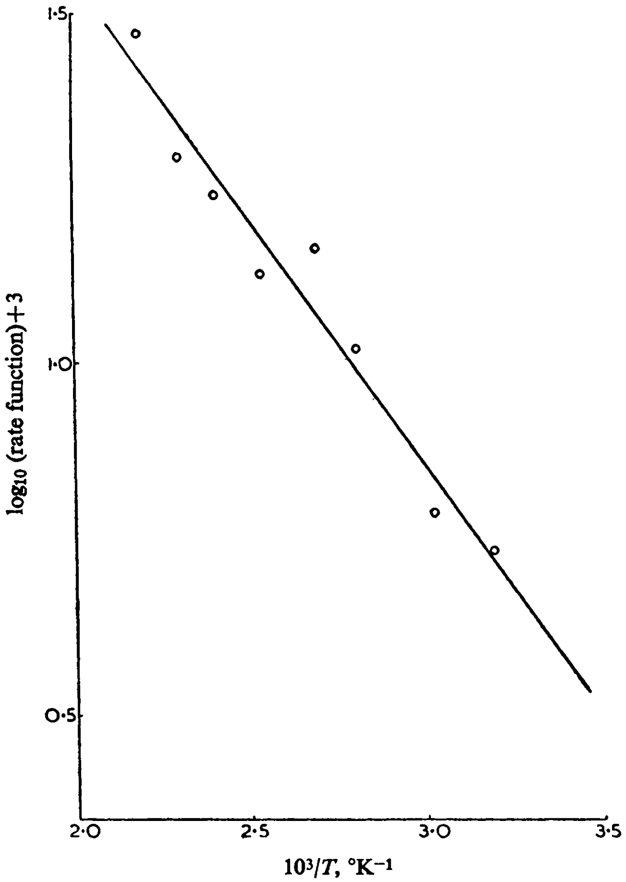

Fig. 4.—Arrhenius plot for chlorine abstraction by CF_2Cl radicals.

EFFECT OF WAVELENGTH

As in the case of the photolysis of 1, 3-dichlorotetrafluoroacetone, the relative amounts of the halogenated ethanes and methanes were markedly affected by the wavelength of the incident radiation. Table 2 includes the results of a photolysis carried out with light of wavelength 2537 Å from a low pressure mercury arc. The yield of the three halogenated ethanes is greatly decreased while the yields of the two halogenated methanes has increased. There is also a slight fall in the quantum yield of carbon monoxide. It is possible that these effects are due to mercury photosensitization rather than direct absorption but this is not supported by the results of flash photolysis which also show a marked increase in the ratio of the quantum yields of the halogenated methanes to ethanes.[5] The interpretation of the wavelength effect is uncertain but it would appear that the increased energy imparted by the light of shorter wavelength is capable of increasing the rate of chlorine abstraction. A more detailed study of the effect of wavelength upon the reactions of the radicals produced in the primary step is in progress at the present time.

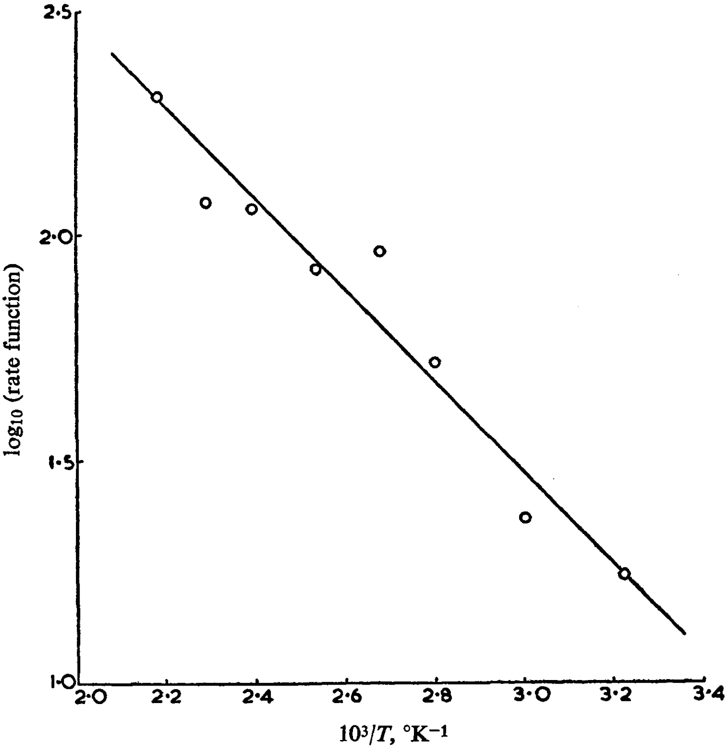

FIG. 5.—Arrhenius plot for chlorine abstraction by $CFCl_2$ radicals.

The effect of adding a foreign gas was investigated by introducing an excess of perfluoroethylcyclohexane to the ketone before photolysis. The formation of the halogenated methanes was suppressed and there was a slight enhancement in the quantum yields of the three halogenated ethanes (table 2). Once again it would appear that removal of energy from the halogenated methyl radicals results in a reduced ability to participate in the abstraction or disproportionation reactions leading to the formation of the halogenated methanes. It can be predicted by simple collision theory,[7] that when two unlike radicals R_1 and R_2 combine with themselves and each other the amounts of R_1R_1, R_1R_2 and R_2R_2 formed are such that

$$\frac{[R_1R_2]}{([R_1R_1][R_2R_2])^{\frac{1}{2}}} = 2,$$

the ratio on the left being known as the ϕ factor.[8]

In the present work it was not easy to obtain precise values for ϕ because of the analytical difficulties associated with the determination of the comparatively involatile

1, 1, 1, 2-tetrachlorodifluoroethane by gas chromatography. Further, this difficulty could not be overcome by the use of mass spectrometry because of the need to study the reactions at low conversion with the result that the reaction products constituted only a small percentage of the sample to be analyzed. Despite these difficulties it was shown that the ϕ factor did not depart substantially from the theoretical value and this suggests that the combination process is not affected by the polar nature of the radicals.

In contrast to the constancy of the ϕ factor in the gas phase, it was shown previously [2] that the combination of the same two radicals in the liquid phase was markedly affected by their physical and chemical environment, resulting in values for ϕ differing considerably from the theoretical value of 2. If the value of 2 is assumed for radical combination in the gas phase, then a determination of the activation energy for chlorine abstraction by CCl_2F radicals, which does not involve a measurement of the concentration of the tetrachlorodifluoroethane may be made.

Fig. 5 shows a plot of $\Phi[CFCl_3] \times 2\Phi[C_2F_4Cl_3]^{\frac{1}{2}}/\Phi[C_2F_3Cl_3][CF_2ClCOCFCl_2]$ against $1/T$ From the slope the difference in activation energies for chlorine abstraction and combination may be determined. The result of 4·6 kcal/mole is slightly higher than the value of 3 kcal/mole obtained for chlorine abstraction by CF_2Cl radicals.

The decrease in quantum yields of all three halogenated ethanes with rise in temperature is difficult to explain, particularly as it is accompanied by a similar drop in the quantum yield of carbon monoxide. These results are the exact opposite of those reported for trifluoro [9] and hexafluoro [10] acetone. The only feasible explanation which can be advanced is that at the higher temperatures carbon chlorine bonds are being broken with the formation of stable halogenated acetonyl radicals. The reaction products of the halogenated acetonyl radicals with other radicals, result in the formation of products which are too involatile to be detected with the present analytical system.

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