# Photodecomposition of Halogenated Ketones

Part 4.--Reaction of CF<sub>2</sub>Cl Radicals with Cyclopentane

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1,3-Dichlorotetrafluoro acetone has been photolyzed in the presence of cyclopentane and the quenching efficiency of the hydrocarbon for excited ketone molecules compared with that of  $C_5F_{10}$ ,  $C_6H_6$  and  $C_6F_6$ . The CF<sub>2</sub>Cl radicals formed by photolysis, abstract hydrogen from cyclopentane and the energy of activation for this process is 5.3 kcal mole<sup>-1</sup>. This reaction has been compared with that of addition to  $C_6H_6$  and  $C_6D_6$  and the ratio  $k_{abs.(C_5H_{10})}/k_{addn.(C_6H_6)}$  found to be 0.38. The activation energy for the thermal decomposition of the adduct formed between CF<sub>2</sub>Cl radicals and  $C_6D_6$  is 11.2 kcal mole<sup>-1</sup>.

1,3-Dichlorotetrafluoro acetone dissociates into two CF<sub>2</sub>Cl radicals and a molecule of carbon monoxide <sup>1</sup> on irradiation with light of wavelength 3130 Å. The interaction of the CF<sub>2</sub>Cl radicals with benzene is a complex process involving the formation of an unstable addition compound, addition to the aromatic system and hydrogen abstraction.<sup>2</sup>

The present investigation was undertaken in order to compare the reaction of  $CF_2Cl$  radicals under conditions comparable with those used in the study of the reactions of  $CF_3$  radicals <sup>3</sup> and to explore the possibility of utilizing the process of abstraction as a basis for a sector determination of the lifetime of  $CF_2Cl$  radicals.

# EXPERIMENTAL

### MATERIALS

1,3-Dichlorotetrafluoro acetone was obtained from L. Light and Co. Ltd. It was purified by bulb-to-bulb distillation in a vacuum system. Cyclopentane was obtained from L. Light and Co. Ltd. After distillation its purity was checked by mass spectrometry. Perfluoro cyclopentane was isolated from a sample of the azeotrope of cyclopentane and perfluoro cyclopentane supplied by Prof. J. C. Tatlow. Perdeuterobenzene ( $C_6D_6$ ) was obtained from Koch Chemicals Ltd.

#### PROCEDURE

The analytical procedure has been described in earlier papers of this series. The 1,3dichlorotetrafluoro acetone was photolyzed in the presence of cyclopentane and the yield of carbon monoxide measured with a sensitive McLeod gauge. The condensable products were then transferred to the inlet system of a gas-chromatography apparatus. The effluent from the base of the column was trapped in a U-tube cooled in liquid nitrogen and transferred to the inlet system of a mass spectrometer (A.E.I. MS2) in order to determine the ratio  $[CF_2ClH]/[C_2F_4Cl_2].$ 

# **RESULTS AND DISCUSSION**

# QUENCHING OF EXCITED 1,3-DICHLOROTETRAFLUORO ACETONE MOLECULES

When a molecule of 1,3-dichlorotetrafluoro acetone absorbs a quantum of light of wavelength 3130 Å, the most probable mode of decomposition involves

the production of a molecule of carbon monoxide and two CF<sub>2</sub>Cl radicals: 1

# $ClCF_2COCF_2Cl^* \rightarrow 2CF_2Cl + CO.$

When cyclopentane is added to the photolysis cell, the yield of carbon monoxide is reduced and it is assumed that this is because the excited ketone molecules are deactivated by collision with cyclopentane molecules. Fig. 1 shows a plot of the rate of formation of carbon monoxide against added cyclopentane pressure; there is little decrease in carbon monoxide yield after the addition of 5 mm of cyclopentane.



FIG. 1.—Quenching of excited 1,3-dichlorotetrafluoroacetone molecules by  $C_5H_{10}$  and  $C_5F_{10}$ . Ketone concentration =  $24 \cdot 22 \times 10^{-7}$  moles/cm<sup>3</sup>. Temp. =  $25^{\circ}$ C.

A similar effect is observed when perfluoro cyclopentane is added to the photolysis cell and fig. 1 illustrates the decrease in the rate of formation of carbon monoxide with added perfluoro cyclopentane pressure. Comparison of these two graphs reveals that the efficiency of perfluoro cyclopentane in quenching excited 1,3-dichlorotetrafluoro acetone molecules is only a third of that of cyclopentane molecules. It is difficult to explain this difference in view of the close structural similarity, and it must either be assumed that a molecular complex is formed between the excited ketone molecule and the cyclopentane, or that there is some coincidence in energy levels within the two species which facilitates energy transfer. The latter assumption appears unlikely because it would be expected that such coincidences would be favoured by similar chemical bonding whereas it is the hydrocarbon and not the fluorocarbon which is the more efficient quenching agent. A similar effect has been noted for benzene and hexafluoro benzene.<sup>2</sup> Table 1 shows the

# TABLE 1.---QUENCHING OF EXCITED 1,3-DICHLOROTETRAFLUORO ACETONE

foreign gas	quenching efficiency relative to C <sub>6</sub> F <sub>6</sub>
hexafluoro benzene	1
benzene	13.2
cyclopentane	10.8
perfluoro cyclopentane	7.2

relative efficiencies of these species in quenching excited 1,3-dichlorotetrafluoro acetone. The quenching by nitrogen is such an inefficient process that an atmosphere of added nitrogen pressure gave a barely perceptible alteration in the rate of decomposition.

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#### HYDROGEN ABSTRACTION PROCESS

Because of the efficiency of cyclopentane in quenching excited 1,3-dichlorotetrafluoro acetone molecules and reducing the carbon monoxide yield, it was necessary to express the yields of all radical products as fractions of the carbon monoxide yield, when studying their variation with change in experimental parameters.

Fig. 2 shows the variation of  $[C_2F_4Cl_2]/[CO]$  and  $[CF_2ClH]/[CO]$  with partial pressure of added cyclopentane, at room temperature. As expected, the yields of  $C_2F_4Cl_2$  and  $CF_2Cl_2$  fall with increase in cyclopentane pressure, while the yield



FIG. 2.—Variation of product yield with cyclopentane concentration. Ketone conc. =  $24 \cdot 22 \times 10^{-10}$  moles/cm<sup>3</sup>. Temp. 25.0°C.

 $\bullet = CF_2ClCF_2Cl \qquad \Box = CF_2ClH \qquad \blacksquare = CF_2Cl_2$ 

of CF<sub>2</sub>ClH produced by hydrogen abstraction, rises steadily. The fate of the cyclopentyl radical produced by such a reaction has not been determined experimentally, because of the involatility of the final product. However, at room temperatures, there was a mass balance between the sum of the yields of  $C_2F_4Cl_2$  and  $CF_2ClH$ . This suggests that for every molecule of  $CF_2ClH$  formed, a further  $CF_2Cl$  radical is lost, presumably by combination with a cyclopentyl radical. A disproportionation process may be ruled out since no cyclopentene was detected.

The rate constant ratio  $k_{abs.}/k_{comb.}^{\dagger}$  should be invariant, but when it is plotted against cyclopentane pressure, using the relationship,

$$\frac{k_{\text{abs.}}}{k_{\text{comb.}}^{\frac{1}{2}}} = \frac{R_{\text{CF}_2\text{CIH}}}{R_{\text{C}_2\text{F}_4\text{CI}_2}^{\frac{1}{2}}} \frac{1}{[\text{C}_5\text{H}_{10}]},$$

a curve is obtained as shown in fig. 3. This suggests that cyclopentane may be an efficient third-body for the recombination of  $CF_2Cl$  radicals, so that

and

$$R_{C_2F_4Cl_2} = k_{comb.}[CF_2Cl]^2[C_5H_{10}]$$

$$\frac{k_{\text{abs.}}}{k_{\text{comb.}}^{\frac{1}{2}}} = \frac{R_{\text{abs.}}}{R_{\text{comb.}}^{\frac{1}{2}}} \frac{1}{[C_5 H_{10}]^{\frac{1}{2}}}.$$

When  $k_{abs.}/k_{comb.}^{\frac{1}{2}}$  is reported on this basis, fig. 3 shows that, within experimental error, the rate constant ratio is invariant. This explanation may also apply to the effect noted by Whittle <sup>4</sup> in the interaction of CF<sub>3</sub> radicals with benzene and toluene described by Kutschke.<sup>5</sup>



In fig. 4, the ratios  $[C_2F_4Cl_2]/[CO]$  and  $\cdot [CF_2ClH]/[CO]$  are plotted against temperature. After an initial curvature, the latter function rises linearly with temperature, with corresponding fall in the value of the former ratio. Here there is no longer a balance between the  $C_2F_4Cl_2$  lost and the  $CF_2ClH$  formed, as at room temperature. Instead, much more  $CF_2ClH$  is found in the system, suggesting that most of the cyclopentyl radicals now disappear by dimerization.

An Arrhenius plot of

$$\log_{10} \{ R_{CF_2CH} / (R_{C_2F_4Cl_2})^{\frac{1}{2}} [C_5H_{10}] \}$$

against 1/T is illustrated in fig. 5. From the slope, a value of  $5\cdot3\pm0\cdot4$  kcal mole<sup>-1</sup> is obtained for the energy of activation of the hydrogen abstraction reaction, assuming that the energy of activation for recombination of CF<sub>2</sub>Cl radicals is zero.

The hydrogen abstraction reaction may be compared with the addition of  $CF_2Cl$  radicals to benzene using a competitive system in which the recombination of  $CF_2Cl$  radicals is eliminated. This greatly simplifies the reaction system since  $CF_2ClH$  is the only volatile reaction product formed. If it is assumed that the  $CF_2ClH$  is formed only by hydrogen abstraction from cyclopentane, and none



arises from the benzene, a value for the ratio of the rate constants (at 25°C),  $k_{abs.}/k_{addn.}$ , of 0.38 is obtained. This value is about the same as those reported by Szwarc <sup>3</sup> for CF<sub>3</sub> radicals in the presence of benzene and iso-octane. The ratio  $k_{abs.}/k_{comb.}^{\dagger}$  obtained in the presence of cyclopentane alone was  $3.22\pm0.08\times10^{-3}$  sec<sup>-1</sup>. Division of these ratios gives a value of  $8.57\pm0.3\times10^{-3}$  sec<sup>-1</sup> for  $k_{addn.}/k_{comb.}^{\dagger}$  Previous work gave  $9.8\pm0.6\times10^{-3}$  sec<sup>-1</sup>. This agreement shows that the assumptions inherent in the previous calculation of  $k_{addn.}/k_{comb.}^{\dagger}$  are substantially justified.

The previous work also showed that some  $CF_2ClH$  was formed from benzene, especially at high temperatures. In order to distinguish between  $CF_2ClH$  formed from cyclopentane, and that arising from benzene, it was decided to carry out a series of experiments at different temperatures, in which cyclopentane and perdeuterobenzene,  $C_6D_6$ , were used as the competing species. Again, no  $C_2F_4Cl_2$  was formed,  $CF_2ClH$  and  $CF_2ClD$  being the only volatile products.

0.2



FIG. 6.—Arrhenius plot of  $\log_{10} \frac{R_{adduct}[C_5 r_{10}]}{R_{CF_2CIH}[C_6 D_6]}$  against 1/T,  $K^{-1}$ .

In none of the runs was the ratio  $[CF_2CID]/[CF_2CIH]$  greater than 0.06, indicating that deuterium abstraction from the deuterobenzene was not important even at the highest temperatures used. This leads to the speculation that the CF<sub>2</sub>ClH observed in the original system was the result of disproportionation of the substituted cyclohexadienyl radical and a further CF<sub>2</sub>Cl radical, rather than direct hydrogen abstraction from the benzene, at least at temperatures up to 160°C.

In order to estimate the size of the isotope effect, competitive runs were carried out for mixtures of  $C_6H_6$  and  $C_6D_6$  and the amounts of  $CF_2ClD$  and  $CF_2ClH$  estimated. The rate ratio

$$R_{\rm CF_2CID}[\rm C_6H_6]/R_{\rm CF_2CIH}[\rm C_6D_6]$$

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was only 0.77. Thus it is justifiable to extend the conclusions drawn from the study of the  $C_6D_6+C_5H_{10}$  system to the incompletely characterized  $C_6H_6+C_5H_{10}$  system.

At room temperature, the value of  $k_{abs.}/k_{addn.}$  for perdeuterobenzene was 0.37, in close agreement with the value for benzene. Fig. 6 shows an Arrhenius plot of

 $\log_{10} \{ R_{adduct} [C_5 H_{10}] / R_{CF_2 CIH} [C_6 D_6] \}$ 

against 1/T. The inflection in this graph is assumed to be due to the thermal decomposition of the CF<sub>2</sub>Cl—C<sub>6</sub>D<sub>6</sub> adduct, as reported previously for benzene. The slope at lower temperatures gives a value for the difference in activation energy between the hydrogen abstraction process and the addition process of 0.5 kcal mole<sup>-1</sup>, which is within the experimental error of the separately determined values, of  $5\cdot3\pm0\cdot4$ , for both the abstraction reaction and the addition process to benzene.

From the slope of the Arrhenius plot at temperatures above 100°C it is possible to obtain an estimate of the energy of activation for the breakdown of the CF<sub>2</sub>Cl— $C_6D_6$  adduct. The value of  $10.7\pm0.4$  kcal mole<sup>-1</sup> is similar to that obtained in the benzene system.

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<sup>1</sup> Bowles, Majer and Robb, Trans. Faraday Soc., 1962, 58, 1541.

- <sup>2</sup> Majer and Phillips, unpublished work.
- <sup>3</sup> Dixon and Szwarc, Trans. Faraday Soc., 1963, 59, 112.
- <sup>4</sup> Charles, Pearson and Whittle, Trans. Faraday Soc., 1963, 59, 1156.
- <sup>5</sup> Holmes and Kutschke, Trans. Faraday Soc., 1962, 58, 333.