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HYDROGEN ABSTRACTION FROM FLUORINATED ALIPHATIC ACIDS

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SUMMARY

1,3-Dichlorotetrafluoroacetone has been photolysed at a wavelength of 313nm in the presence of fluorinated aliphatic acids, such as trifluoroacetic acid, pentafluoropropionic acid, heptafluorobutyric acid and chlorodifluoroacetic acid. From the rates of formation of chlorodifluoromethane and 1,2-dichlorotetrafluoroethane, the rate constants and energies of activation for the hydrogen abstraction reaction were calculated. No products were observed which could arise from the decomposition of the alkyl carboxyl radical produced during the hydrogen abstraction reaction

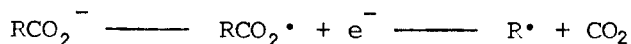


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## INTRODUCTION

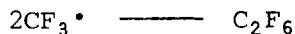
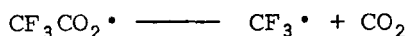
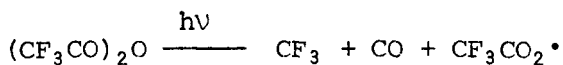
In the Kolbe synthesis of symmetrical alkanes<sup>1</sup> such as ethane by the electrolysis of the salts of carboxylic acids, it has been suggested that the radical anion  $\text{RCO}_2^-$  is discharged at the electrode to form the uncharged radical  $\text{RCO}_2^\bullet$  which is unstable and breaks down into the radical  $\text{R}^\bullet$  and carbon dioxide.



The symmetrical alkane is then formed by the dimerisation of the radical  $\text{R}^\bullet$ . The intervention of the radical  $\text{R}^\bullet$  is confirmed by the addition of unsaturates (M) such as 1,3-dienes<sup>2</sup> to the electrolysis cell. There follows the reactions

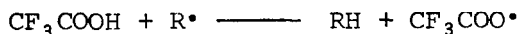


The assumption that the radical  $\text{RCO}_2^\bullet$  is unstable is supported by experiments of the photolysis of hexafluoroacetic anhydride with light in the near ultra violet region. The excited molecule decomposes cleanly into a mixture of carbon monoxide, carbon dioxide and hexafluoroethane.<sup>5</sup> The decomposition may only be interpreted in the following reaction sequence

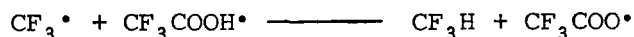
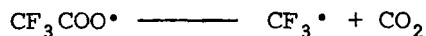


assuming that the  $\text{CF}_3\text{CO}_2\cdot$  radical decomposes when formed.

From these considerations it appeared possible to carry out the radical sensitised decomposition of acids, particularly those containing only a single proton such as trifluoroacetic acid. At elevated temperatures any radical R would be expected to abstract the hydrogen atom producing the supposedly unstable  $\text{CF}_3\text{CO}_2\cdot$



Upon decomposition the  $\text{CF}_3\text{COO}\cdot$  radical would produce a molecule of carbon dioxide and a  $\text{CF}_3\cdot$  radical to continue the chain by hydrogen abstraction



In order to study the possibility of initiating such a chain reaction a radical source was chosen which would

generate radicals other than those which would propagate the chain. The  $\text{CF}_2\text{Cl}$  radical was chosen because of the considerable amount of information now available about its reactions with a variety of substrates.<sup>3</sup> It is the purpose of the present paper to investigate hydrogen abstraction from fluorinated aliphatic acids by chlorodifluoromethyl radicals and the fate of the resulting fluorinated alkyl carboxy radical.

## EXPERIMENTAL

### Materials

1,3-Dichlorotetrafluoroacetone, trifluoroacetic acid, pentafluoropropionic acid, heptafluorobutyric acid and chlorodifluoroacetic acid were obtained from Koch-Light and Co. Ltd. They were distilled before use and their purity checked by mass spectrometry.

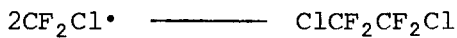
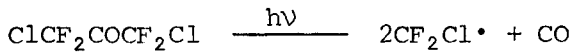
### Procedure

All photolyses were carried out in silica cells attached to a conventional vacuum line. 60mm pressure of 1,3-dichloro-

tetrafluoroacetone and 60mm of the appropriate acid were introduced into the reaction vessel at a temperature of 120°. The cell was irradiated with light from a medium pressure mercury vapour lamp (Philips HPK), filtered so as to isolate the 313nm line and so ensure that only the ketone absorbed radiation. The photolysis was carried out at a variety of temperatures above 120° for a fixed period of 1 hour. After irradiation, the contents of the reaction cell were frozen into a U tube by immersing it in liquid air, and the non-condensable gases pumped to a McLeod gauge. Analysis of a sample of the non-condensable gases by mass spectrometry gave a spectrum of pure carbon monoxide. The pressure of carbon monoxide was therefore used as a measure of the degree of conversion. The condensable products were then vapourised and transferred to the inlet system of a gas chromatograph for analysis. Samples of the effluent from the base of the gas chromatographic column were analysed using an A.E.I. MS9 mass spectrometer and shown to be mixtures of chlorodifluoromethane and 1,2-dichlorotetrafluoroethane. The amounts of these two species present were measured by comparison of gas chromatographic peak areas with those obtained using known pressures of authentic specimens.

## RESULTS AND DISCUSSION

The only products passing through the gas chromatograph were 1,2-dichlorotetrafluoroethane which is produced by the dimerisation of the chlorodifluoromethyl radicals



and chlorodifluoromethane which is produced by hydrogen abstraction



The rate constant for the dimerisation of chlorodifluoromethyl radicals is known<sup>6</sup> and so the rate constant for the hydrogen abstraction reaction can be calculated. From the equation

$$\frac{\text{Rate}_{\text{CF}_2\text{ClH}}}{\text{Rate}_{\text{C}_2\text{F}_4\text{Cl}_2}^{\frac{1}{2}}} = \frac{k_{\text{T}}}{k_{\text{C}}^{\frac{1}{2}}} [\text{RCOOH}]$$

and expanding  $k_{\text{T}}$  and  $k_{\text{C}}$  in the Arrhenius form values for the energies of activation for the hydrogen abstraction reaction can be calculated. The results for the four different acids are given in the following table.

Table 1

Arrhenius Factors for Hydrogen Abstraction from Fluorinated Aliphatic Acids

Acid	E kcalmole <sup>-1</sup>	A ℓmole <sup>-1</sup> sec <sup>-1</sup> x 10 <sup>5</sup>
Trifluoroacetic acid	3.3 ± 0.4	0.6 ± 0.3
Pentafluoropropionic acid	7.5 ± 0.3	3.5 ± 0.3
Dichlorofluoroacetic acid	4.9 ± 0.7	2.2 ± 0.4
Heptafluorobutyric acid	3.0 ± 0.3	1.3 ± 0.2

The values for the energy of activation are low when compared with the value of 13.3 kcalmole<sup>-1</sup> obtained for the corresponding hydrogen abstraction reaction from fluoroform.<sup>4</sup> This is unexpected when one considers the large bond strength in aliphatic acids and the possibility of an alternative mode of production of chlorodifluoromethane is not ruled out. However, the most surprising feature of the investigation was the total absence of carbon dioxide from the reaction product mixture and the failure to observe any product which could arise by the interaction of trifluoromethyl radicals. This suggests that the halogenated alkyl carboxy radicals are more stable than had previously been considered and that

they survive the elevated temperatures used in studying the abstraction reaction ( $120^{\circ}$  -  $270^{\circ}$ ). Dissociation of the fluorinated alkyl carboxy radical in the Kolbe reaction must therefore be promoted by the recombination energy made available at the electrode. In the case of the photolysis of perfluoroacetic anhydride the energy available in the quantum of light absorbed must be sufficient to break the carbon-carbon bond and to provide an excess in the resulting  $\text{CF}_3\text{COO}^{\bullet}$  radical sufficient to ensure its decomposition. If the failure to detect the decomposition product of the fluorinated alkyl carboxy radicals is due to their thermal stability then this behaviour is in contrast with that of the corresponding fluorinated acyl radicals which decompose spontaneously.

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