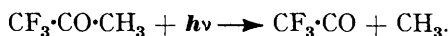


### 817. The Photolysis of Trifluoroacetone.

By E. A. DAWIDOWICZ and C. R. PATRICK.

The photolysis of trifluoroacetone has been re-investigated. Contrary to former conclusions it is shown that an important primary act of photolysis produces the acetyl and trifluoromethyl radicals. No product arising from the trifluoroacetyl radical was found. Other features of the overall reaction are discussed.

SIEGER and CALVERT<sup>1</sup> concluded from a study of the photolysis of trifluoroacetone, using light of wavelength of 3130 Å, that the predominant primary process is:



There is considerable evidence that the acetyl radical is a relatively stable entity, and is formed in the photolysis of acetone and acetaldehyde.<sup>2-4</sup> Products formed from trifluoroacetyl and other perhalogenoacetyl radicals have not generally been detected amongst the products of photolysis of appropriate ketones,<sup>5-8</sup> although recently Whittle and Tucker<sup>9</sup> have suggested that the trifluoroacetyl radical is formed in the photolysis of hexafluoroacetone. As hexafluorobiacetyl is known to be a relatively stable compound,<sup>10</sup> and there is no reason to suppose that there is an exceptionally low efficiency for the recombination of trifluoroacetyl radicals, it is difficult to understand why this compound is not formed, unless the lifetime of the trifluoroacetyl radical is small compared with that of acetyl radicals; in view of this, the suggested process appears unusual. Furthermore, the analysis of products reported by Sieger and Calvert accounts for only about two-thirds of the ketone decomposed. It was therefore decided to reinvestigate the photolysis of trifluoroacetone so as to obtain more information about the primary act of photolysis.

#### EXPERIMENTAL

Trifluoroacetone was prepared by McLoughlin's method.<sup>11</sup> The crude product always contained some of trifluoroacetone hydrate; this was difficult to dehydrate even with fresh phosphorus pentoxide. The ketone was purified by vacuum-distillation and its purity was assessed by gas chromatography and mass spectrometry. The hydrate could be detected, when present, by gas chromatography. It was found impossible to distinguish between the mass-spectrometric cracking pattern of the ketone and that of its hydrate.

The ultraviolet spectrum of the ketone vapour showed a maximum at 2780 Å ( $\epsilon = 8 \text{ mole}^{-1} \text{ cm}^{-1}$ ). The extinction coefficient fell to about half its maximum value at about 2500 Å and 3100 Å. This is in good agreement with the results of Ausloos and Mourad.<sup>12</sup> Reactions were carried out in a silica vessel closed by Springham greaseless taps. The cell was fitted at the further side of the taps with cones so that it could be detached from the vacuum line and attached to the inlet of the mass spectrometer or a gas-chromatography column. The cell was irradiated by a medium-pressure mercury-vapour lamp (Phillips 125w type HPK). The average temperatures of the vessel during these experiments were within  $45 \pm 5^\circ$ . Satisfactory resolution of the product was obtained by using a gas-chromatography column at room temperature with dinonyl phthalate as stationary phase.

<sup>1</sup> Sieger and Calvert, *J. Amer. Chem. Soc.*, 1954, **76**, 5197.

<sup>2</sup> Barak and Style, *Nature*, 1935, **135**, 307.

<sup>3</sup> Davis, *Chem. Rev.*, 1947, **40**, 207.

<sup>4</sup> Blacet and Blaedel, *J. Amer. Chem. Soc.*, 1940, **62**, 3374.

<sup>5</sup> Ayscough and Steacie, *Proc. Roy. Soc.*, 1956, *A*, **234**, 476.

<sup>6</sup> Giacometti, Okabe, Price, and Steacie, *Canad. J. Chem.*, 1960, **38**, 104.

<sup>7</sup> Bowles, Derbyshire, Majer, and Patrick, *Nature*, 1960, **185**, 683.

<sup>8</sup> Bowles, Majer, and Robb, *Trans. Faraday Soc.*, 1962, **58**, 2394.

<sup>9</sup> Tucker and Whittle, *Proc. Chem. Soc.*, 1963, 93.

<sup>10</sup> Moore and Clark, *Proceedings of 2nd International Symposium on Fluorine Chemistry*, 1962, p. 285.

<sup>11</sup> McLoughlin, Ph.D. Thesis, Birmingham University, 1959.

<sup>12</sup> Ausloos and Mourad, *J. Phys. Chem.*, 1961, **65**, 1519.

The products were analysed with an AEI MS2 mass spectrometer. Quantitative measurements were made by using the following mass peaks:  $m/e = 86$  ( $\text{CH}_3\cdot\text{CO}$ ) $_2^+$  for biacetyl;  $m/e = 30$  ( $\text{C}_2\text{H}_6$ ) $^+$  for ethane;  $m/e = 119$  ( $\text{C}_2\text{F}_6$ ) $^+$  for hexafluoroethane;  $m/e = 65$  ( $\text{CH}_3\cdot\text{CF}_2$ ) $^+$  for 1,1,1-trifluoroethane;  $m/e = 58$  ( $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2$ ) $^+$  for acetone; and  $m/e = 97$  ( $\text{CF}_3\cdot\text{CO}$ ) $^+$  for trifluoroacetone.

## RESULTS

The following compounds were found in the reaction mixture: biacetyl, ethane, hexafluoroethane, 1,1,1-trifluoroethane, acetone, 2,2-difluoropropane, and a dimer of trifluoroacetone. Methane and trifluoromethane were present in small amounts revealed by gas chromatography, but these could not be unambiguously detected by mass spectrometry. After a number of runs a brown substance (3.6 mg.) (representing less than 5% of the total amount of ketone photolysed) was found on the walls of the vessel.

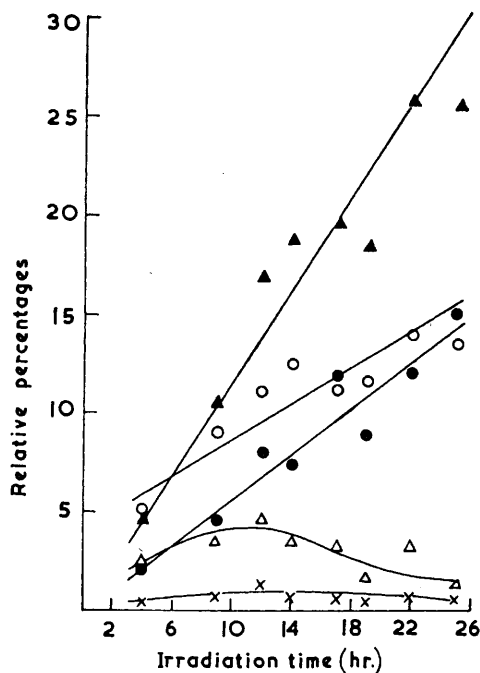


FIG. 1. Variations of relative amounts of products with time of irradiation.

[ $\times$ ,  $(\text{CH}_3\cdot\text{CO})_2$ ;  $\Delta$ ,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ ;  $\bullet$ ,  $\text{C}_2\text{H}_6$ ;  $\circ$ ,  $\text{C}_2\text{F}_6$ ;  $\blacktriangle$ ,  $\text{CF}_3\cdot\text{CH}_3$ .]

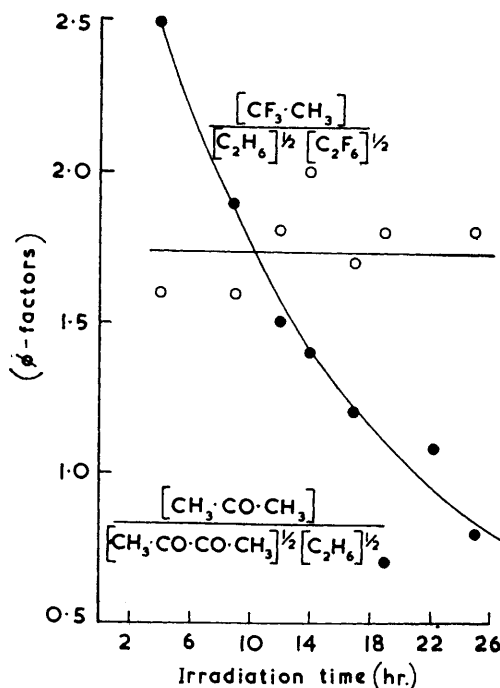


FIG. 2. Variations of  $\phi_1$  and of  $\phi_2$  with time of irradiation.

The presence of biacetyl confirms the view that the acetyl radical is formed in the reaction system. This radical must be produced in the primary process  $\text{CF}_3\cdot\text{CO}\cdot\text{CH}_3 + h\nu \rightarrow \text{CH}_3\cdot\text{CO} + \text{CF}_3\cdot$ . The observed significant conversion (about 20%) of the ketone into products containing the acetyl radical, rather than the trifluoroacetyl or simply methyl residues, demonstrates that the process is an important mode of photolytic breakdown of the ketone. It is impossible to ascertain from these experiments whether the methyl radical is formed directly in an alternative type of photolytic act or by the decomposition of acetyl radicals. This important finding is contrary to that of Sieger and Calvert, who observed that the total yield of products containing the trifluoromethyl radical was less by about one-half than those containing the methyl radical. In this investigation, the total amount of products containing the methyl (including the acetyl) residue and those containing the trifluoromethyl residue were, within experimental error, equal, particularly

at low conversions. Products containing the trifluoroacetyl residue, although sought, were not detected.

The relative amounts of the major products formed were measured as a function of both duration of reaction (see Fig. 1) and of initial ketone pressure (see Fig. 3). Whereas the amounts of the three ethanes increased with time of reaction, those of acetone and biacetyl did not. The behaviour of the amount of acetone is striking in that it passes through a maximum as the irradiation time is increased; a probable explanation is that both acetone and biacetyl are consumed in some reaction. Although photolysis of these two products is possible, it is more plausible to suppose that these are consumed in abstraction reactions with the several radical species that are present in the reaction system. Some evidence in support of this contention is available from the consideration of the relative rates of abstraction from these compounds and from ethane reported by several authors.<sup>13</sup> It is, however, very difficult to understand why the amount of acetone passes through a maximum as the duration of the reaction increases. It would seem impossible to do so on the basis of this material's either being photolysed or disappearing in abstraction reactions.

The complexity of the rates of formation of the compounds is reflected by the behaviour of the quantities \*

$$\phi_1 = [\text{CF}_3 \cdot \text{CH}_3] / [\text{C}_2\text{H}_6]^{1/2} [\text{C}_2\text{F}_6]^{1/2}$$

$$\text{and } \phi_2 = [\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3] / [\text{CH}_3 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}_3]^{1/2} [\text{C}_2\text{H}_6]^{1/2},$$

where the quantities in square brackets are the concentrations of the appropriate products formed at the chosen times of reaction (proportional to the average rates of formation of these substances during the period of reaction). These quantities ( $\phi$ -factors), which measure the preference for cross-combination of dissimilar radicals, should on simple statistical grounds equal two when no energy of activation is involved; considerable experimental evidence obtained in gas-phase studies conforms closely to this ideal behaviour.<sup>14</sup> The values of these quantities are plotted in Fig. 2 as a function of the duration of the reaction. Whereas  $\phi_1$  is constant, and is about 1.7,  $\phi_2$  varies considerably, which is contrary not only to simple statistical theory, but also to the more general requirement that

$$\phi_2 = k_2 / (k_3 k_4)^{1/2}$$

(where the quantities  $k$  are rate coefficients for the reactions between the radicals denoted by subscripts \*) should be constant. Wijnen has reported a value of 1.7 for this quantity.<sup>15</sup>

The variation of the rates of formation of the several products with initial pressure of ketone is represented in Fig. 3, which shows that the rate of photolysis decreases with increasing pressure, probably because of a collisional deactivation of the photoexcited ketone similar to that found in the photolysis of hexafluoroacetone,<sup>5</sup> and perfluorodiethyl ketone.<sup>6</sup>

The differential effect of the pressure of ketone on the rates of formation of the several products is shown by the variation of the apparent  $\phi$  values shown in Fig. 4. The constancy of the factor  $\phi_1$  suggests that the rates of formation of the ethanes are similar to one another, but the variation of  $\phi_2$  shows that the rates of formation of the products containing the acetyl residue are affected differently by the variation of pressure.

The constancy in these experiments of the quantity  $\phi_1$  is significant. The value

\* Subscripts are used:

1, for reaction between  $\text{CH}_3$  and  $\text{CF}_3$ .

2, for reaction between  $\text{CH}_3 \cdot \text{CO}$  and  $\text{CH}_3$ .

3, for reaction between  $\text{CH}_3$  and  $\text{CH}_3$ .

4, for reaction between  $\text{CH}_3 \cdot \text{CO}$  and  $\text{CH}_3 \cdot \text{CO}$ .

<sup>13</sup> Trotman-Dickenson, *Quart. Rev.*, 1953, **7**, 198.

<sup>14</sup> Kerr and Trotman-Dickenson, "Progress in Reaction Kinetics," Vol. I., ed. Porter, Pergamon, 1961, p. 105.

<sup>15</sup> Wijnen, *J. Chem. Phys.*, 1958, **28**, 271.

obtained, 1.7, is smaller than that reported by Pritchard and Dacey,<sup>16</sup> namely 2.2, but is nevertheless close enough to be consistent with the latter value, the considerable experimental error of which must be taken into account. The variation of  $\phi_1$  with temperature reported by these workers has associated with it so great a scatter as to make very uncertain the energy of activation ascribed to the quantity in question. Furthermore, it may be noted that the supposed vindication<sup>17</sup> of the principle underlying the calculation of rate coefficients from the transition-state theory, which is claimed on the basis of these results, is invalid owing to its use of an erroneous value for the entropy of hexafluoroethane (for a more correct value see, for instance, ref. 18).

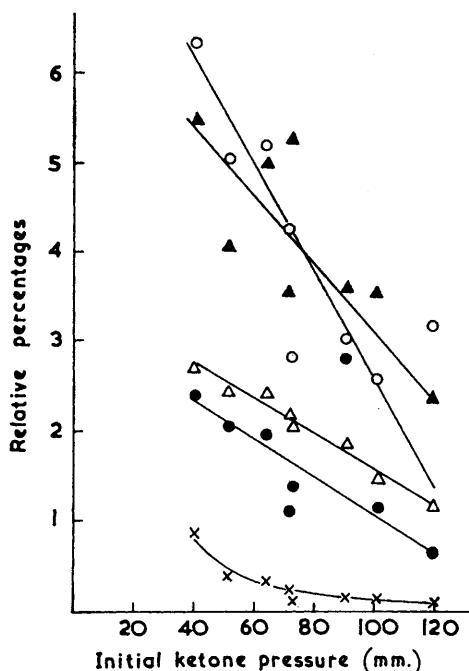


FIG. 3. Variations of relative amounts of products with initial pressure of trifluoroacetone.

[x,  $(\text{CH}_3\text{CO})_2$ ;  $\Delta$ ,  $\text{CH}_3\text{CO}\cdot\text{CH}_3$ ;  $\bullet$ ,  $\text{C}_2\text{H}_6$ ;  $\circ$ ,  $\text{C}_2\text{F}_6$ ;  $\blacktriangle$ ,  $\text{CF}_3\cdot\text{CH}_3$ .]

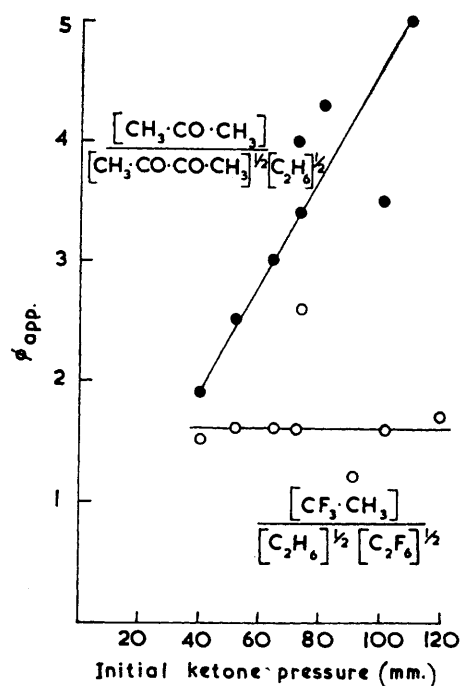


FIG. 4. Variations of  $\phi_1$  and of  $\phi_2$  with initial pressure of ketone.

The volatile dimer of trifluoroacetone, and the solid polymer, possibly of a polymer of trifluoroacetone, are of some interest, although little can be deduced about their structures or means of formation; the formation of similar dimers has not been reported in the photolysis of other ketones. The ultraviolet spectrum of the polymer, in ethanol, showed a continuously rising absorption as the wavelength was reduced below about 3500 Å. Involatile products have been found to accumulate in reaction systems in which 1,3-dichlorotetrafluoroacetone has been photolysed; these have been stated tentatively to be polytetrafluoroethylene, formed by the condensation of difluoromethylene radicals in the reaction system.<sup>19</sup> It is difficult to suggest a structure for the dimer. No information about it was available from any source other than from the mass-spectrometric cracking pattern. It was detected merely by finding in the cracking pattern of the reaction products

<sup>16</sup> Pritchard and Dacey, *Canad. J. Chem.*, 1960, **38**, 182.

<sup>17</sup> Pritchard, Pritchard, Miller, and Dacey, *Canad. J. Chem.*, 1960, **38**, 319.

<sup>18</sup> Bryant, *J. Polymer Sci.*, 1962, **56**, 277.

<sup>19</sup> Bowles, Majer, and Robb, *Trans. Faraday Soc.*, 1962, **58**, 1541.

a component having the appropriate  $m/e$  ratio for the ion arising from such a dimer; this ion was absent from the cracking pattern obtained when unirradiated trifluoroacetone was examined.

An interesting minor product observed in these reactions is 2,2-difluoropropane, which was detected by using the ion  $m/e = 61$  ( $C_3H_6F^+$ ). 1,3-Dichlorohexafluoropropane was found among the products of photolysis of 1,3-dichlorotetrafluoroacetone by Bowles, Majer, and Robb.<sup>19</sup> This was said to be formed by the addition of difluoromethylene radicals to chlorodifluoromethyl radicals to form a chlorotetrafluoroethyl radical, which subsequently reacted with a chlorodifluoromethyl radical. The difluoromethylene radicals were believed to be formed in the reaction system of Bowles, Majer, and Robb by the disproportionation of chlorodifluoromethyl radicals. A similar sequence of reactions could take place in the present reaction system. It would, however, be necessary to suppose that the difluoromethylene radicals were formed by the disproportionation of trifluoromethyl radicals. Carbon tetrafluoride, which would also be formed, is difficult to detect by mass spectrometry in this system. The difficulty with the suggested reaction sequence is that it requires specifically that the difluoromethylene radical should react only with a methyl radical, and that the 1,1-difluoroethyl radical so produced, should react specifically with another methyl radical, since no other propanes containing more fluorine atoms, were observed. Such propanes would have been formed, had reactions with trifluoromethyl radicals in the suggested reaction sequence been possible. An alternative view is to suppose that the propanes are formed by reaction between a photo-excited molecule of the ketone and another molecule, but the actual mechanism would be difficult to ascertain owing to the relatively small extent to which this reaction proceeds.

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