282. *The Photolysis of Trifluoroacetaldehyde.*

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The photolysis of trifluoroacetaldehyde has been studied over a wide range of temperatures and pressures by use of light of wavelength 3130 Å. The products are trifluoromethane, hexafluoroethane, hydrogen, and carbon monoxide. Quantum yields of the first and last up to 60 indicate a chain reaction involving trifluoromethyl radicals produced in the initial step. An alternative primary process yielding trifluoromethane and carbon monoxide directly has a probable quantum efficiency of 0·021. Rate constants are given for the abstraction by trifluoromethyl radicals of hydrogen from trifluoroacetaldehyde, methane, *iso*butane, and acetaldehyde. The association of two trifluoromethyl radicals has been shown not to depend significantly upon total pressure down to 0·5 mm. Side reactions, evident at low temperatures, are discussed.

PHOTOLYTIC reactions of acetone, azomethane, and acetaldehyde have been extensively studied both for their own interest and to investigate the reactions of methyl radicals. Analogous interest lies in the fluorinated compounds and the photolyses of trifluoroacetone,[1] hexafluoroacetone,[2] and hexafluoroazomethane[3,4] have been reported. The first yields methyl radicals; the course of photolysis of the third is complicated by the addition of trifluoromethyl radicals to the parent compound, and evidently hexafluoroacetone is the best source of trifluoromethyl radicals. We now describe the photolysis of trifluoroacetaldehyde, $CF_3{\cdot}CHO$; evidence is given for the participation of trifluoromethyl radicals in a chain reaction, and a rate constant is evaluated for the abstraction of the hydrogen atom from the aldehyde. Figures are given[5] for the rate of abstraction by trifluoromethyl radicals of hydrogen from other compounds and, where there has been duplication, the results agree well with those[4,6] obtained from the use of other radical sources.

Combination of methyl radicals to form ethane requires the presence of a third body[7,8] which, by energy transfer on collision, stabilises the excited ethane molecule first formed. This led us to seek a similar pressure dependence in the combination of trifluoromethyl radicals. Down to pressures of 0·5 mm. of trifluoroacetaldehyde it appears that there are sufficient collisions to sustain the rate of formation of hexafluoroethane at the same value as at higher pressures. A lower limit is given for the mean life of the excited C_2F_6 complex.

Evidence is given for two primary processes, one leading directly to the formation of trifluoromethane and carbon monoxide, the other a dissociation into $CF_3{\cdot}$ and ${\cdot}CHO$ radicals.

As in the photolysis of acetaldehyde, the part played by the formyl radical, ${\cdot}CHO$, is not readily discerned. Quantum yields suggest that at high temperatures its main fate is decomposition with the subsequent appearance of a trifluoromethyl radical; there is little evidence about its fate at low temperatures: a wall reaction is possible. Just as a wall reaction leading to methane has been noticed at low temperatures in the photolysis of acetone and acetaldehyde, so it appears that a similar reaction yields trifluoromethane in addition to its homogeneous production.

[1] Sieger and Calvert, *J. Amer. Chem. Soc.*, 1954, **76**, 5197.
[2] Ayscough and Steacie, *Proc. Roy. Soc.*, 1956, *A*, **234**, 476.
[3] Dacey and Young, *J. Chem. Phys.*, 1955, **23**, 1302.
[4] Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849.
[5] Dodd and Smith, *Research*, 1956, **8**, s63.
[6] Ayscough, Polanyi, and Steacie, *Canad. J. Chem.*, 1955, **33**, 743; Ayscough and Steacie, *ibid.*, 1956, **34**, 106.
[7] Kistiakowsky and Roberts, *J. Chem. Phys.*, 1953, **21**, 1135.
[8] Dodd and Steacie, *Proc. Roy. Soc.*, 1954, *A*, **223**, 283.

EXPERIMENTAL

The photolysis of gaseous trifluoroacetaldehyde was studied with light predominantly of wavelength 3130 Å. The ranges of pressure, temperature, and intensity of light were respectively 0·5—100 mm., 18—400°, and (0·2—9) × 10^{-11} einsteins cm.$^{-3}$ sec.$^{-1}$. The two cylindrical reaction vessels (one of Vitreosil, length 8 cm., volume 237 c.c., and the other of Pyrex, length 80 cm., volume 1330 c.c.) were equipped with plane end-windows. Provision was made for the larger reaction system to be further increased in volume, for pressures below 2 mm., by including a 3 l. bulb through which the contents were circulated by a mercury-vapour pump. The vessels were electrically heated and the temperature was maintained within 1° along their lengths. Pressures were measured by a constant-volume mercury manometer, a magnifying manometer (mercury and dibutyl phthalate, magnification about ×10), and a McLeod gauge. Reaction times varied from a few minutes to 48 hr.

The light source was a British Thomson-Houston ME/D 250 w high-pressure mercury arc. Aqueous potassium chromate was used as a filter. A Pyrex plate was used as an additional filter in front of the Vitreosil vessel. The ultraviolet absorption spectrum of trifluoroacetaldehyde begins at about 3500 Å and rises to a broad maximum at about 3020 Å (ε 5·8 at 3020 and 5·3 at 3130 Å in hexane) with a second region of strong absorption commencing at 2450 Å. From the absorption spectrum of the aldehyde, the known transmission of the filters, and the measured output of the lamp it was estimated that virtually all the absorption took place in the reaction system between 2900 and 3400 Å, with 80% in the range 3070 to 3200 Å.

Light was collected either by a quartz flask filled with water or (for most of the work) by a large polished aluminium reflector giving a slightly converging beam. The illuminated volumes were taken to be equal to the volumes of the reaction vessels, not including side-arms. Relative light intensities were measured with an EEL selenium cell (screened by Chance OX7 filter glass and a filter solution of nickel and cobalt sulphates) whose area was sufficient to receive most of the light passing through the vessel. The amount of light absorbed was calculated, with corrections for reflection from the rear windows of the vessel and the furnace, from the transmitted intensity by interpolation in a Beer's-law graph. Calibration was made against the quantum yield of carbon monoxide formation (Φ_{CO} = 1·0) in the photolysis of acetone vapour at 125°. The calibration was frequently checked and was revised whenever the system was adjusted. Relative to the standard the accuracy of measurement was of the order of ±5%.

Materials.—Trifluoroacetaldehyde was prepared from trifluoroacetic acid by Rosenmund reduction of the acid chloride,[9] in the preparation of which [10] it was found best to maintain the mixture of the acid and benzoyl chloride at 60° until most of the acid chloride had been evolved (about 1 hr.) and then to raise the temperature to 150°, instead of raising the temperature gradually during 24 hr. The acid chloride was condensed and allowed to evaporate (20 g. in 2—3 hr.) into a stream of hydrogen (10 l. per hr.), which carried it over the reducing palladised-asbestos catalyst. This was maintained at 230°; use of this temperature prevented production of the tar obtained at the temperature (250°) used by Brown and Musgrave.[9] To prevent production of hydrate the cylinder hydrogen was passed through palladised asbestos at 250° to remove oxygen, and thence through a trap cooled in liquid air. The colourless solid product, evidently polymeric, was warmed to 50° with a few drops of concentrated sulphuric acid and low-temperature fractionation of the evolved gas demonstrated the presence of hydrogen chloride. A subsequent fraction which distilled at 0·5 mm. at −130° was monomeric trifluoroacetaldehyde (b. p. −20°) which could now be condensed and kept without danger of polymerisation. That some polymerisation occurred on the inner surface of the apparatus at room temperature was evident from the formation of white feathery crystals of hydrate whenever leakage admitted moist air. Molecular-weight measurements and the infrared spectrum (identical with that published by Husted and Albrecht [11]) showed the sample to be substantially pure.

The mass spectrum of the aldehyde (Table 1) showed the expected peaks, including that corresponding to the $CF_3{\cdot}CHO^+$ ion and two rearrangement peaks at mass numbers 32 and 51. The latter is of unusual magnitude, but the absence of other unaccountable peaks and the constant

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[9] Brown and Musgrave, *J.*, 1952, 5049.

[10] Henne, Alm, and Smook, *J. Amer. Chem. Soc.*, 1948, **70**, 1968.

[11] Husted and Albrecht, *ibid.*, 1952, **74**, 5420.

relative intensity of the peak at mass number 51 convinced us that it could not be due to impurity in the aldehyde.

Methane (from a cylinder) was passed over active copper at 200°, condensed at −196°, and, after pumping, distilled at −184°. After several distillations mass-spectrometric analysis showed a satisfactory purity.

TABLE 1. *Mass spectrum of trifluoroacetaldehyde.*

m/e	Ion	Peak height (cm.)	*m/e*	Ion	Peak height (cm.)	*m/e*	Ion	Peak height (cm.)
19	F	1·0	31	CF	52·0	63	$CF_2{\cdot}CH$	3·5
20	HF	2·0	32	CFH	18·5	69	CF_3	80·8
24	C_2	1·1	43	C_2F	2·5	78	$CF_2{\cdot}CO$	5·7
25	C_2H	1·0	44	C_2FH	4·8	79	$CF_2{\cdot}CHO$	14·0
28	CO	36·1	50	CF_2	128·0	82	$CF_3{\cdot}CH$	2·2
29	CHO	414·0	51	CF_2H	240·0	98	$CF_3{\cdot}CHO$	34·4

*iso*Butane (98% pure) was subjected to trap-to-trap distillation between −130° and −196°.

Acetaldehyde was distilled from anhydrous calcium sulphate at 21° and then at low temperature *in vacuo*.

Trifluoromethane and hexafluoroethane (kindly supplied by Imperial Chemical Industries Limited, General Chemicals Division) were used to calibrate the mass spectrometer and were first roughly fractionated and then distilled at −160°/0·5 mm.

Analysis of Products.—Systematic analysis was made for carbon monoxide, hydrogen, trifluoromethane, and hexafluoroethane: these were separated by low-temperature fractionation, the fractions being measured by a combined Toepler pump and gas-burette. The non-condensable gases, carbon monoxide and hydrogen, were measured and then oxidised on copper oxide, the carbon monoxide being measured as dioxide. In experiments with added methane analysis of the non-condensable gases by this means was not feasible. Trifluoromethane and hexafluoroethane could not be separated since their vapour-pressure curves practically coincide; they formed the two constituents of a fraction taken off at −160° and relative proportions were then assessed by mass-spectrometry or infrared absorption. A mass-spectral analysis based on peaks 51 for trifluoromethane and 119 for hexafluoroethane was complicated by the fact that the sensitivity at the peak 119 was affected by the presence of trifluoromethane. Hexafluoroethane was therefore estimated from the residual peak at mass 69 after subtraction of the contribution from trifluoromethane. Reproduciblity to within 0·5% was obtained for normal mixtures but when the ratio $CF_3H : C_2F_6$ became as high as 30 : 1 the errors in mass-spectral analysis became large. Infrared absorption for trifluoromethane based on bands at 1250 cm.$^{-1}$ for hexafluoroethane and 1150 cm.$^{-1}$ for trifluoromethane was used satisfactorily for such mixtures.[12]

When ethane was expected among the products, small amounts could be detected in the fluorocarbon fraction as a difference between the total pressure and the combined partial pressures, measured spectrophotometrically, of trifluoromethane and hexafluoroethane. Mass-spectral examination of the products was made for carbon tetrafluoride, silicon tetrafluoride, and also for possible fluorocarbons of higher molecular weight.

Rates of production (mole cm.$^{-3}$ sec.$^{-1}$) are referred to as follows: carbon monoxide, R_{CO}; hydrogen, R_H; trifluoromethane, R_M; hexafluoroethane, R_E. Intensity of light absorbed, I_a, was measured in einsteins cm.$^{-3}$ sec.$^{-1}$.

RESULTS AND DISCUSSION

Photolysis above 150°.—Preliminary experiments indicated a reaction considerably slower than the photolysis of acetaldehyde under the same conditions. Non-condensable products were entirely carbon monoxide and small quantities of hydrogen. The only condensable products which could be identified were trifluoromethane and hexafluoroethane: their presence was first indicated by vapour-density measurements and was confirmed and their concentration estimated by their mass and infrared spectra.

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[12] Ayscough, *Canad. J. Chem.*, 1955, **33**, 1566.

Insignificant traces of silicon tetrafluoride were occasionally detected by mass spectometry : there was no real evidence of thermal decomposition or attack on Pyrex glass or silica at temperatures up to 400°.

Quantum yields as high as 60 indicated a chain reaction and the rate of formation of carbon monoxide was proportional to the square-root of the light intensity. This and the nature of the products suggested a reaction mechanism similar to that for acetaldehyde, *viz.* :

$$CF_3{\cdot}CHO + h\nu \longrightarrow CF_3{\cdot} + {\cdot}CHO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$CF_3{\cdot} + CF_3{\cdot}CHO \longrightarrow CF_3{\cdot}CO{\cdot} + CF_3H \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$CF_3{\cdot}CO{\cdot} \longrightarrow CF_3{\cdot} + CO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$CF_3{\cdot} + CF_3{\cdot} \longrightarrow C_2F_6 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

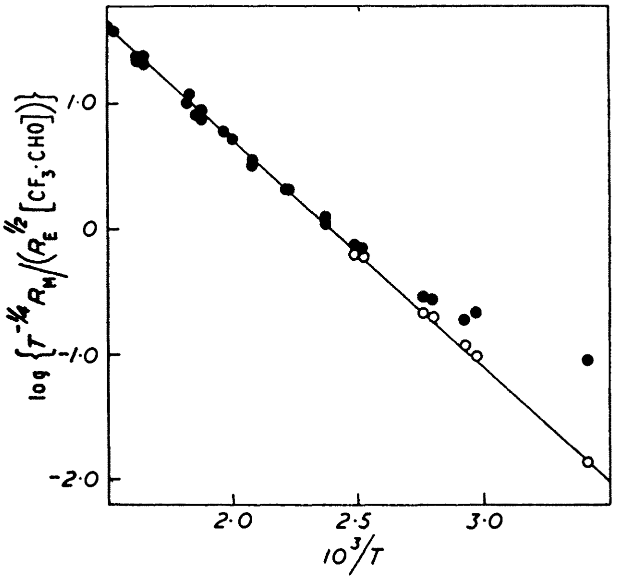

FIG. 1. *Dependence of* $R_M/R_E^{1/2}[CF_3{\cdot}CHO]$ *on temperature.*

●, uncorrected values.

Fluorine-abstraction reactions such as :

$$CF_3{\cdot} + CF_3{\cdot}CHO \longrightarrow CF_4 + {\cdot}CF_2{\cdot}CHO$$

or

$$CF_3{\cdot} + CF_3{\cdot} \longrightarrow CF_4 + CF_2{\cdot}$$

were discounted by the absence of carbon tetrafluoride, in agreement with similar findings with trifluoroacetone, hexafluoroacetone, and hexafluoroazomethane.

If reactions (2) and (4) are the sole contributors to the rates of formation of trifluoromethane and hexafluoroethane, then

$$\rho = R_M/(R_E^{1/2}[CF_3{\cdot}CHO]) = k_2/k_4^{1/2} \quad . \; . \; . \; . \; . \; . \; . \quad (i)$$

should be independent of light intensity and of aldehyde pressure and should conform to a linear Arrhenius plot of $\log_{10} \rho T^{-1/2}$ against $1/T$. At 262° and about 50 mm. pressure the values of ρ were 41·7 and 41·0 mole$^{-1/2}$ cm.$^{3/2}$ sec.$^{-1/2}$ for absorbed intensities $3{\cdot}22 \times 10^{-11}$ and $2{\cdot}2 \times 10^{-12}$ einsteins cm.$^{-3}$ sec.$^{-1}$, *i.e.*, a fourteen-fold intensity variation. At the same temperature, pressures of 9, 50, and 90 mm. gave values of ρ of 40·8, 41·2, and 41·1. Although below 150° there was some variation with pressure and a marked variation with intensity these figures agree with the above assumptions at the stated temperature. The

Arrhenius plot is shown in Fig. 1 and it is clear that there is linearity above 150°. The line corresponds to

$$k_2/k_4^{\frac{1}{2}} = (1{\cdot}95 \times 10^4)T^{\frac{1}{2}} \exp(-8200/\boldsymbol{R}T)$$

Thus $E_2 - \frac{1}{2}E_4 = 8{\cdot}2 \pm 0{\cdot}5$ kcal./mole and, collision diameters 5·7 and 4·0 Å for $CF_3{\cdot}CHO$ and CF_3 respectively being assumed, the ratio of the probability factors $P_2/P_4^{\frac{1}{2}} = 5{\cdot}3 \times 10^{-3}$. Ayscough[13] has shown that $E_4 < 1{\cdot}5$ kcal./mole and that $P_4 = 0{\cdot}16$ if $E_4 = 0$. Hence E_2 is close to 8·2 kcal./mole and P_4 to $2{\cdot}1 \times 10^{-3}$.

Abstraction of Hydrogen by Trifluoromethyl Radicals.—Photolysis of trifluoroacetaldehyde in the presence of compounds containing hydrogen, *viz.*, methane, *iso*butane, and acetaldehyde, gave a higher proportion of trifluoromethane in the products, clearly owing to an additional reaction

$$\mathrm{CF_3{\cdot} + RH \longrightarrow CF_3H + R{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2')$$

and consequently

$$\rho = R_{\mathrm{M}}/(R_{\mathrm{E}}^{\frac{1}{2}}[\mathrm{CF_3{\cdot}CHO}]) = k_2/k_4^{\frac{1}{2}} + k_{2'}[\mathrm{RH}]/(k_4^{\frac{1}{2}}[\mathrm{CF_3{\cdot}CHO}]) \quad . \; . \quad \text{(ii)}$$

Knowledge of $k_2/k_4^{\frac{1}{2}}$ allowed $k_{2'}/k_4^{\frac{1}{2}}$ to be deduced from the measurements of ρ in the presence of appropriate amounts of RH. Fig. 2 shows the Arrhenius plots for $k_{2'}/k_4^{\frac{1}{2}}$ for the compounds cited: the curves correspond to $k_{2'}/k_4^{\frac{1}{2}} = 1{\cdot}96 \times 10^4 T^{\frac{1}{2}} \exp(-10{,}400/\boldsymbol{R}T)$ for methane, $5{\cdot}4 \times 10^3 T^{\frac{1}{2}} \exp(-4500/\boldsymbol{R}T)$ for *iso*butane, and $2{\cdot}5 \times 10^3 T^{\frac{1}{2}} \exp(-4000/\boldsymbol{R}T)$ for acetaldehyde. The values of $E_{2'} - \frac{1}{2}E_4$ and of $P_{2'}/P_4^{\frac{1}{2}}$ have already been reported.[5] The excellent agreement between our values of $k_{2'}$ for methane and *iso*butane and those derived for the same compounds in experiments with hexafluoroacetone as the source of trifluoromethyl radicals[6] is valuable confirmation of our interpretation of the linear portion of Fig. 1.

In discussing the reaction of methyl radicals with tetrafluoroethylene, Danby and Raal[14] have postulated a reaction (2″) in which the trifluoromethyl radical induces the decomposition of acetaldehyde without itself suffering any change:

$$\mathrm{CF_3{\cdot} + CH_3{\cdot}CHO \longrightarrow CF_3{\cdot} + CH_4 + CO} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2'')$$

Their data indicate that $1{\cdot}41(k_{2''}/k_4^{\frac{1}{2}})(k_\beta^{\frac{1}{2}}/k_\alpha) = 12{\cdot}8$ (the ratio of their constants C''/C') where k_α and k_β refer to the reactions

$$\mathrm{CH_3{\cdot} + CH_3{\cdot}CHO \longrightarrow CH_4 + CH_3{\cdot}CO{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\alpha)$$

$$\mathrm{CH_3{\cdot} + CH_3{\cdot} \longrightarrow C_2H_6} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\beta)$$

$k_\alpha/k_\beta^{\frac{1}{2}}$ has been measured[15] and has a probable value at 300° of 191 mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$. Hence $k_{2''}/k_4^{\frac{1}{2}}$ would be $0{\cdot}707 \times 12{\cdot}8 \times 191 = 1730$ mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$, which is four times faster than the hydrogen-abstraction reaction (2′) between trifluoromethyl radicals and acetaldehyde which we have measured ($k_{2'}/k_4^{\frac{1}{2}} = 427$ at 300°). Unfortunately we did not analyse the non-condensable gases in our experiments with acetaldehyde, and therefore lack evidence on the occurrence of reaction (2″), which would produce four times as much methane as the extra trifluoromethane given by (2′). Nor is it clear that inclusion of reaction (2′) would significantly affect Danby and Raal's interpretation of their results (except to increase the complexity of the theoretical expressions) although they state that their experimental results require no loss of fluoromethyl radicals. They did not analyse for trifluoromethane.

Pressure-dependence of Trifluoromethyl Radical Combination.—If the combination of trifluoromethyl radicals required third-body collisions for deactivation of the active $C_2F_6^*$

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[13] Ayscough, *J. Chem. Phys.*, 1956, **24**, 944.

[14] Danby and Raal, *J.*, 1950, 1596.

[15] Volman and Brinton, *J. Chem. Phys.*, 1952, **20**, 1764; Ausloos and Steacie, *Canad. J. Chem.*, 1955, **33**, 31; Dodd, *ibid.*, 1955, **33**, 699.

complex there should be a pressure below which collisions are insufficiently frequent to sustain the rate constant $k_4 = R_E/[CF_3\cdot]^2$ at its high-pressure value. Consequently ρ should begin to increase as the aldehyde pressure is decreased and should show the form of dependence upon pressure which has been found [8] at low pressures in the photodecomposition of acetone where the recombination of methyl radicals is similarly involved. Experiments at 124° gave values of ρ which rose from 3·5 at high pressures to between 7 and 8 at 1 mm. When it later became apparent that a correction had to be applied, as discussed below, the corrected values, though showing a rather large spread at the low pressures, gave no indication of a trend to higher values. Eight corrected values between 0·75 and 7·5 mm. averaged 3·2 ± 0·7 and ten between 7·5 and 25 mm. averaged 2·9 ± 0·1. At 209°, where the correction is negligible, values were found as in Table 2.

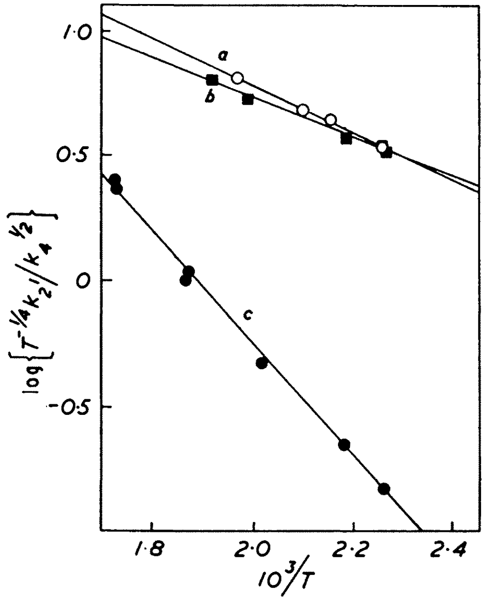

FIG. 2. *Abstraction of hydrogen by trifluoromethyl radicals from* (a) iso*butane,* (b) *acetaldehyde, and* (c) *methane.*

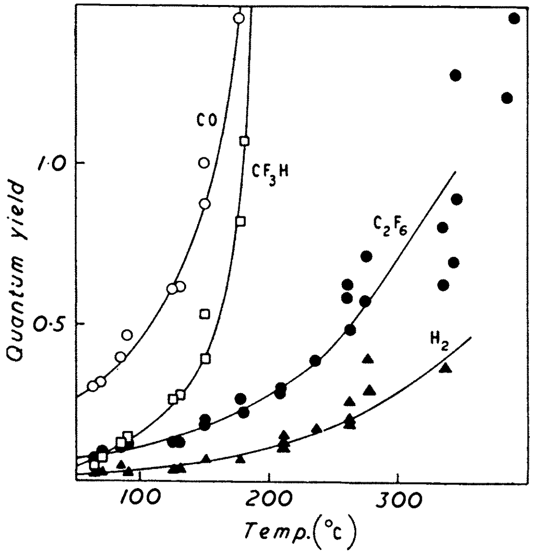

FIG. 3. *Variation of quantum yields with temperature.*

TABLE 2. *Pressure variation at* 209°.

$CF_3\cdot CHO$ (mm.) ...	42	30	27	8·9	6·9	3·1	2·4	1·1	0·5
ρ	16·2	16·6	17·2	17·5	19·9	19·3	19·2	19·3	19·7

A slight increase in ρ can be seen but not the appreciable increase found for methyl radicals at 0·5 mm. of acetone. There is thus no real evidence of dependence upon pressure down to 0·5 mm. of aldehyde. The data of Table 2 imply that the unimolecular rate constant for decomposition of the active C_2F_6* complex at 209° is less than $3{\cdot}3 \times 10^6$ sec.$^{-1}$, or that the mean life of the complex is greater than 3×10^{-7} sec. This may be compared with the lower limit of $1{\cdot}6 \times 10^{-8}$ sec. estimated [8] for the active C_2H_6* complex at 247°. It is plausible to suppose that the longer lifetime of the C_2F_6* complex is related to the fact that in hexafluoroethane all other vibrational levels lie close to or below that involving predominantly the stretching of the carbon–carbon bond. The accumulation of critical energy in that mode is therefore less likely than it is in the case of hexafluoroethane where a larger number of the other vibrational levels lie above that attributed to C–C stretching.

Quantum Yields.—The quantum yields of carbon monoxide, trifluoromethane, hexafluoroethane, and hydrogen at various temperatures are shown in Fig. 3. These were determined in the same experiments as recorded in Fig. 1, mainly at about the same pressure of aldehyde (30—40 mm.) and at intensities in the range (1·6—5) × 10^{-11} einsteins cm.$^{-3}$ sec.$^{-1}$. Quantum yields at the room temperature at various intensities are given in Table 3.

TABLE 3. *Quantum yields at room temperature.*

$I_a \times 10^{11}$	8·66	3·94	1·45	0·57	0·55	0·44	0·155
CO	0·18	0·17	0·18	0·20	0·19	0·19	0·23
CF_3H	0·030	0·033	0·040	0·055	0·057	0·064	0·073
C_2F_6	0·060	0·054	0·055	0·055	0·055	0·062	0·064
H_2	0·016	0·019	0·013	—	0·016	0·014	0·018

The yields, Φ_E, of hexafluoroethane are of particular interest. It is not clear why the spread of the values should be so great above 250° and we are not prepared to defend the three values greater than unity. There is, however, sufficient evidence that $\Phi_E > \frac{1}{2}$ above about 250°, although the sequence of reactions (1)—(4) requires that $\Phi_E = k_1 \leqslant 0{\cdot}5$. There is evidently a further source of trifluoromethyl radicals and reactions (5) and (6) are suggested.

$$\cdot CHO \longrightarrow H\cdot + CO \qquad \ldots\ldots\ldots\ldots \qquad (5)$$

$$H\cdot + CF_3\cdot CHO \longrightarrow H_2 + CF_3\cdot CO\cdot \qquad \ldots\ldots\ldots\ldots \qquad (6)$$

If reactions (5), (6), and (3), respectively, are the only fates of the species ·CHO, H·, and CF_3·CO·, then $\Phi_E = k_1 \leqslant 1$. Thus k_1 is probably close to unity above 350°. The quantum yield of hydrogen, Φ_H, should then be equal to Φ_E but we were not able to measure this with even moderate accuracy above about 280°.

At lower temperatures Φ_E would be expected to fall to half its value at high temperatures, since reaction (5), which strongly depends upon temperature (E_5 = 14—15 kcal./mole), will be replaced by an alternative reaction for formyl radicals : for example, the wall reaction postulated by Calvert and Steacie [16] as occurring in the photolysis of formaldehyde. The observed value, 0·06, of Φ_E at room temperature implies not only that reactions (5) and (6) no longer participate, but that either k_1 is itself small ($= 2\Phi_E = 0{\cdot}12$) at 20° or trifluoromethyl radicals are consumed in reactions other than (4). We were able to detect at about 4465 Å some fluorescence arising from irradiation of the aldehyde at 3130 Å. This implies that $k_1 < 1$; but there is also evidence discussed below for other reactions in which trifluoromethyl radicals are lost.

The deviation from linearity which can be seen in Fig. 1 at temperatures below 150° is an indication of a significant contribution to R_M from a reaction other than (2) and less dependent upon temperature. Such would be a primary intramolecular rearrangement, as is also probable in the photolysis of acetaldehyde, *viz.* :

$$CF_3\cdot CHO + h\nu \longrightarrow CF_3H + CO \qquad \ldots\ldots\ldots\ldots \qquad (1')$$

This would naturally imply that $k_1 \leqslant 1$. It would also require that ρ be proportional to intensity, or that :

$$\Phi_M = R_M/I_a = (k_2/k_4^{\frac{1}{2}})R_E^{\frac{1}{2}}[CF_3\cdot CHO]/I_a + k_{1'} \qquad \ldots\ldots \qquad (iii)$$

Hence a plot of R_M/I_a against $R_E^{\frac{1}{2}}[CF_3\cdot CHO]/I_a$ should give a straight line of slope $k_2/k_4^{\frac{1}{2}}$ and intercept $k_{1'}$. The results in Table 3 have been tested in this way (Fig. 4, curve *A*). Equation (iii) is apparently obeyed, the intercept having the value $k_{1'} = 0{\cdot}021$. On the other hand the slope (0·148) is greater than the value (0·063) of $k_2/k_4^{\frac{1}{2}}$ which is obtained by extrapolation from the linear portion of Fig. 1. Curve *C* represents equation (iii) with $k_2/k_4^{\frac{1}{2}} = 0{\cdot}063$. The quantity $\Phi_M - (k/k_4^{\frac{1}{2}})R_E^{\frac{1}{2}}[CF_3\cdot CHO]/I_a$ should be constant ($= k_{1'}$)

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[16] Calvert and Steacie, *J. Chem. Phys.*, 1951, **19**, 176.

but in Fig. 4, curve *B*, is shown to be proportional to $R_E^{\frac{1}{2}}[CF_3{\cdot}CHO]/I_a$. The earlier discussion has demonstrated that reaction (4) is the only significant source of hexfluoroethane at higher temperatures : it is unlikely that it should not be so at lower temperatures and therefore $R_E^{\frac{1}{2}}$ is a measure of the concentration of trifluoromethyl radicals. Thus there is implied a third reaction leading to trifluoromethane whose rate is proportional to

$$CF_3{\cdot} + {\cdot}CHO \longrightarrow CF_3H + CO \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$CHO + CF_3{\cdot}CHO \longrightarrow CF_3H + CO + {\cdot}CHO \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

$[CF_3]$. (The dependence on aldehyde pressure was not examined, for all the experiments were performed at one pressure.) Reactions such as (7) and (8) do not explain this proportionality, which suggests a reaction (9) between trifluoromethyl radicals and aldehyde adsorbed on the walls of the vessel :

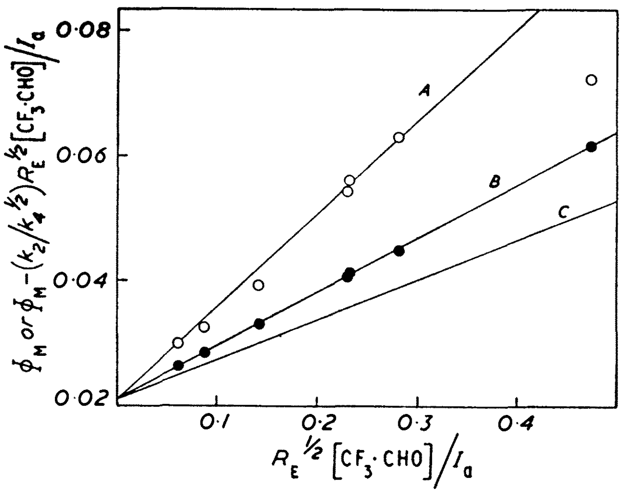

FIG. 4. *Dependence of quantum yield of trifluoromethane upon intensity.*

A, eqn. (iii), slope 0·148.
B, eqn. (iv), slope 0·085.
C, eqn. (iii), slope 0·063.

$$CF_3{\cdot} + CF_3{\cdot}CHO \text{ (wall)} \longrightarrow CF_3H + \text{products} \quad . \; . \; . \; . \; . \; . \quad (9)$$

Equation (iii) then becomes :

$$\Phi_M - (k_2/k_4^{\frac{1}{2}})R_E^{\frac{1}{2}}[CF_3{\cdot}CHO]/I_a = k_{1'} + \{k_9/(k_4^{\frac{1}{2}}[CF_3{\cdot}CHO])\} \times \{R_E^{\frac{1}{2}}[CF_3{\cdot}CHO]/I_a\} \quad \text{(iv)}$$

The slope (0·085) of curve *B* in Fig. 4, the aldehyde concentration ($2{\cdot}33 \times 10^{-6}$ mole cm.$^{-3}$), and the value of k_4 ($2{\cdot}34 \times 10^{13}$ mole^{-1} cm.^{3} sec.$^{-1}$ [13]) permit a calculation of $k_9 = 0{\cdot}96$ sec.$^{-1}$. This can be compared with the value, 422 sec.$^{-1}$, obtained if every trifluoromethyl radical were to react at every collision with the wall (geometrical area 154 cm.^{2}) in a volume of 237 cm.^{3}. Defined as $R_M/[CF_3{\cdot}]$ for reaction (9), k_9 includes the fraction of surface occupied by adsorbed aldehyde as well as the likelihood of reaction of a radical with an adsorbed aldehyde molecule. The ratio $0{\cdot}96/422 = 2{\cdot}3 \times 10^{-3}$ therefore seems entirely reasonable. At increased temperatures a decrease in the fraction adsorbed and an increase in the reaction rate would act in opposition and thus k_9 should be more or less independent of temperature. Above 20° the deviations in ρ were not measured with sufficient accuracy to allow reliable estimates of k_9. That the deviations vary little with temperature and become relatively unimportant above 150° is shown by applying the above value of k_9 (obtained at room temperature) as a correction [by use of equation (iv)] to all the points in Fig. 1 below 150°. The open points thus obtained lie well on the extrapolated Arrhenius line for $k_2/k_4^{\frac{1}{2}}$.

The wall reaction (9) provides an alternative fate for trifluoromethyl radicals which would reduce Φ_E at room temperature: its effect is small. Thus, in a typical experiment ($I_a = 1{\cdot}45$ in Table 3) the contributions to Φ_M from reactions (1′), (2), and (9) are respectively 0·021, 0·008, and 0·011 and hence $\Phi_E = \frac{1}{2}(k_1 - 0{\cdot}011) = 0{\cdot}055$. k_1 is thus estimated to be 0·12, but the term arising from (9) is small as is necessary to agree with the fact that Φ_E does not vary significantly with intensity. On this interpretation we should expect the quantum yield of carbon monoxide, arising from reactions (1′), (3), and probably (9), to be greater than Φ_M by an amount (not greater than k_1) which depends upon the fate of the ·CHO radicals. The results from the same experiment thus give $k_1 \geqslant 0{\cdot}18 - 0{\cdot}04 = 0{\cdot}14$. Since k_1 obtained from Φ_E has about the same value, it is implied that the major contribution to Φ_{CO} is from the formyl radicals all of which must appear as carbon monoxide. Moreover, since $\Phi_H = 0{\cdot}016$ (average), they must do so by a reaction path such that only a fifth of them yield molecular hydrogen. It is not clear how this may be.

Similar reasoning applied to other reactions which might be suggested for the low value of Φ_E does not lead to any greater value of k_1. Thus if it is assumed that reaction (3) does not occur at low temperatures but that (10) does, the value of k_1 obtained for Φ_E is 0·13. The effect of (10) is no greater because the yield of $CF_3{\cdot}CO{\cdot}$ radicals is only equal to the contribution, 0·008, of reaction (2) to Φ_M. Ayscough and Steacie[2] give some evidence for the immediate decomposition of any trifluoroacetyl radicals which may be formed photolytically from hexafluoroacetone. Reaction (10) is evidently not required to explain our present results. No evidence could be found for hexafluoroacetone, which would be produced in (10), on mass-spectrometric examination of the higher-boiling products.

$$CF_3{\cdot} + CF_3{\cdot}CO \longrightarrow CF_3{\cdot}CO{\cdot}CF_3 \qquad \text{. . . . . (10)}$$

The above arguments based upon material balance show that the yields of carbon monoxide agree with those of trifluoromethane and hexafluoroethane but that the apparent efficiency of the primary split is low. We did not study the effect of inert gases on quantum yield and there is insufficient evidence to show whether a relatively stable activated complex, $CF_3{\cdot}CHO^*$, is responsible for a low value of k_1 or whether there is a considerable degree of recombination between trifluoromethyl and formyl radicals.

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