

The Recombination of Trifluoromethyl Radicals at High Temperature

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THE recombination of methyl radicals at temperatures around 500° is the subject of some debate.¹ Whereas in the decomposition of acetaldehyde^{2,3} this reaction appears to be of third order, results on the decomposition of ethane⁴⁻⁶ indicate that the recombination should be of second order.

Possibly in part this is due to the differences between the energy levels available for coupling with the different third bodies.

The recombination of trifluoromethyl radicals has been examined in studies on the thermal decomposition of trifluoroacetaldehyde.⁷ The

¹ M. H. Back, M. Eusuf, and K. J. Laidler, "Symposium on the Kinetics of Pyrolytic Reactions," University of Ottawa, 1964.

² M. Eusuf and K. J. Laidler, *Canad. J. Chem.*, 1964, **42**, 1851.

³ R. W. Dexter and A. B. Trenwith, *J. Chem. Soc.*, 1964, 5459.

⁴ C. P. Quinn, *Proc. Roy. Soc.*, 1963, *A*, **275**, 190.

⁵ M. C. Lin and M. H. Back, "Symposium on the Kinetics of Pyrolytic Reactions," University of Ottawa, 1964.

⁶ R. W. Dexter and A. B. Trenwith, *Proc. Chem. Soc.*, 1964, 392.

⁷ N. L. Arthur and T. N. Bell, unpublished.

decomposition yields mainly trifluoromethane and carbon monoxide with lesser amounts of hexafluoroethane and hydrogen. The experimental rate equation is:

$$\text{Rate} = k[\text{CF}_3\text{CHO}]^{1.5}$$

A chain mechanism which can account for the observed facts is:

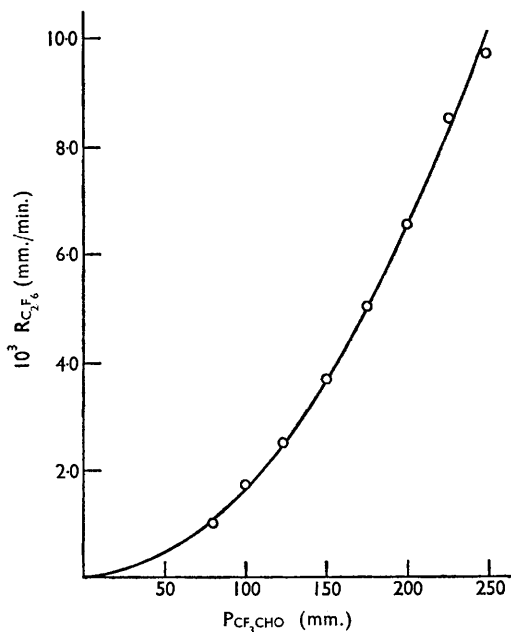
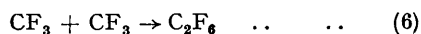
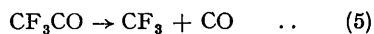
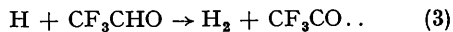
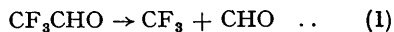
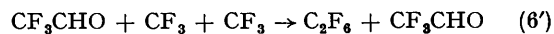
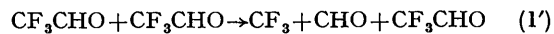


FIG. 1. Variation of $R_{\text{C}_2\text{F}_6}$ with $P_{\text{CF}_3\text{CHO}}$

The overall kinetics give no indication as to the absolute order of reactions (1) and (6). This has been examined by measuring the rate of formation of hexafluoroethane at 500°, and the results are shown in Figures 1 and 2. The second-order dependence of $R_{\text{C}_2\text{F}_6}$ on the pressure of trifluoroacetaldehyde is quite conclusive; thus (1) and (6) must be rewritten:



$$\text{Whence, } R_{\text{C}_2\text{F}_6} = k_1[\text{CF}_3\text{CHO}]^2$$

We conclude that whilst at 200° no real evidence⁸ exists for the pressure dependence of the trifluoromethyl recombination, at 500° this reaction is in its third-order region at pressures of trifluoroacetaldehyde up to 250 mm.

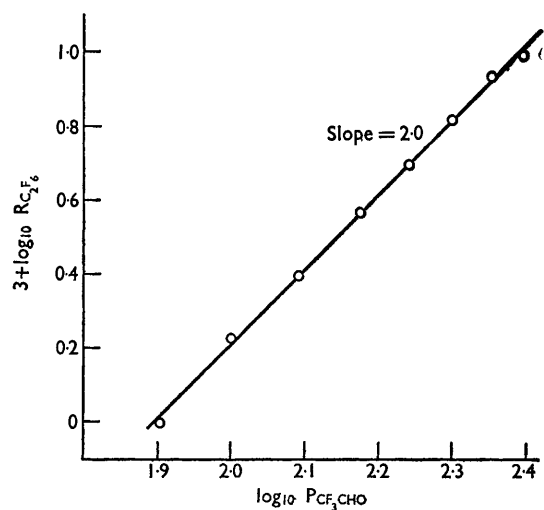


FIG. 2. Variation of $\log_{10} R_{\text{C}_2\text{F}_6}$ with $\log_{10} P_{\text{CF}_3\text{CHO}}$

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⁸ R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1957, 1465.