The Combination of Trichloromethyl Radicals

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THE rate of combination of trichloromethyl radicals to yield hexachloroethane was first reported by Melville, Robb, and Tutton,[1] from studies of the photochemical addition of bromotrichloromethane to cyclohexene. Rate measurements were made by dilatometry and the absolute rate was determined using the normal rotating sector method. Very similar studies have been reported by Bengough and Thomson.[2] The values for k_1

$$CCl_3\cdot + CCl_3\cdot \xrightarrow{k_1} C_2Cl_6$$

determined by both groups of workers was log $k_1 = 8{\cdot}0$ l. moles^{-1} sec.$^{-1}$ at 298°K which is two powers of ten lower than the combination rates of methyl or trifluoromethyl radicals in the gas phase. No direct measurement of k_1 has been attempted in the gas phase although Goldfinger and co-workers[3] were able to make an estimate from studies on the chlorination of chloroform. Their estimated value log $k_1^{298} = 8{\cdot}8$ l. moles^{-1} sec.$^{-1}$ was close to the liquid-phase rate of Melville and co-workers.

The standard rotating-sector technique has been applied to the photochemical addition of bromotrichloromethane to ethylene (details of the establishment of the reaction mechanism and of the experimental method without the sector have already been reported[4]). A series of twenty-six runs ($[CH_2CH_2] = 4{\cdot}40 \times 10^{-4}$ moles l.$^{-1}$; $[CCl_3Br] = 1{\cdot}10 \times 10^{-3}$ moles l.$^{-1}$, temperature 175°; reaction time 3 hours) has been carried out at fourteen different sector speeds (dark : light ratio = 3; max. speed 3787 revs. mins.$^{-1}$ gave a rate ratio (intermittent : steady) of 0·516; min. speed 0·025 revs. mins.$^{-1}$ gave a rate ratio of 0·233). These results have been plotted against the theoretical sector curve and an uncorrected value of log $k_1^{448} = 10{\cdot}5$ l. moles^{-1} sec.$^{-1}$ has been obtained. Assuming the reaction has no activation energy this value is a hundred times faster than the previous estimate for the gas-phase reaction. It brings the combination of trichloromethyl radicals into line with methyl, trifluoromethyl, and other alkyl radicals.[5]

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[1] H. W. Melville, J. C. Robb, and R. C. Tutton, *Discuss. Faraday Soc.*, 1951, **10**, 154.

[2] W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, 1961, **57**, 1928.

[3] R. Eckling, P. Goldfinger, G. Huybrechts, G. Martens, L. Meyers, and S. Smoes, *Chem. Ber.*, 1960, **93**, 3014.

[4] J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, 1964, **60**, 1769.

[5] J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics", Vol. 1, p. 107, ed., G. Porter, Pergamon Press, 1961.