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THE EFFECT OF PRESSURE ON THE QUENCHING OF FLUORESCENCE

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The effect of pressure on the quenching of fluorescence was measured in order to study the effect of hydrostatic pressure on very fast reactions in the liquid phase. It follows from kinetic considerations that the rate of a reaction becomes viscosity dependent when the time required by the reacting molecules to diffuse together becomes comparable with the time required to form the transition state.[1] This condition will occur in ordinary solvents only for reactions with very low activation energies but has been shown to arise in extremely viscous media also for reactions with the higher activation energies common in ionic reactions. The reaction between an excited molecule and a strong quenching agent has a very low activation energy and although it is very fast its rate can be studied by observing relative fluorescence intensities. The quenching of the fluorescence of anthracene by carbon tetrabromide has been investigated by Bowen and Metcalf[2] in some detail and was found to be kinetically comparatively simple. The rate of the quenching reactions was measured by these authors in mixed paraffin solvents and found to be approximately inversely proportional to the viscosity of the solvent, except at very high viscosities, where it decreased much faster than $1/\eta$. Bowen and Sahu[3] later showed that the fluorescence yields of substituted anthracenes are themselves a function of viscosity and that it is necessary to correct for this effect when comparing quenching reactions in solvents of different viscosities.[4] We have examined the quenching of anthracene fluorescence at pressures up to 2500 atm. and found a similar relation between the quenching constant and viscosity of a single solvent when this was increased by the applied pressure.

In each solvent the quenching constant was determined at a number of concentrations of carbon tetrabromide and its value at zero concentration, k_0, was found by extrapolation (*cf.* ref. 2). Figure 1 shows the value of k_0 (in l. mole^{-1}) found in methylcyclohexane, *n*-hexane, and Dow-Corning silicone 200–100 at

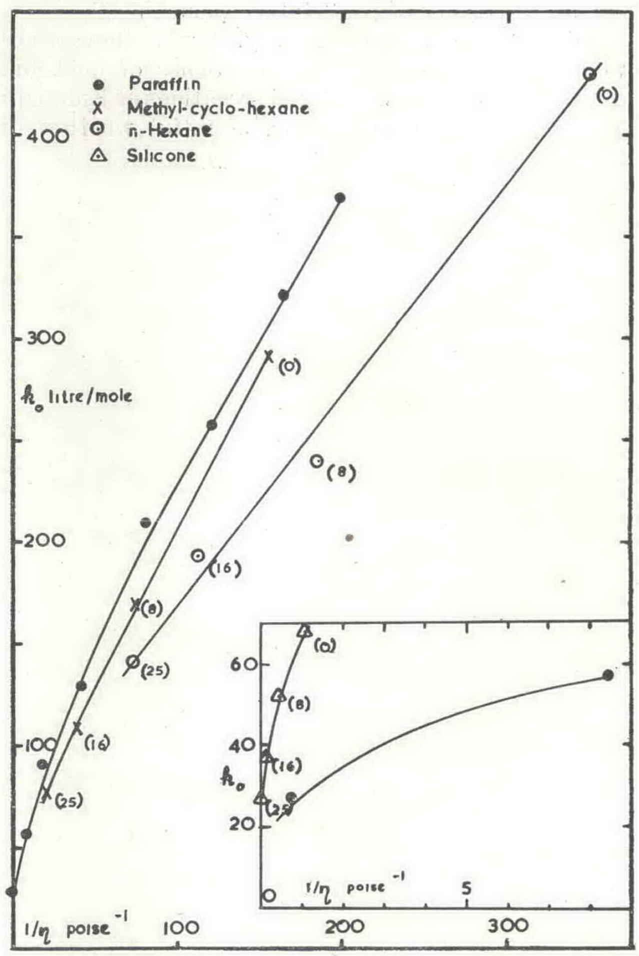

Fig. 1.—The quenching of anthracene by carbon tetrabromide in various solvents. Results in paraffin according to ref. 2. Insert shows high viscosity region on a larger scale. The pressures at which the measurements were made are given in hundreds of atmospheres in parentheses. ●, paraffin; ×, methylcyclohexane; ⊙, *n*-hexane; △, silicone.

30° and at the pressures given in parentheses in hundreds of atmospheres. Also shown are the values found by Bowen and Metcalf in mixed paraffin solvents at 20°. Viscosities of the solvents at high pressure were measured by Bridgman.[5]

The experiments consisted in a direct comparison of quenched and unquenched solutions of anthracene (0.283×10^{-3} mole kg.$^{-1}$) placed in high pressure cells in a modified spectrophotometer. The solutions were thoroughly degassed and the carbon tetrabromide-concentration was varied between 0.01 and 0.07 mole l.$^{-1}$.

(1) S. D. Hamann, *Trans. Faraday Soc.*, **54**, 507 (1958).
(2) E. J. Bowen and W. S. Metcalf, *Proc. Roy. Soc.* (London), **A206**, 438 (1951).
(3) E. J. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959).
(4) The author is grateful to Dr. Bowen for pointing this out when commenting on this note and for informing him of some relevant values of the fluorescent yield of anthracene in paraffin solvents.
(5) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **61**, 57 (1926).

The monochromator was used to isolate the 365 nm line from the light emitted by a 125-watt high pressure mercury lamp, and the fluorescence intensity was measured after the residual exciting radiation had been absorbed in an effective ultraviolet filter. Corrections for stray light and for slight differences in the optical paths of the two cells were applied.

The results of the experiments show that in any one solvent the quenching constant is approximately inversely proportional to the viscosity, as simple diffusion theory would lead one to expect for a diffusion-controlled reaction. However, the results also show that the proportionality factor increases with the initial viscosity of the solvent. This effect remains unchanged if one takes account of the "static" quenching.[2]

The solutions in poly-dimethylsiloxane showed very weak fluorescence even in the absence of quenching agent, in agreement with the observations of Kallmann[6] and of Porter,[7] and it seems doubtful whether the quenching mechanism in this solvent is strictly comparable with that in the other solvents.

The effect of pressure on the quenching reaction thus seems to be primarily that of increasing the viscosity of the solvent, while that due to the different volumes of the initial and the transition state is quite negligible. If one assumes this effect to be general for fast reactions between neutral molecules, one would expect to find it also for the fast reactions involved in free radical recombinations and in the termination step of free radical polymerizations. The effect of pressure on the latter has been deduced by Nicholson and Norrish[8] from an analysis of the polymerization of styrene under pressure. The rate of the termination reaction was stated by these authors to be inversely proportional to the square root of the viscosity of the solvent, but the actual results do not rule out an inverse dependence on the first power of the viscosity.

(6) H. Kallmann, *Discussions Faraday Soc.*, **27**, 101 (1959).
(7) G. Porter, *ibid.*, **27**, 102 (1959).
(8) A. E. Nicholson and R. G. W. Norrish, *ibid.*, **27**, 104 (1959).