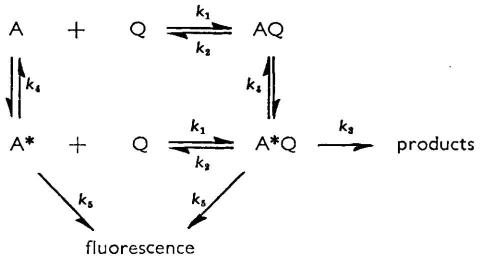
870. *Effect of Pressure on the Rate of Fast Reactions*

By D. W. Haworth and W. S. Metcalf

The rate of reaction of excited molecules of 9,10-diphenylanthracene with oxygen dissolved in methylcyclohexane or in toluene is fast enough to be limited by the diffusion together of the reagents. At high pressures, the solvents become highly viscous, and the reaction rate falls. The rate of reaction with carbon tetrachloride is too slow to be limited by diffusion; in this case, the reaction rate increases with pressure, but falls again at very high pressures.

The rate of reaction of optically excited molecules with added substances is inferred from the rate of decay of their fluorescence and the fall in its intensity when such quenching substances are added.[1] The more important processes [2] involved are shown in the Scheme below.



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[1] O. Stern and M. Volmer, *Phys. Z.*, 1919, **20**, 183.
[2] W. S. Metcalf, *J.*, 1960, 3726.

They are the absorption of light and its emission as fluorescence, internal degradation of excitation energy, the formation of "encounters"[3] (AQ and A*Q) between reagent species in the course of their diffusive motion, and the reaction of the optically excited molecules (A*) with quencher molecules (Q) during the course of such encounters.

Analysis[2] of this scheme yields the following expression for the observed quenching coefficient k, defined by

$$k = (f_0/f - 1)/[\mathrm{Q}]$$

where f_0 and f are the fluorescence intensities when the quencher concentration is zero and [Q], respectively:

$$\frac{1}{k} = \frac{1}{(k_1\tau_0 + K) + k_1\tau_0 K[\mathrm{Q}]} + \frac{1 + K[\mathrm{Q}]}{k_3\tau_0 K} \tag{1}$$

where $K = k_1/k_2$, is an equilibrium constant describing the concentration of encounters, and $\tau_0 = 1/(k_4 + k_5)$, is the mean life of excited molecules in the absence of quencher, a separately measurable quantity.[4] In the present experiments, it is 9 nanoseconds.

Pressure is predicted to have a large effect on k_1 but not on k_3, τ_0, or K. k_1 describes the rate of formation of encounters during the diffusive motion of A* and Q, or of A and Q, and several theoretical approaches[5] predict it to be approximately proportional to their diffusion coefficients. Diffusion coefficients, in turn, are approximately proportional to the fluidity of the solvent,[6] which is very sensitive to pressure.[7]

Two extreme cases commonly occur: in the first, quenching in encounters is almost certain. $k_3 \gg k_2 + k_4 + k_5$. The first term in equation (1) is dominant, so that

$$k = k_1\tau_0 + K + k_1\tau_0 K[\mathrm{Q}]$$

or, more approximately,[5g] $k = k_1\tau_0$. In this case, quenching rapidly falls (and fluorescence rises) as the pressure rises. The quenching of the fluorescence of anthracene by carbon tetrabromide is such a case,[5g] for which Ewald[8] has shown the effect of pressure to be as expected. Another example is the quenching of the fluorescence of 9,10-diphenylanthracene by oxygen in methylcyclohexane (Figures 1 and 2) and in toluene (Figure 3).

In the second extreme case, quenching during an encounter is an unlikely event. $k_3 \ll k_2 + k_4 + k_5$. The second term in equation (1) is dominant, so that

$$k = k_3\tau_0 K/(1 + K[\mathrm{Q}])$$

This expression contains no terms highly sensitive to pressure. The weak quenching of the fluorescence of 9,10-diphenylanthracene by carbon tetrachloride is such a case. In fact (Figures 1—3) the quenching rises a little and then falls as the pressure increases. At very high viscosities, diffusion limitations can appear, as, for example, in the quenching of the fluorescence of anthracene[9] by ethyl iodide, and by carbon tetrachloride. In the present experiments, there is so much carbon tetrachloride present that it is implausible to postulate diffusion as a limiting process.

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[3] E. Rabinovitch and W. C. Wood, *Trans. Faraday Soc.*, 1936, **32**, 1381.

[4] E. A. Bailey and G. K. Rollefson, *J. Chem. Phys.*, 1953, **21**, 1315.

[5] (*a*) M. V. Smoluchowski, *Z. phys. Chem.*, 1917, **92**, 129; (*b*) S. J. Wawilow, *Z. Physik*, 1929, **53**, 665; (*c*) B. Sveshnikoff, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 257; (*d*) E. Rabinovitch, *Trans. Faraday Soc.*, 1937, **33**, 1225; (*e*) E. W. Montroll, *J. Chem. Phys.*, 1946, **14**, 202; (*f*) F. C. Collins and G. E. Kimball, *J. Colloid. Sci.*, 1949, **4**, 425; (*g*) E. J. Bowen and W. S. Metcalf, *Proc. Roy. Soc.*, 1951, *A*, **206**, 437; (*h*) R. M. Noyes, *Prog. Reaction Kinetics*, 1961, **1**, 129.

[6] A. Einstein, *Z. Electrochem.*, 1908, **14**, 235.

[7] P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, Ltd., London, 1949, p. 341.

[8] A. H. Ewald, *J. Phys. Chem.*, 1963, **67**, 1727.

[9] W. H. Melhuish and W. S. Metcalf, *J.*, 1954, 976.

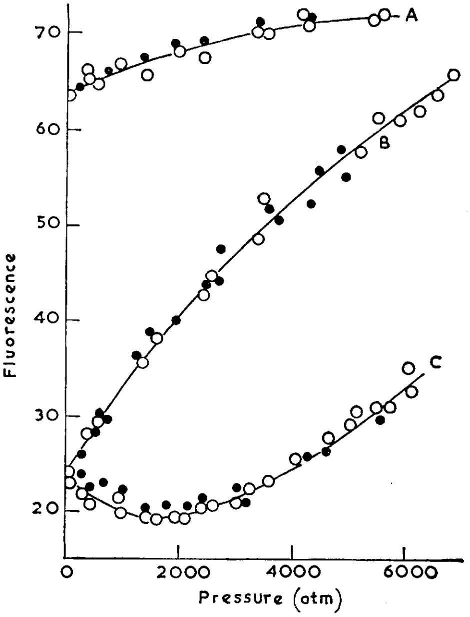

FIGURE 1. (A) 9,10-Diphenylanthracene (5×10^{-5}M) in methylcyclohexane at 20°. (B) Oxygen (10^{-2}M at 1 atm.) added. (C) Carbon tetrachloride (1·3M) present

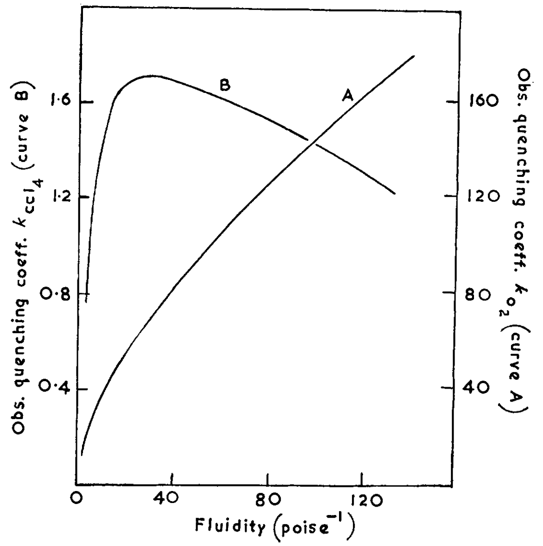

FIGURE 2. The quenching of the fluorescence of 9,10-diphenylanthracene (5×10^{-5}M) in methylcyclohexane by (A) oxygen, right-hand scale, and (B) carbon tetrachloride, left-hand scale, as a function of fluidity

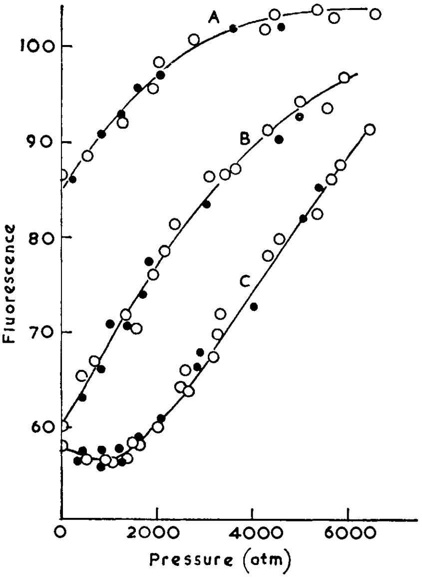

FIGURE 3. (A) 9,10-Diphenylanthracene (5×10^{-5}M) in toluene at 20°. (B) Oxygen (7×10^{-3}M) present. (C) Carbon tetrachloride (0·13M) present

In Figures 1—3, open circles refer to successively rising pressure steps and filled circles to successively falling pressure steps

EXPERIMENTAL

The pressure vessel (Figure 4), designed and made at the Dominion Physical Laboratory, follows the design of Poulter [10] except that a flanged plug of aluminium alloy (" Hiduminium ") precedes the piston, and the three window supports, shown on a larger scale in Figure 5, are also flanged. In consequence, no great tightness of the retaining threads is needed to prevent leakage. The piston guide, whose importance was stressed by Poulter, allows at least 35 tons

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[10] T. C. Poulter, *Phys. Rev.*, 1932, **40**, 860.

to be applied to a piston of 14-mm. diameter without fracture. The pressure inside is then 21,000 atm. The apparatus has not been tested to the point of failure.

Because of friction, which is remarkably reproducible, the pressure inside (indicated by a manganin resistance gauge[11]) is about 500 atm. below that calculated from the force applied to the piston as the pressure is increased, and the same amount above as it is released. The internal pressure is taken as the mean, and the manganin gauge (Figure 6) so calibrated is used for interpolation.

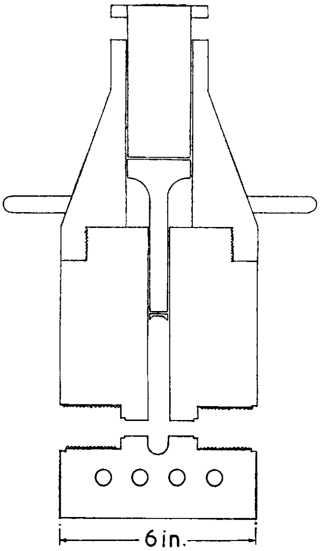

FIGURE 4. Pressure vessel

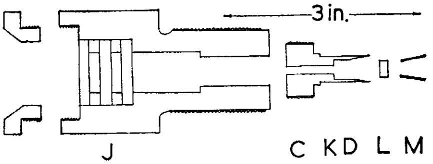

FIGURE 5. Window support, one of three. J, safety windows separated by rubber rings; C, thread to engage withdrawing tool; K, window position; D, tight-fitting tapered flange; L, window to Poulter's specification; M, nylon retainer.

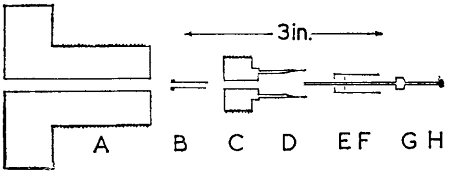

FIGURE 6. Manganin gauge support. A, retaining block; B, fibre insulator; C, thread to engage withdrawing tool; D, tight-fitting tapered flange; E, mica insulating disc; F, steel terminal cylinder; G, bobbin for manganin wire; H, terminal

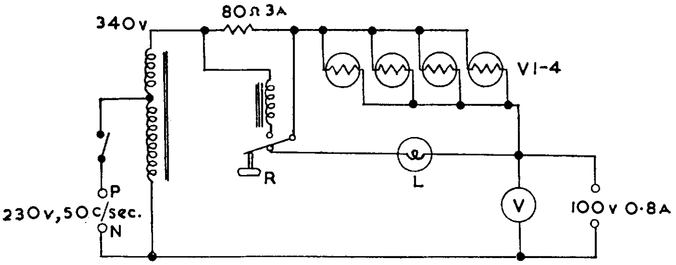

FIGURE 7. Constant-current power supply. V 1—4, barretters, Philips C8; L, incandescent lamp, 230 v, 60 w; R, relay, reset manually when V indicates 100 v

The pressure-transmitting liquid is light medical paraffin, purified (if it is fluorescent) by being washed with fuming sulphuric acid, and then clarified by passage through aluminium oxide powder; the product is not a lubricant. The piston must be lubricated by a grease composed of a mixture of this paraffin and stearic acid, in order to prevent it seizing to the cylinder irreparably.

The light source is an 80-w high-pressure mercury arc (Philips 56201 E) operated from a 50 c./sec. current-regulated supply (Figure 7). A nickel oxide glass filter (Chance OX 2·5 mm.) isolates the group of lines near 3650 Å. The sample is in a glass tube (i.d. 6 mm. bore, wall 2 mm., length 30 mm.), attached at the top to a stoppered plastic tube, which collapses under pressure. The fluorescence is separated from scattered exciting light by a filter which does not itself fluoresce excessively (Kodak 2B) and is viewed by an electron multiplier phototube

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[11] Ref. 7, p. 72.

(RCA 931 A) whose output is amplified by a phase-sensitive device which takes advantage of the 100-c./sec. modulation of the exciting light. This amplifier and detector were designed and made by Canterbury University Industrial Development Division.

The viscosities (η) at 20° used in Figure 2 are extrapolated from the measurements of Bridgman [12] at 30 and 70° according to the equation $\log \eta = A + B/T$. The compressibility of methylcyclohexane required for the calculation of [Q] is not available, and is taken as equal to that of n-hexane. Compressibilities of similar liquids [13] do not differ any more than the spread of the points in Figures 1 and 3.

We gratefully acknowledge a grant, for the purchase of equipment, from the New Zealand Universities Research Committee.

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[*Received, February* 17*th*, 1965.

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[12] Ref. 7, p. 343.

[13] Ref. 7, p. 129.