Phosphorescence Quenching by Diffusion in an Isopentane Glass[1]

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Summary The quenching of toluene phosphorescence by *cis*-piperylene at 77 K in an isopentane glass obeys Stern–Volmer kinetics; this is in contrast to the "static quenching" previously reported for rigid (*i.e.* predominantly ethanol) glasses.

As part of a general study[2] of alkylbenzene emission and emission quenching, we have examined phosphorescence quenching by dienes in glasses at 77 K. Such triplet quenching is well known,[3] but has usually been observed in alcohol or solvent mixtures (such as ethanol–ether), under which conditions the data are best treated by a "sphere of quenching action" model.[4,5] In such a model, the medium is considered to be completely rigid, diffusion is considered negligible and the excited triplet is quenched only by energy transfer to species within the "sphere of quenching action" at the instant of excitation.

We now report that when isopentane is used as the glassy medium, phosphorescence quenching data may be treated by the usual Stern–Volmer kinetics, whereby $I_0/I = 1 + k_q\tau[Q]$ (with I and I_0 representing phosphorescence emission intensities with and without quencher present). Although several different systems have been studied,[2] the data for *cis*-piperylene quenching of toluene phosphorescence suffice to illustrate the technique. These data are shown plotted in the Figure, with the slope ($k_q\tau$) of the (least-squares derived) line found to be 942 ± 106 M^{-1} (error represents standard deviation of the data). Under identical conditions for (freeze, pump, thaw) degassing, our measured lifetime, (τ), for toluene at 77 K in isopentane, is 3·50 ± 0·07 s.[6] Thus, the rate constant for quenching, k_q, is found to be 269 ± 30 $\text{s}^{-1}\text{M}^{-1}$, some 47% of the diffusion controlled rate constant ($k_{\text{diff}} = 568\ \text{s}^{-1}\text{M}^{-1}$) calculated using the modified Debye equation[7] (η for isopentane at 77 K taken as *ca.* 3 × 10^4 poise).[8] The observation of a k_q equal to *ca.* 47% k_{diff} may be compared with measurements at room temperature in solution, wherein for example, k_q for naphthalene quenching of the benzophenone triplet is reported[9] to be about 12% k_{diff}.

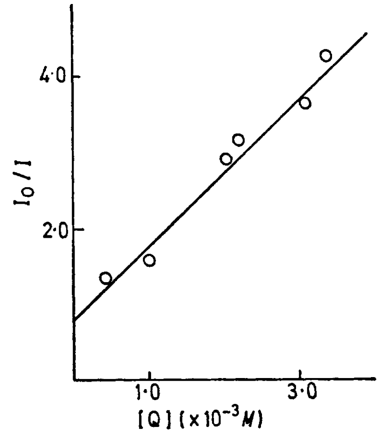

FIGURE. *Stern–Volmer quenching plot relating toluene phosphorescence intensity at* 77 K *in an isopentane glass, to* cis-*piperylene concentration.*

The validity of our treatment of these data is confirmed by several observations. Thus, if one assumes rigidity of the medium and a "sphere of quenching action", the radius of this sphere may be calculated using equation (1).[3]

$$V_c\ (\text{cm}^3) = \frac{1000 \ln I_0/I}{\text{N}[Q]} \qquad (1)$$

Typical radii[3] for triplet energy transfer are of the order of 12—15 Å. A similar treatment of our data gives a radius of *ca.* 55 Å, certainly not a realistic figure for triplet quenching by the close-contact, exchange mechanism.[3] Furthermore, although toluene fluorescence is efficiently quenched at room temperature by *cis*-piperylene at these concentrations, no fluorescence quenching is observed at 77 K; this again argues against the "instantaneous quenching" assumed by the "quenching sphere" model. Finally, though 3·37 × 10^{-3}M *cis*-piperylene in an isopentane glass quenches 77% of toluene phosphorescence, a considerably larger (*i.e.* 8·4 × 10^{-3}M) concentration of the diene in an ethanol glass was found to quench only 19% of the toluene emission.†‡

Thus it appears that bimolecular processes requiring diffusion can occur at 77 K in an isopentane glass.

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† The quenching observed in ethanol corresponds to a "sphere of quenching" radius of 21 Å, a value slightly higher but comparable to those observed for other triplet-transfer systems.[3]

‡ Concentrations used in this report are uncorrected for solvent contraction at 77 K. Such contraction amounts to *ca.* 20% for isopentane[10] and correction for this factor reduces the Stern–Volmer slope and the calculated "radii" by *ca.* 10%.

[1] For previous paper in the series "Organic Photochemistry," see S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, in the press.

[2] P. Froehlich, Ph.D. thesis, Purdue University, Lafayette, Indiana, August, 1971.

[3] For a useful summary, see A. Lamola in "Technique of Organic Chemistry", Volume XIV, eds. A. Lamola and N. Turro, pp. 44–50.

[4] F. Perrin, *Compt. rend.*, 1924, **178**, 1968.

[5] S. I. Vavilov, *Zhur. eksp. teor. Fiz.*, 1943, **13**, 13.

[6] Such values will vary with degassing technique, solvent purity *etc.* A value of 6·42 s was reported for toluene in a methylpentane–isopentane mixture: J. W. Rabalais, H. J. Maria, and S. P. McGlynn, *J. Chem. Phys.*, 1969, **51**, 2259.

[7] P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265; A. Beckett, A. Osborne, and G. Porter, *Trans. Faraday Soc.*, 1964, **60**, 873; J. T. Dubois and R. L. Van Hemert, *J. Chem. Phys.*, 1964, **40**, 923.

[8] J. W. Hilpern, G. Porter, and L. J. Steif, *Proc. Roy. Soc.*, 1964, **277A**, 437.

[9] G. Porter and F. Wilkinson, *Proc. Roy. Soc.*, 1961, **264A**, 1.

[10] K. Rosengren, *Acta Chem. Scand.*, 1962, **16**, 1421.