The Photoisomerization of *o*-Xylene

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WORK on the photoisomerization of simple aromatic molecules has led to several postulates on the mechanism of the reaction(s). It is generally believed that the electronically excited aromatic molecule forms a non-aromatic isomer which has limited stability and can re-aromatize to give the observed shifts of substituents. For benzene itself, and for di- and tri-substituted rings a benzvalene form has been suggested as the most likely as the intermediate. The mechanism of its formation has led to differing views. Most authors favour formation of this intermediate from the first excited aromatic singlet state.[1] Noyes and Harter[2] consider the triplet may be involved in the case of *o*-xylene. Ward[3] discounts both excited singlet and triplet state participation in favour of a highly vibrationally excited ground-state molecule.

In our work on the 2537 Å induced isomerization of *o*- → *m*-xylene in isopentane, we find that sufficient *trans*-but-2-ene to quench practically all the aromatic triplet states has little effect on the *m*-xylene yield. *trans*-But-2-ene does not quench the fluorescence from the excited singlet state of *o*-xylene significantly ($k_q = 2 \times 10^5$ M^{-1} sec.$^{-1}$).

Further information can be obtained from the quenching of the excited singlet state by xenon which results from the heavy-atom enhancement of intersystem crossing to the triplet state.[4] This quenching could be conveniently monitored by suppression of fluorescence. Precise measurement of low quantum yields presents many problems but it can be seen from Figure 1 that the production of *m*-xylene from 0·5 M *o*-xylene in isopentane at 60° is suppressed by xenon in a similar way to fluorescence. Kinetic treatment of the results shows that both quenchings have the same Stern–Volmer constant. This eliminates any form of the triplet in the *o*- → *m*-isomerization reaction, independently of the but-2-ene results. At the concentration of *o*-xylene used excimer formation is small.[5] The effect of dilution on the isomerization yield is not consistent with an excimer route for the rearrangement.

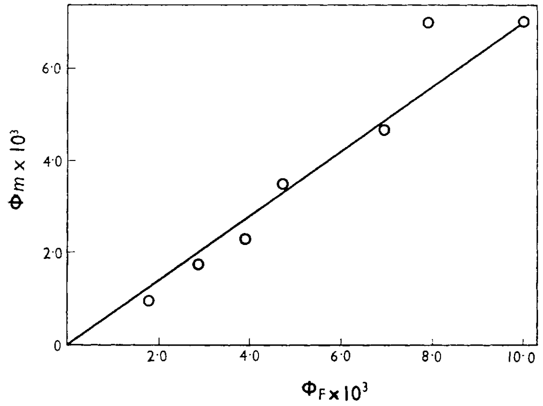

FIGURE 1. ϕ_m (m-*xylene quantum yield*) *vs.* ϕ_F (*total fluorescence yield*) *at various xenon concentrations.*

The yield of *m*-xylene increases with temperature and follows an Arrhenius relationship as shown in Figure 2 which gives an activation energy, E_A, of 7·7 ± 0·6 kcal. mole^{-1}. Since isomerization is clearly in direct competition with fluorescence, we may write the rate constant for production of the intermediate, presumably benzvalene, as

$$k_{\text{isomer}} = \frac{B\phi_m}{\tau_F} = Ae^{-E_A/RT}$$

where B is the re-aromatization branching ratio, $\phi_{\text{inter}}/\phi_m$, and τ is the observed fluorescent lifetime. To determine the A factor a value must be assigned to B. Consideration of the various isomeric benzvalenes which may be produced suggests a value of 4 on a purely statistical basis. Allowing for steric and other effects of substituents liberal limits $2 < B < 8$ may be set. Taking this and the uncertainty in E_A into account and taking (at 25°) $\tau_F = 3 \times 10^{-8}$ sec.[6] and $\phi_m = 0{\cdot}0015$ we calculate A between 2×10^{10} and 4×10^{11} sec.$^{-1}$.

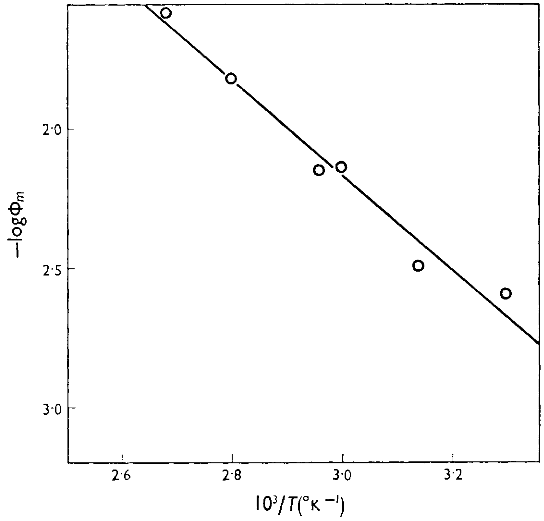

FIGURE 2. *Temperature dependence at* ϕ_m

The low value of the A factor may be due to a low probability for excitation of vibrational modes needed to form the benzvalene structure.

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[1] *E.g.* K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1964, **86**, 2307; K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, 1968, **90**, 1116; D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 1966, 593.

[2] Quoted by W. A. Noyes, jun. and C. S. Burton, International Conference on Photochemistry, Munich 1967.

[3] H. R. Ward, *J. Amer. Chem. Soc.*, 1967, **89**, 2367.

[4] A. R. Horrocks, A. Kearvell, K. Tickle, and F. Wilkinson, *Trans. Faraday Soc.*, 1966, **62**, 3393.

[5] M. D. Lumb and D. A. Weyl, *J. Mol. Spectroscopy*, 1967, **23**, 365.

[6] Estimated from data given by J. B. Birks and I. H. Munro, *Progr. Reaction Kinetics*, 1967, 239.