Thermal *cis–trans*-Isomerization of Substituted Azobenzenes: a Correction of the Literature

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RECENT interest in the mechanism of thermal isomerization around double bonds[1] prompts us to call attention to uncertainties in the literature with regard to the rates and mechanism of the thermal, uncatalyzed *cis–trans*-isomerization of substituted azobenzenes.[2] The results of Le Fèvre and Northcott[3] with five monosubstituted azobenzenes have been claimed by Jaffé[4] to follow the Hammett '$\sigma\rho$' equation,[5] whereas the work of Schulte-Frohlinde[6] appears to militate against such a smooth relationship. However, in almost all of these kinetic studies, the starting materials were merely mixtures of *cis-* and *trans*-forms obtained photochemically[7] from the *trans*-forms. Since rates thus measured involve a limited conversion and do not exclude the influence of adventitious catalysts that may be formed during the irradiation, we have re-examined this isomerization reaction with a much larger number of substituents, always starting with pure *cis*-isomers. Our work leads us to question the validity of some of the results of Le Fèvre and Northcott and their correlation by Jaffé, both of which have attracted attention,[8] and to reject all mechanisms hitherto suggested for this reaction.

The *cis*-isomers were isolated by irradiation[†] of solutions of *trans*-isomers[‡] in chloroform, followed by chromatography on silicic acid in a dark room. The isomerizations were allowed to proceed in a dark room to at least 90% completion and followed spectrophotometrically by the decrease in absorbance in the visible region of the spectrum. Although we have measured all rates in ethanol, benzene, and n-heptane as solvents, we present here only our data in benzene, since this is the solvent used by previous investigators. Rate constants ($k_1 \times 10^4$ min.$^{-1}$)[§] obtained for the various monosubstituted azobenzenes at 35° are given below, alongside the substituent:[9] H, 3·58;[10] *m*-Me, 5·13; *m*-Et, 4·06; *m*-Pr^i, 3·23; *m*-Bu^t, 3·06; *m*-COMe, 2·68; *m*-Cl, 3·48; *m*-OMe, 3·81; *m*-NO$_2$, 3·16; *p*-Me, 5·59; *p*-Et, 5·54; *p*-Pr^i, 8·02; *p*-Bu^t, 6·35; *p*-COMe, 11·75; *p*-Cl, 5·56; *p*-OMe, 10·3; *p*-NO$_2$, 93·3. Values of E_a are in the range 21·1—23·8 kcal./mole and log A (A in sec.$^{-1}$) in the range 12·0—13·5.

The most striking feature of the above data is that all *para*-substituted azobenzenes isomerize faster than the parent compound, regardless of the nature of the substituent. Thus, contrary to the conclusion of Jaffé, we find no linearity in a Hammett plot using either σ, σ^+, or σ^-.[11] In fact, the isomerization of *para*-nitroazobenzene, which was claimed by Le Fèvre and Northcott to be the slowest of all the isomerizations studied by them, is actually found to be the fastest in our study which encompasses the same substituents. The overall effect of substituents in this reaction is not very large, and the effect of a change in solvent even less, the maximum change in rate observed being only threefold in going from n-heptane to absolute ethanol (generally a decrease), a change in Z-value[12] of almost 20. Although a detailed discussion of these observations will be deferred to the full Paper, the following comments may be made with regard to the mechanism of the reaction. Schulte-Frohlinde[6] apparently considered his results to be in accord with a twisting around the N=N bond, involving a rupture of the π-bond to yield a singlet transition state. Although the observation of pre-exponential factors as high as 10^{12}—10^{14} sec.$^{-1}$ precludes the intervention of triplet excited states formed by intersystem crossover, the activation energies are too low to be compatible with a singlet transition state. The corresponding isomerization of the stilbenes[13] which are considered to involve singlet states has a characteristic activation energy of about 34—37 kcal./mole in the liquid phase. Since the barrier to rotation around the N=N bond has been calculated to be higher than that for rotation around the C=C bond by about 24 kcal. in the gas phase,[1g] one would expect an activation energy of at least 55 kcal./mole for the azobenzenes if the singlet mechanism were to

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[†] A Hanovia 100 w "Inspectolite" lamp (catalogue No. 16180) was used, and the solutions irradiated in quartz vessels at 0° for 3—5 hours.

[‡] Satisfactory analyses were obtained for all new compounds.

[§] Computed by the method of least squares from excellent first-order plots and found to be reproducible within ±4%. Activation parameters were then calculated from the least-squares slope of an Arrhenius plot.

prevail.[14] On this presumption, the observation of activation energies as low as 21—24 kcal./mole would require considerable destabilization of the double bond by the substituents *via* dipolar resonance structures[15] and/or a special role of solvent[15b] in the azo-compounds not encountered in the stilbenes. The absence of large solvent or substituent effects effectively rules out all of these possibilities. The only other path available to the azobenzenes then involves a linear transition state in which one or both nitrogen atoms undergo a change in hybridization to the *sp*-state, the π-bond remains intact, and the nonbonded electron pair occupies a *p*-orbital, a mechanism not available to the stilbenes. Such a mechanism has been postulated for the *cis–trans*-isomerization of imines[1a] which have similar activation energies.

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[1] (a) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, 1966, **88**, 2775; (b) D. Y. Curtin and C. G. McCarty, *Tetrahedron Letters*, 1962, 1269; (c) D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, 1961, **83**, 3474; (d) S. Andreades, *J. Org. Chem.*, 1962, **27**, 4163; (e) H. A. Staab, F. Vögtle, and A. Mannschreck, *Tetrahedron Letters*, 1965, 697; (f) N. P. Marullo and E. H. Wagener, *J. Amer. Chem. Soc.*, 1966, **88**, 5034; (g) J. Binenboym, A. Burcat, A. Lifshitz, and J. Shamir, *ibid.*, p. 5039.

[2] First studied by G. S. Hartley, *Nature*, 1937, **140**, 281; *J. Chem. Soc.*, 1938, 633.

[3] R. J. W. Le Fèvre and J. Northcott, *J. Chem. Soc.*, 1953, 867.

[4] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[5] L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, 1940, p. 186.

[6] D. Schulte-Frohlinde, *Annalen*, 1958, **612**, 131, 138.

[7] The proportion of *cis*-isomer in such mixtures, in our experience, rarely exceeds 50%. See also ref. 9, and W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Amer. Chem. Soc.*, 1952, **74**, 4641.

[8] E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt-Dryden, New York, 1959, p. 222; R. B. Cundall, *Progr. Reaction Kinetics*, 1964, **2**, 179.

[9] Values for the last three *meta*- and last three *para*-substituted azobenzenes are quoted from the Ph.D. thesis of E. R. Talaty, The Ohio State University (University Microfilms, No. 58573, Ann Arbor, Michigan).

[10] Compare with value of $3{\cdot}51 \times 10^{-4}$ min.$^{-1}$ obtained by extrapolation of data of J. Halpern, G. W. Brady, and C. A. Winkler, *Canad. J. Research*, 1950, **28B**, 140.

[11] Requisite values are collected by J. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, 1962, ch. 4.

[12] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.

[13] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 1938, 2078; M. Calvin and H. W. Alter, *J. Chem. Phys.*, 1951, **19**, 768.

[14] The barrier to rotation around the N=N bond in aliphatic azo-compounds in their ground states has been calculated to be about 66 kcal./mole (D. R. Kearns, *J. Phys. Chem.*, 1965, **69**, 1062).

[15] (a) Assumed by Hartley (ref. 2); (b) Considered by M. G. Horowitz and I. M. Klotz, *J. Amer. Chem. Soc.*, 1955, **77**, 5011.