178. *The Effects of Substituents and Solvents on the* cis ⟶ trans *Change of Azobenzene.*

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The rates of geometrical inversion of azobenzene in seven solvents, and of azobenzene together with five *p*-substituted azobenzenes in benzene, have been studied by dielectric capacity–time measurements. All show Arrhenius equations similar to those previously found applicable to aromatic diazocyanides. A rough connection between the energy of activation recorded for $X \cdot C_6 H_4 \cdot N_2 \cdot Ph$ and $\mu_{Ph X}$ is demonstrable *via* the empirical equation $E = E_0 + 1316(\mu + 0 \cdot 226\mu^2)$. A correlation between the kinetic data and the square roots of the internal pressures of the solvents has been examined, and also one depending on the solute–solvent interaction energy. The second gives indications of being less unsatisfactory than the first.

FOLLOWING an investigation of the effects of substituents and solvents on the velocities of the *cis* to *trans* thermal changes of various aromatic diazocyanides (Le Fèvre and Northcott, *J.*, 1949, 944) it became of obvious interest to compare our findings with those parallel for the corresponding azobenzenes. Some relevant information had already been recorded by Hartley (*J.*, 1938, 633) for the parent azobenzene and five of its derivatives having respectively the OH, NH_2, NMe_2, OMe, and $^+NMe_3$ groups in the 4-position, the majority of these having been studied in light petroleum, benzene, and acetone, although in some cases water, acetic acid, aqueous acids and other mixtures were used.

However, since neither these media nor the substituents overlapped extensively with those taken by us for the diazocyanides, and because his measurements had been spectro-photometric at dilutions of 3—8 × 10⁻⁴ mole/l., we have re-examined, at higher concentrations in benzene, azobenzene and 4-methoxyazobenzene and added 4-chloro-, 4-bromo-, and 4-nitro-azobenzene. Halpern, Brady, and Winkler (*Canad. J. Res.*, 1950, **28**, *B*, 140) have provided full data for azobenzene in sixteen homogeneous solvents with dielectric constant ranging from that of heptane to that of water.

EXPERIMENTAL

Azobenzene was twice recrystallised from alcohol after a solution in this solvent had been boiled under reflux for 1 hour. All operations were performed in the absence of direct daylight. The material, m. p. 68°, was stored in an opaque desiccator. The *cis*-isomer, prepared according to Hartley (*loc. cit.*) and recrystallised from light petroleum by cooling below room temperature, had m. p. 71—72°.

The *trans*-substituted azobenzenes were obtained by direct condensation of nitrosobenzene with the appropriate aniline derivative in acetic acid (cf. Beilstein, " Handbuch etc.," Vol. XVI). *cis-p*-Chloro-, *-p*-bromo-, and *-p*-methoxy-azobenzene were isolated by procedures similar to those used for azobenzene. M. p.s of the azobenzenes were : 4-chloro-, *cis* 32°, *trans* 90—91° ; 4-bromo-, *cis* 39°, *trans* 88—89° ; 4-methoxy-, *cis ca.* 25°, *trans* 53—54°.

As with the diazocyanides, dielectric-capacity changes have been used to follow the reactions. To secure greater constancy than is possible with batteries for long times, an oscillator was built around a 6SJ7 pentode associated with a stabilised HT supply and having a Phillips type 1941 barrettor in series with the heater circuit. Fig. 1 shows the arrangement. The cell, thermostat, other ancillary details, and procedures have been described previously (*J.*, 1948, 1949; 1949, 333, 944) except that the variable condenser C_3 utilised in the present work was a Sullivan second-grade instrument from which all but two of the rotating vanes had been removed;
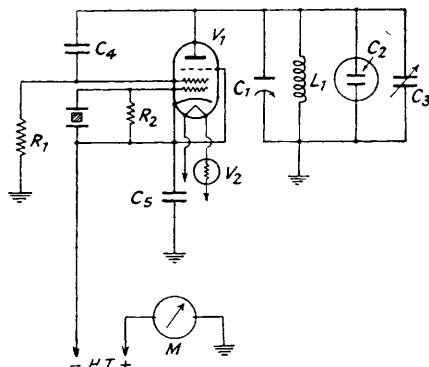

Fig. 1.

C_1, *Radio variable condenser.* C_2, *Cell.* C_3, *Precision variable condenser.* C_4, *15μμF Mica condenser.* C_5, *225μμF Mica condenser.* R_1, *5000 ohms 2 watt Resistor.* R_2, *4500 ohms 2 watt Resistor.* V_1, *6SJ7 Pentode.* V_2, *Barrettor (Phillips Type 1941).* M, *0—25 Milliameter.*

when checked against a " stepped rod " condenser, built on the lines shown in Fig. 4 of *J.*, 1950, 276, C_3 displayed a rectilinear dependence of capacity on scale-reading over the central two-thirds of its range; its maximum usable variation was 16—20 μμF, requiring for traversal some 40 revolutions of a geared worm-drive counter-head, 0·01 turn of which caused a detectable change in the milliammeter M.

Since the reactions under study were of the first order, in all cases solutions of the *trans*-forms in benzene (of the quality used for dipole-moment determinations; cf. *J.*, 1948, 2270) or other solvents (purified as in *J.*, 1949, 944) were exposed to direct sunlight in clear glass flasks for 1 hour, then introduced into the cell C_2, and observations on C_3 were recorded as soon as thermal equality with the bath-liquid had been attained. In some instances (marked * in Tables 1 and 2) comparative runs were also made with freshly dissolved pure *cis*-isomerides; data so obtained always confirmed those secured from the photo-generated *cis–trans*-mixtures.

TABLE 1.   cis *to* trans *Inversion of* $R·C_6H_4·N:N·C_6H_5$ *in benzene.*

R	$k_{25°}$	$k_{45°}$	$k_{70°}$	A (sec.$^{-1}$)	E (kcal./mole)
H	0·0058 *	0·0727 *	—	$4·5 \times 10^{11}$	23·7
Me	0·0159	0·217	—	5×10^{12}	24·5
p-Cl	0·0107	0·116 *	—	$8·5 \times 10^{10}$	22·4
p-Br	0·0101 *	0·122	—	$1·2 \times 10^{11}$	22·6
p-NO$_2$	*ca.* 0·004	0·045	0·662	*ca.* 1×10^{11}	23·2
p-MeO	0·0232 *	0·247	—	$1·3 \times 10^{11}$	22·1

TABLE 2.   cis *to* trans *Inversion of* $C_6H_5·N:N·C_6H_5$ *in different solvents.*

Solvent	$k_{25°}$	$k_{45°}$	$k_{70°}$	A (sec.$^{-1}$)	E (kcal./mole)
*cyclo*Hexanone	—	0·0301 *	0·707$_3$	$5·6 \times 10^{13}$	27·3
o-C$_6$H$_4$Cl$_2$	0·0046	0·084 *	1·976	$1·5 \times 10^{14}$	27·3
C$_6$H$_6$	0·0058 *	0·0727 *	—	$4·5 \times 10^{11}$	23·7
CHCl$_3$	0·0071	0·0916 *	—	7×10^{11}	23·9
CCl$_4$	0·0074	0·0896 *	—	$4·1 \times 10^{11}$	23·5
*cyclo*Hexane	0·0075	0·0849 *	—	$8·7_5 \times 10^{10}$	22·6
PhCl	0·0078	0·112 *	—	$5·45 \times 10^{12}$	25·0

RESULTS

Table 1 sets out the values for the rate constants, k (in hr.$^{-1}$), at the indicated temperatures, of azobenzene and five of its derivatives in benzene, together with the corresponding frequency

factors, A, and the energies of activation, E, required by the equation $k_t = A e^{-E/RT}$. Table 2 presents similar data for the parent molecule in seven solvents.

DISCUSSION

The A and E values now reported for the azobenzenes fall over ranges which are approximately those already found for the aromatic diazocyanides (*J.*, 1949, 944), namely, 10^{11}—10^{15} sec.$^{-1}$ and 21—26 kcal./mole, respectively. They illustrate again the difference, previously noted, between these $-N\colon N-$ containing molecules and the stilbenes, for the interconversion of which in the liquid phase $A = 2\cdot7 \times 10^{10}$ sec.$^{-1}$ and $E = 36\cdot7$ kcal./mole (cf. Taylor and Murray, *J.*, 1938, 2078). For comparison, the corresponding change with the piperonaldoximes in benzene shows $A = 2\cdot5 \times 10^{13}$ sec.$^{-1}$ and $E = 22\cdot6$ kcal./mole (Le Fèvre and Northcott, *J.*, 1949, 2235).

Hartley (*loc. cit.*) quotes " times for half-change " in benzene at two or more temperatures only for azobenzene; from these figures we calculate $A = 4\cdot2 \times 10^{11}$ sec.$^{-1}$ and $E = 23\cdot6$ kcal./mole. For the same system Halpern, Brady, and Winkler (*loc. cit.*) give $2\cdot1 \times 10^{11}$ sec.$^{-1}$ and $E = 23\cdot3$ kcal./mole. In the case of 4-methoxyazobenzene, examined by Hartley in our solvent at 25°, a half-life of 29·9 hours is required by the k_{25} listed in Table 1; Hartley found 30 hours; we conclude therefore that the present results are reasonably in congruence with his.

Regarding the effects of substituents, a rough parallelism exists between the diazocyanides and the azobenzenes. Fig. 2, in which $3 + \log k_{\text{azobenzene}}$ is plotted against $2 + \log k_{\text{diazocyanide}}$, suggests the same trend. Figs. 3 and 4 are of interest also in displaying

FIG. 2.	FIG. 3.	FIG. 4.

Benzene-diazocyanide.   *3′-Substituted diphenyl.*   *4′-Substituted diphenyl.*
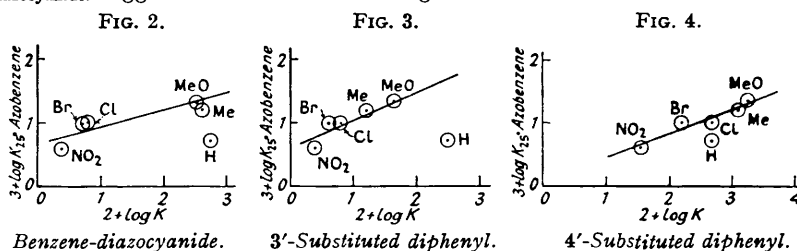
an approximately rectilinear relation between the logarithms of the rate constants of the azobenzenes with those for the racemisations (in acetone) of various 3′- or 4′-substituted 2′-methoxy-2-nitrodiphenyl-6-carboxylic acids (Adams *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 1788; 1935, **57**, 1565). In all three diagrams the points for azobenzene itself are not reconcilable with those for its derivatives. These questions were explored since each of the reactions concerned involves a mutual twisting of two halves of a molecule. Among the azobenzenes the energy of activation rises with p-substitution, the order of groups being from MeO, through Cl, Br, NO_2, H, to Me. We cannot see any direct correlation of this fact with known properties of the radicals named, although, as with the diazocyanides (Le Fèvre and Northcott, *loc. cit.*; Le Fèvre and Freeman, *J.*, 1950, 3128), the empirical equation $E = E_0 \pm C(\mu + \alpha\mu^2)$ appears roughly to apply (here E and E_0 are the activation energies for the derived and parent compounds respectively, μ is the dipole moment of the corresponding monosubstituted benzene, and C and α are constants; cf. *J.*, 1933, 890, 1248; *Trans. Faraday Soc.*, 1938, **34**, 163). Thus writing $E = E_0 + 1316(\mu + 0\cdot226\mu^2)$ gives the figures in the third column of Table 3. The analogous

TABLE 3. *Calculation of E for substituted azobenzenes by equation.*
$$E = E_0 + 1316(\mu + 0\cdot226\mu^2).$$

p-Subst.	μ_{PhX}	E (calc.)	E (obs.)	p-Subst.	μ_{PhX}	E (calc.)	E (obs.)
H	0 D.	23·7	23·7	NO_2	−4·0	23·2	23·2
Cl	−1·6	22·4	22·4	MeO	−1·3	22·5	22·1
Br	−1·6	22·4	22·6	Me	+0·4	24·3	24·5

expression, used previously, for the diazocyanides was $E = E_0 + 1604(\mu + 0\cdot209\mu^2)$.

Finally, we wish to comment on the effects of solvents on these *cis* to *trans* changes. Halpern, Brady, and Winkler (*loc. cit.*) conclude that for azobenzene itself $E_{\text{obs.}}$ is a straight-line function of the square root of the internal pressure of the solvent. With p-chloro-

benzenediazocyanide (Le Fèvre and Northcott, *loc. cit.*) we had tried this possibility incidentally with others, some of which seemed more satisfactory. Through the absence from the literature of heats of vaporisation for several of the media used we could not always compute the internal pressures required as the ratio (energy of vaporisation)/(molecular volume); instead we used (*a*) an empirical expression due to Hildebrand (cf. Glasstone, " Text Book of Physical Chemistry," Van Nostrand, 2nd Edn., 1946, p. 480), thus taking the internal pressure, P_i, at 25° as $(24\cdot5T_b - 1400)/V_{25}$, where $T_b =$ b. p. in °K, and $V =$ molecular volume, and (*b*) the " solubility parameter values "

FIG. 5.	FIG. 6.
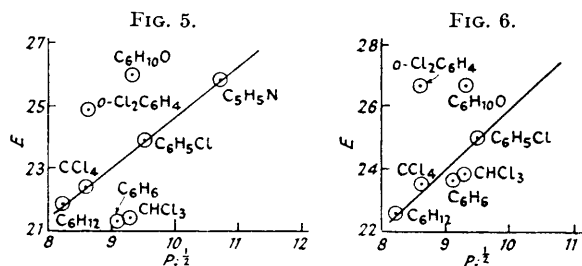
(assumed equal to $P_i^{\frac{1}{2}}$) listed by Hildebrand and Scott (" Solubility of Non-Electrolytes," Reinhold Publ. Corp., 3rd Edn., 1950, p. 436). The P_i figures indicated by method (*a*) or (*b*) agreed with those by $(E_{\text{vap.}})/V$ in the cases where $H_{\text{vap.}}$ data were available.

In Fig. 5 the energies of activation for 4-chlorobenzenediazocyanide (Le Fèvre and Northcott, *loc. cit.*) in eight solvents are plotted against $(P_i)^{\frac{1}{2}}$; the rectilinearity is not better than in other graphs in *J.*, 1949, 944. Fig. 6 shows a similar graph for azobenzene in the seven solvents named in Table 2; both Figs. 5 and 6 fail notably to include *o*-dichlorobenzene and *cyclo*hexanone. Accordingly we have again followed the idea used in *J.*, 1949, 944, *i.e.*, that electrostatic forces between solute and solvent molecules tend to

FIG. 7.
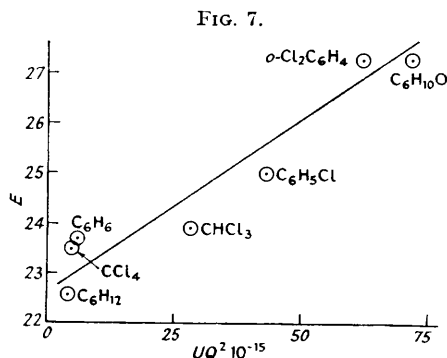
resist the inversion process : if the actual moment of a solvent molecule contiguous to a solute molecule is proportional to $\mu_M = \mu_{\text{solvent}} + 2 \times \alpha_{\text{solvent}} \cdot \mu_{\text{solute}}/(r_{\text{solute}} + r_{\text{solvent}})^3$ (α being the polarisability, μ the dipole moment, and *r* the radius of the molecules considered, *i.e.*, 3 Å for azobenzene and as listed in *J.*, 1949, 944 for the solvents), and if μ_{solute} and μ_{solvent} are taken as acting at the centres of the molecules concerned, then the interaction energy between solute and solvent is also proportional to $U = \mu_M \cdot \mu_{\text{solute}}/(r_{\text{solute}} + r_{\text{solvent}})^3$, *i.e.*, to Q^2U (where $\mu_{\text{actual}} = Q\mu_{\text{gas}}$; cf. Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1496). Fig. 7 shows E plotted against Q^2U computed on the simple lines just given; remembering the speculative nature of the quantitative assumptions upon which it is based, we submit that Fig. 7 offers indications of a relation smoother than those depicted in Fig. 5 or 6.

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