203. *Effects of Solvents and Structure on the Thermal Transformation of* cis- *into* trans-*Diazocyanides.*

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The rates of thermal *cis–trans*-interconversion of ten diazocyanides in one solvent (benzene), and of one diazocyanide (*p*-chlorobenzenediazocyanide) in eight different solvents, have been compared. The reactions show first-order kinetics with frequency factors between 10^{12} and 10^{15} sec.$^{-1}$, and energies of activation from 21 to 26 kcals./g.-mol. The lower A and E values apply in the case of non-polar solvents, changing to the higher as the polarity of the solvent increases. No regular correlation of either k or E with solvent properties can be discerned. For various diazocyanides in benzene the influence of substituents can be expressed by the equation: $E = E_0 + 2{\cdot}9\boldsymbol{R}T(\mu + 0{\cdot}209\mu^2)$, where E_0 is the energy of activation observed for benzenediazocyanide, and μ is the dipole moment of the appropriate C_6H_5X compound.

Reactions which proceed by first-order kinetics *in solution* have hitherto received rather infrequent attention (cf. Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1933), and of the cases reported the most numerous conform to the type A = B + C [*e.g.*, decompositions of diazonium or sulphonium salts, carboxylic acids, etc. (*op. cit.*, pp. 156, 157)]. Before 1938, direct *cis-* to *trans*-geometrical inversions had been studied only in the *gaseous* phase (Kistiakowsky and associates, various papers; *e.g., J. Amer. Chem. Soc.*, 1935, **57**, 269), with the one exception of certain oxime inversions (*J.*, 1908, **93**, 1041; 1912, **101**, 26, 2100; 1941, 606) which Patterson and his co-workers had followed polarimetrically in mixed solvents containing ethyl tartrate.

Ten years ago, as a side issue to their structural investigation, the isomeric diazocyanides and azobenzenes (Le Fèvre and Vine, *J.*, 1938, 431; Hartley, *ibid.*, p. 633; Le Fèvre and Hartley, *ibid.*, 1939, 531) were found to undergo interconversion in organic solvents at rates that could be conveniently measured either dielectrically or photometrically. The opportunity was therefore taken to commence the examination of the rôles of substituents and media in reactions involving the $-N{=}N-$ group.

By August, 1939, when the work had to be suspended, preliminary surveys (with Vine and Saboor, Ph.D. Theses, London, 1938 and 1941, respectively; Saboor, *Indian J. Physics*, 1943, **17**, 223) had satisfactorily indicated that, in a number of solvents, the time of half-change was generally independent of the initial concentration of the less stable form; *i.e.*, the reactions were apparently of the first order. The k values could therefore be obtained from the times of half change read from a dielectric constant–time curve.

This paper records the comparison of ten diazocyanides in one solvent (benzene), and of one (*p*-chlorobenzenediazocyanide) in eight different solvents.

In some instances, *slight* indications have been found of " initial disturbances." It is difficult to decide whether these arise from experimental errors near the beginning of a " run ", or from the fact that the isomerisation really involves a pair of consecutive changes (*e.g.*, $cis \xrightarrow{k_1}$ active intermediate $\xrightarrow{k_2} trans$, in which k_2 is the rate-determining factor). The latter is a possibility, but (compare Walker, *Proc. Roy. Soc. Edin.*, 1898, **22**, 23) *unless* k_1 and k_2 are widely different in magnitude, " first-order kinetics " cannot appear, and *if* the separate constants *are* widely different, the rate-determining constant and the " overall " (observed) constant will be practically undistinguishable.

Our measurements are summarised in Table I.

Discussion.—As a preliminary we have evaluated, from the data in Table I, the frequency factors (A) and the energies of activation (E) from the equation $k = Ae^{-E/\boldsymbol{R}T}$. The results are shown in Table II. For the thermal *cis-* to *trans*-conversion of azobenzene, either alone (fused) or dissolved in acetone or benzene, Hartley (*loc. cit.*) records a mean activation energy of 23 kcals./g.-mol., and for the *p*-dimethylamino-derivative, a value 2 kcals./g.-mol. lower. The similarity between the diazocyanides and azobenzene is therefore clear. It is accordingly of interest to compare the data of Table II with the studies, mentioned above, of analogous

TABLE I.

Thermal isomerisation of cis-*aromatic diazocyanides.*

Diazocyanide.	Solvent.	k^{25} (hr.$^{-1}$).	k^{45} (hr.$^{-1}$).	$k^{t°}$ (hr.$^{-1}$).
Benzene-	C_6H_6	5·55	—	1·43 (15°)
p-Toluene-	C_6H_6	4·12	—	1·03 (15°)
α-Naphthalene-	C_6H_6	0·224	2·568	—
β-Naphthalene-	C_6H_6	0·165	1·926	—
p-Chlorobenzene-	$C_6H_{10}O$ *	$0{\cdot}015_5$	0·25	—
,,	$C_5H_5N_5$	0·029	0·46	—
,,	*o*-$C_6H_4Cl_2$	0·041	0·58	—
,,	C_6H_6	0·065	0·63	—
,,	$CHCl_3$	$0{\cdot}074_5$	0·73	—
,,	CCl_4	0·071	0·77	—
,,	C_6H_{12} †	$0{\cdot}084_5$	0·87	—
,,	C_6H_5Cl	0·078	0·99	—
p-Bromobenzene-	C_6H_6	0·058	—	2·08 (57·5°)
o- ,,	C_6H_6	0·028	—	—
p-Nitrobenzene-	C_6H_6	0·026	0·27	—
p-Methoxybenzene-	C_6H_6	3·47	—	0·97 (15°)
2 : 4 : 6-Tribromobenzene-	C_6H_6	—	—	0·11 (57·5°) 0·396 (70·0°)

* *cyclo*Hexanone. † *cyclo*Hexane.

TABLE II.

Diazocyanide.	Solvent.	*A* (sec.$^{-1}$).	*E.* (kcals./g.-mol.).
Benzene-	C_6H_6	*ca.* 1×10^{15}	23·0
p-Toluene-	C_6H_6	*ca.* 2×10^{15}	$23{\cdot}5_5$
α-Naphthalene-	C_6H_6	5×10^{13}	22·9
β-Naphthalene-	C_6H_6	4×10^{13}	23·1
p-Chlorobenzene-	$C_6H_{10}O$	$6{\cdot}8 \times 10^{14}$	26·1
,,	C_5H_5N	$1{\cdot}0 \times 10^{15}$	$25{\cdot}9_5$
,,	*o*-$C_6H_4Cl_2$	$2{\cdot}2 \times 10^{14}$	24·9
,,	C_6H_6	$9{\cdot}5 \times 10^{11}$	$21{\cdot}3_5$
,,	$CHCl_3$	$1{\cdot}2 \times 10^{12}$	21·4
,,	CCl_4	$5{\cdot}5 \times 10^{12}$	22·4
,,	C_6H_{12}	$3{\cdot}2 \times 10^{12}$	21·9
,,	C_6H_5Cl	$7{\cdot}1 \times 10^{13}$	$23{\cdot}8_5$
p-Bromobenzene-	C_6H_6	$1{\cdot}5 \times 10^{12}$	21·6
p-Nitrobenzene-	C_6H_6	*ca.* 1×10^{12}	$21{\cdot}9_5$
p-Methoxybenzene-	C_6H_6	*ca.* 3×10^{13}	21·7
2 : 4 : 6-Tribromobenzene-	C_6H_6	$5{\cdot}6 \times 10^{11}$	23·0

geometrical changes in the gaseous phase of such molecules as maleic ester, *cis*-but-2-ene, *cis*-methyl cinnamate, *cis*-stilbene, and its mono-and dichloro-derivatives (see Moelwyn-Hughes, *op. cit.*, Chap. II, for summary). Our results at once suggest a marked contrast between the $-N{=}N-$ and the $-C{=}C-$ containing compounds, since for the latter the reactions appear to fall into two groups distinguished by their *A* and *E* values. In the first, these quantities are around 10^{14} sec.$^{-1}$ and 25 kcals./g.-mol., while in the second, the corresponding data are *ca.* 10^{11} and 45. The dissolved diazocyanides (and azobenzene, so far as data exist) are thus found to be intermediate, in that their frequency factors range from 10^{12} to 10^{15} sec.$^{-1}$ and their energies of activation from 21 to 26 kcals./g.-mol. It is possible that the distinction just emphasised would be understandable by a theoretical treatment similar to that sketched for the ethylenic case by Glasstone, Laidler, and Eyring ("The Theory of Rate Processes," McGraw-Hill, 1941, 325) but at present this cannot be applied since the torsional frequency for the $-N{=}N-$ system is unavailable.

We therefore restrict our discussion to (*a*) the effects of solvents on the *cis–trans-p*-chlorobenzenediazocyanide change, and (*b*) the effects of substituent groups on the *cis–trans*-benzenediazocyanide change.

Effects of Solvents.—A number of attempts to correlate the influences of different solvents on particular reactions, with certain physical properties of the solvent or of the solution, are on record (cf. Moelwyn-Hughes, *op. cit.*, Chap. VI). The literature shows, however, that the relative velocities of a given reaction in a series of solvents are seldom reproduced for a different chemical reaction in the same media. This seems to be true both for the A = B + C decomposition type and the A = B molecular rearrangement type (*e.g.*, camphene hydrochloride to *iso*bornyl chloride, Meerwein *et al.*, *Ber.*, 1922, **55**, 2507; *Annalen*, 1924, **435**, 211; also the racemisation—compare, however, Conant and Carlson, *J. Amer. Chem. Soc.*, 1929, **51**, 3464;

Savich and Goldblatt, *ibid.*, 1945, **67**, 2027—of *d*-pinene, Smith, *ibid.*, 1927, **49**, 43, etc.) for which the degree of solvent dependency is variable, sometimes marked, but sometimes nil (as in Smith's case; or the thermal breakdown of dinitrogen pentoxide, Eyring and Daniels, *ibid.*, 1930, **52**, 1472).

To set our results against this background, we note that *cis-p*-chlorobenzenediazocyanide isomerises at about the same speed in carbon tetrachloride as in chloroform, while Beckmann changes of the picryl ethers of benzophenone and acetophenone oximes (which likewise proceed spontaneously in pure solvents, and by first-order kinetics, Chapman and Howis, *J.*, 1933, 806) have rates which are *much* less in the former solvent than in the latter.

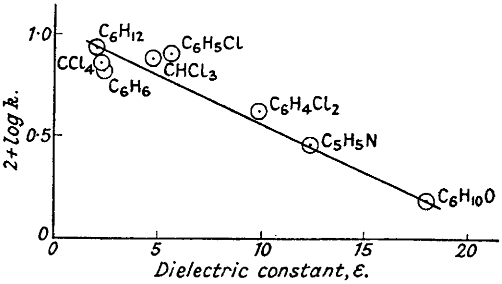
Even towards two closely similar reactions [*e.g.*, the formation of $(Et_4N)Br$ and $(Et_4N)I$; cf. Mellor, " Chemical Statics and Dynamics ", Longmans, 1909, 341] the catalytic powers of a series of liquids may not be quantitatively the same. It is accordingly not surprising that our observed orders for 25° and 45° should differ :

at 25° : *cyclo*hexane$>C_6H_5Cl>CHCl_3>CCl_4>C_6H_6>o\text{-}C_6H_4Cl_2>C_5H_5N>$*cyclo*hexanone

at 45° : $C_6H_5Cl>$*cyclo*hexane$>CCl_4>CHCl_3>C_6H_6>o\text{-}C_6H_4Cl_2>C_5H_5N>$*cyclo*hexanone

In the circumstances, therefore, one can scarcely expect to establish a quantitative correlation between reaction velocity and any *one* solvent property. Where, in the past, apparent relationships have been noticed, some mechanistic feature has often been obvious (*e.g.*, ionisation, where *k* has varied with the dielectric constant, as in the decomposition of sulphonium salts, von Halban, *Z. physikal. Chem.*, 1909, **67**, 129; or cohesion, where an effect of surface tension has been traced, as in the interactions between *N*-chloroacetanilide and hydrochloric acid solutions, Richardson and Soper, *J.*, 1929, 1873). No such guide is provided by the various attempts to describe a model for configurational inversion about a double bond.

Fig. 1.



Nevertheless, in addition to what follows we have also explored the variation of *k* and log *k* with such single solvent properties as viscosity, surface tension, refractive index, molecular and specific refraction, specific dispersion, the coefficient of cubical expansion, cohesion, adiabatic compressibility, internal pressure, parachor, etc. In most cases the absence of a correlation has been clearly visible merely by inspection. The failure with viscosity is significant since the number of collisions between solvent and solute, by simple theory, is $Z = 3\pi\eta\sigma/2m_1$ (cf. Moelwyn-Hughes, *op. cit.*, p. 28), where σ/m_1 refers to the *solute*. Yet there is no relation between *A* (Table II) and *Z* as calculated from η. Taking the effective diameter of *p*-chlorobenzenediazocyanide to be probably between 6 and 12 A. (see later), we find that the observed *A* is always less than *Z* by the above formula. The introduction (Hinshelwood, " Kinetics of Chemical Change," Oxford, 1940, 51) of a temperature-invariant factor, *P*, to represent various unknown conditions modifying Z, would qualitatively rationalise the situation.

The literature contains many references suggesting that connections between reaction velocities and properties are commonly very indirect. The empirical rule of Richardson and Soper (*loc. cit.*) may be cited as one example, and if in our cases the assumption may be made that the transition state resembles the product (as it probably does), but exceeds it in internal pressure, then solvents of high internal pressure should act deceleratively if the second phase of the overall reaction is the rate-determining stage. (Activated, and polar, intermediate forms, *e.g.*, $X\cdot\overset{+}{C}_6H_4{:}N\cdot\overset{-}{N}\cdot CN$, *may* be involved; their moments would be many multiples of those of the *trans*-form which, *e.g.*, when X = Cl, has $\mu = 3{\cdot}7$ D.) Since internal pressure runs roughly parallel to the dielectric constant of a liquid, it is notable that, qualitatively, a general slowing of reaction does in fact seem to accompany a gross increase in the dielectric constant of the medium (compare the speed in *cyclo*hexanone, $\varepsilon = 18$, with that in *cyclo*hexane, $\varepsilon = 2$), although the corresponding rates in benzene, chloroform, carbon tetrachloride, and chlorobenzene ($\varepsilon = 2{\cdot}3, 4{\cdot}7, 2{\cdot}2, 5{\cdot}6$, respectively) clearly indicate that no *accurate* parallelism with this property exists. However, a graph of log *k* against $\varepsilon_{\text{solvent}}$ (Fig. 1) reveals an *approach* to a smooth relationship.

A number of authors have attempted to consider liquid-phase reactions in the light of a quasi-crystalline structure of liquids. Bradley (*J.*, 1934, 1910) assumes a spherical solute molecule, surrounded by 12 others, within which the motion of the central one resembles a high-frequency vibration with a continually changing axis. If v^2 is the mean square velocity of the solute and α its amplitude of vibration, then, for a unimolecular reaction $k = \frac{v}{\alpha}\left(\frac{3\pi}{2}\right)^{\frac{1}{2}} \frac{E}{\boldsymbol{R}T} e^{-E/\boldsymbol{R}T}$. The quantity α might therefore be related to the interstitial spaces in the models of the various solvents; Bradley (*Trans. Faraday Soc.*, 1937, **33**, 1185) equates it to $2(2{\cdot}22/4\pi N)^{\frac{1}{3}}(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})$, where V and V_0 are the molecular volumes at $T°$ and the absolute zero, respectively. Using Sugden's data (*J.*, 1927, 1786) we have computed $(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})$, but find no proportionality between $E_{\text{obs.}}/(V^{\frac{1}{3}} - V_0^{\frac{1}{3}})$ and A (Table II). In combination, however, with the independent approach by Wheeler (*Proc. Indian Acad. Sci.*, 1936, **4**, 291), Bradley's α becomes $0{\cdot}268(\boldsymbol{k}T/r)(V/P)^4$, where P = parachor, r = solvent radius, which (for a hexagonally close-packed arrangement) $= (\frac{3}{4}0{\cdot}74M/N\pi d)^{\frac{1}{3}} = (0{\cdot}2916V)^{\frac{1}{3}} \times 10^{-8}$ cm. Again, however, the solvents are not placed in their correct frequency factor order.

Waring and Becher (*J. Chem. Physics*, 1947, **15**, 488) assign a vibrational frequency, f, to the molecules of the solvent " crystal ", and calculate f as $C(3N/4\pi V)^{\frac{1}{3}}$, where C is the velocity of sound in the medium, and V the molecular volume. The reaction constant is given by

$$k = \frac{nf}{(S-1)!}\left(\frac{E_g}{\boldsymbol{R}T}\right)^{S-1}(e^{-E_{\text{obs.}}/\boldsymbol{R}T})$$

n being the number of molecules surrounding the solute, S the specified number of internal degrees of freedom contributing to the reaction, and E_g the theoretical energy of activation of the reaction in the gaseous phase. Thus according to this theory the logarithms of the observed frequency factors, listed in Table II, should be proportional to (log C — 0·5 log V + log n + constants). We have estimated n in two ways as follows : (i) A scale drawing showed that *cis-p*-chlorobenzenediazocyanide may reasonably be fitted into a prolate spheroid whose major axis ($2a$) is twice its minor. The ratio (molecular volume at 25°)/parachor is roughly 0·45 [this is a fortuitous relation; cf. Sugden, *J.*, 1927, 1780, *re* the analogous apparent relationships between zero and molecular volumes—since Parachor = (molecular volume)(surface tension)$^{\frac{1}{4}}$, and for most organic liquids the surface-tension range is small]. The parachor of *p*-chlorobenzenediazocyanide is about 350 (measured, see Experimental; 342 calculated) whence $V_{25°} =$ *ca.* 158, and $158/(6{\cdot}06 \times 10^{23}) = \pi a^3/3$, whence $a = 6{\cdot}29$ A. Using the virtual radii of the solvents (cf. above) we next evaluated the surface areas of spheroids in which the axes were $2(6{\cdot}29 + r_{\text{solvent}})$ and $2(3{\cdot}14_5 + r_{\text{solvent}})$, respectively. Division by $2\sqrt{3}\,r^2_{\text{solvent}}$ provided n. (ii) As above, except that n was taken as Area/$4r^2$. The results are compared in Table III.

TABLE III.

Estimated numbers of solvent molecules surrounding p-*chlorobenzenediazocyanide.*

	(i).	(ii).		(i).	(ii).
*cyclo*Hexanone	19·7	17·1	$CHCl_3$	21·6	18·7
Pyridine	21·6	18·7	CCl_4	20·2	17·5
o-$Cl_2C_6H_4$	19·2	16·6	*cyclo*Hexane	19·4	16·8
C_6H_6	20·9	18·1	C_6H_5Cl	19·9	17·2

TABLE IV.

Observed.	*ex* Bradley.	*ex* Wheeler.	*ex* Waring & Becher.
C_5H_5N	o-$C_6H_4Cl_2$	o-$C_6H_4Cl_2$	C_5H_5N
*cyclo*Hexanone	*cyclo*Hexanone	*cyclo*Hexanone	C_6H_6
o-$C_6H_4Cl_2$	C_6H_5Cl	C_5H_5N	*cyclo*Hexanone
C_6H_5Cl	C_5H_5N	C_6H_5Cl	C_6H_5Cl
CCl_4	$CHCl_3$	C_6H_6	$CHCl_3$
*cyclo*Hexane	C_6H_6	CCl_4	*cyclo*Hexane
$CHCl_3$	CCl_4	*cyclo*Hexane	o-$C_6H_4Cl_2$
C_6H_6	*cyclo*Hexane	$CHCl_3$	CCl_4

The number varies from 17 to 22; it is considerably more than the 12 adopted by Bradley.

When the appropriate measurements (velocity of sound data from Freyer, Hubbard, and Andrews, *J. Amer. Chem. Soc.*, 1929, **51**, 759; Willard, *J. Acoustic Soc. Amer.*, 1941, **12**, 438; and Bergman, " Ultrasonics ", transl. Hatfield, Wiley, 1939) are introduced into the various expressions, the solvents may be arranged (Table IV) in descending orders of the relative frequency factors forecast. Not only is the experimental sequence not followed, but the calculated quantities are not " spread " nearly sufficiently. A similarly inappropriate result is obtained if the estimated surfaces of the solute ellipsoids (above) are multiplied by the number of solvent molecules striking a unit area per second; *i.e.*, $d_S N/M_S(\boldsymbol{R}T/2\pi M_S)^{\frac{1}{2}}$ (cf. Moelwyn-Hughes, *op. cit.*, p. 28)—an approach which, because of the relative size of the solute, seems *a priori* reasonable.

Glasstone, Laidler, and Eyring (*op. cit.*, p. 420) point out that in certain cases log k has varied with $(\varepsilon - 1)/(2\varepsilon + 1)$, rather than with ε directly (as attempted in Fig. 1). Fig. 2 shows signs of a correlation on this basis *except for the three solvents* whose molecules are ordinarily regarded as non-polar. The position of C_6H_5Cl ($\mu = 1{\cdot}6$ D.) relatively to CCl_4 ($\mu = 0$), C_6H_6 ($\mu = 0$), etc., in Table I negatives an immediate connection with solvent moments as usually measured. We note, however, that Fig. 3, in which $E_{\text{obs.}}$ is shown against ε, brings the two solvent types more nearly on to one line. Moreover, the solute has an appreciable polarity ($\mu = 2{\cdot}9 - 3{\cdot}7$ D. in C_6H_6; Le Fèvre and Vine, *loc. cit.*); it will induce polarity in the surrounding solvent molecules, and hold them by electrostatic attractive forces. Since the latter may need to be overcome during the inversion reaction, some influence, probably on the activation energy, could intuitively be foreseen. This possibility has been explored with the following assumptions: The solute dipole (3 D.) is situated at an average distance = 4·72 A. (*i.e.*, the mean of the major and minor half-axes mentioned above) plus r_{solvent} (calculated from the molecular volumes at 25°; cf. Table VII) from the centres of the surrounding solvent molecules, whose polarisabilities are given by $\alpha = 0{\cdot}0394[R_L]_D \times 10^{-23}$ c.c. The maximum moment, μ_M, acting anti-parallel to μ_{solute}, of each solvent molecule is therefore *ca.* $\mu_{\text{solvent}} + 2(\alpha_{\text{solvent}}\ \mu_{\text{solute}})/(4{\cdot}72 + r_{\text{solvent}})^3$. The interaction energy U (cf. Jeans, " Electricity and Magnetism," Cambridge Univ. Press, 1920, 354) is therefore proportional to $\mu_M \cdot \mu_{\text{solute}}/(4{\cdot}72 + r_{\text{solvent}})^3$. In the last but one column of Table V are shown the values of U which are plotted against $E_{\text{obs.}}$ (*ex* Table II) in Fig. 4.

FIG. 2.

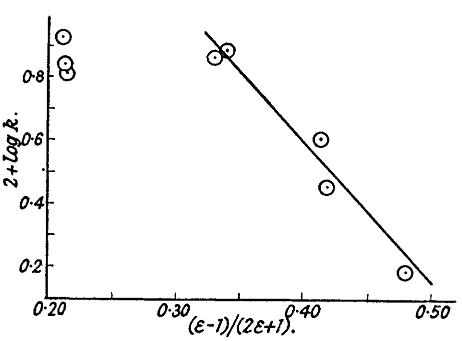


FIG. 3.

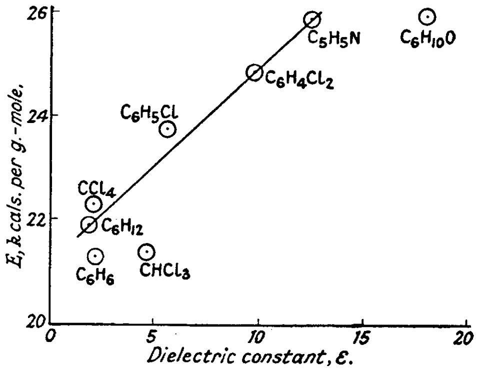


TABLE V.

	μ, D.	$\alpha \times 10^{23}$.	$\mu_M \times 10^{18}$.	$U \times 10^{15}$.	$Q^2U \times 10^{15}$.
*cyclo*Hexanone	2·8	1·09	2·94	18·3	32·4
C_5H_5N	2·3	0·95	2·43	16·7	30·4
o-$Cl_2C_6H_4$	2·3	1·36	2·46	14·8	27·8
C_6H_6	0	1·03	0·14	0·93	1·2
$CHCl_3$	1·0	0·84	1·12	7·7	11·5
CCl_4	0	1·04	0·13	0·83	1·1
*cyclo*Hexane	0	1·09	0·13	0·80	1·0
C_6H_5Cl	1·6	1·22	1·75	11·0	18·6

The result is promising. It will be noted that both polar and non-polar solvents whose molecular shapes are related tend to lie on a straight line. Chloroform shows the greatest disagreement, but since it may aggregate itself around the solute by the three chlorine atoms, its resultant moment might never act co-linearly with that of the diazocyanide; thus the fundamental assumption made above is least applicable in this case. Perhaps the " actual " dipole moments (when surrounded by other molecules in the liquid state) should be considered. Onsager (*J. Amer. Chem. Soc.*, 1936, **58**, 1486) calculates them by $\mu_{\text{actual}}/\mu_{\text{gas}} = (n^2_\infty + 2)(2\varepsilon + 1)/3(2\varepsilon + n^2_\infty) = Q$. We have evaluated Q for each solvent (using n_D as an approximation to n_∞; see Table VII) and roughly corrected the U values (Table V) by multiplying by Q^2. The effect may be seen by comparing Figs. 4 and 5.

FIG. 4.

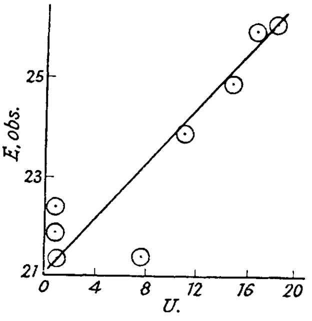
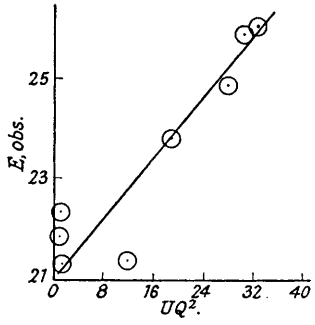


FIG. 5.



Possibility of Adventitious Catalysis.—In view of the demonstration that molecular oxygen can catalyse certain *cis* ⟶ *trans*-reactions in C═C systems (Tamamushi and Akiyama, *Z. Electrochem.*, 1937, **43**, 156) or C═N systems (Taylor and Lavington, *J.*, 1934, 980), it should be pointed out that no such effect is apparent in our experiments. The observed rates are the same in freshly vacuum-distilled solvents as in those which have been standing in contact with air for several weeks, and the order of velocities shown in Table I is quite different from that shown in the International Critical Tables (Vol. III, p. 262) for the solubilities of oxygen in the eight solvents used.

Effects of Substituents.—Because of the conclusions of Brönsted and Pederson (*Z. physikal. Chem.*, 1924, **108**, 185; compare Hinshelwood, *J.*, 1937, 635, and Hammett, *Chem. Reviews*, 1935, **17**, 125; *Trans. Faraday Soc.*, 1938, **34**, 156), a relation was first sought between log k (from Table I) and log K_A, where the latter refers to the dissociation constants of *p*-substituted benzoic acids. On the whole the two sets of values indicate a definite drift. We next attempted the correlation noted by Waters (*Phil. Mag.*, 1929, **8**, 436) and Nathan and Watson (*J.*, 1933, 893), who succeeded in expressing in an approximately linear manner the dipole moments of certain benzene derivatives C_6H_5X with the logarithms of the dissociation constants of various benzoic and acetic acids. This was tolerably successful, but a better fit is obtained by the general equation (Waters, *J.*, 1933, 1551; *Nature*, 1934, **134**, 178; Watson, *Trans. Faraday Soc.*, 1938, **34**, 165) : $E = E_0 \pm C(\mu + \alpha\mu^2)$. The values of E listed in Table II for the *p*-chloro-, *p*-nitro-, and unsubstituted benzenediazocyanides being used, values of $\alpha = 0{\cdot}209$ and $C = 1604$ lead to good agreement between found and calculated values for the energies of activation. The moments of the corresponding $C_6H_5{\cdot}X$ are shown in col. 2 of Table VI.

TABLE VI.

Diazocyanide.	μ(D.).	E (kcals./g.-mol.). calc.	found.
Benzene-	0	23·0	23·0
p-Toluene-	+0·34	$23{\cdot}5_8$	$23{\cdot}5_5$
p-Chlorobenzene-	−1·5	$21{\cdot}3_5$	$21{\cdot}3_5$
p-Nitrobenzene-	−4·0	$21{\cdot}9_5$	$21{\cdot}9_5$
p-Methoxybenzene-	−1·23	$21{\cdot}5_3$	21·7
2 : 4 : 6-Tribromobenzene-	0	23·0	23·0

Nathan and Watson (*J.*, 1933, 890; *Nature*, 1934, **133**, 379; Evans, Morgan, and Watson, *J.*, 1936, 1174) write their equation for the substituted acetic acid case as $E = E_0 + 2{\cdot}4\boldsymbol{R}T(\mu + 0{\cdot}032\mu^2)$. Expressing our results in the same form, we have $E = E_0 + 2{\cdot}9\boldsymbol{R}T(\mu + 0{\cdot}209\mu^2)$.

EXPERIMENTAL.

Solutes.—These were prepared by methods described in earlier papers (Anderson, Le Fèvre, and Savage, *J.*, 1947, 445; Anderson, Bedwell, and Le Fèvre, *ibid.*, p. 457; Le Fèvre and Northcott, this vol., p. 333).

Solvents.—" Thiophen-free " benzene was dried, partially frozen in contact with sodium wire, and decanted; the solid portion remaining, after remelting, was stored over sodium. Carbon tetrachloride was shaken with mercury, washed successively with concentrated sulphuric acid, dilute sodium hydroxide, and water, then dried ($CaCl_2$) and distilled under moderately reduced pressure immediately before use, b. p. 26°/120 mm. Chloroform (A.R.), stored in contact with calcium chloride, was distilled when required, b. p. 28·1°/225 mm. *cyclo*Hexane, purified as above for benzene, had b. p. 81°/760 mm. *cyclo*Hexanone was first precipitated as the bisulphite compound which, after separation, was decomposed by sodium carbonate solution; the liberated ketone, after steam-distillation and drying (Na_2SO_4), was redistilled; b. p. 155·5°/760 mm. Pyridine was kept over potassium hydroxide for several days, then twice boiled under reflux with fresh pellets of potassium hydroxide; it was fractionated as needed; b. p. 115°/759 mm. *o*-Dichlorobenzene was partially frozen, etc., then distilled, and only the middle fraction taken; this was stored over calcium chloride; b. p. 86°/18 mm. A pure stock of chlorobenzene was dried ($CaCl_2$) and redistilled as necessary; b. p. 132°/762 mm.

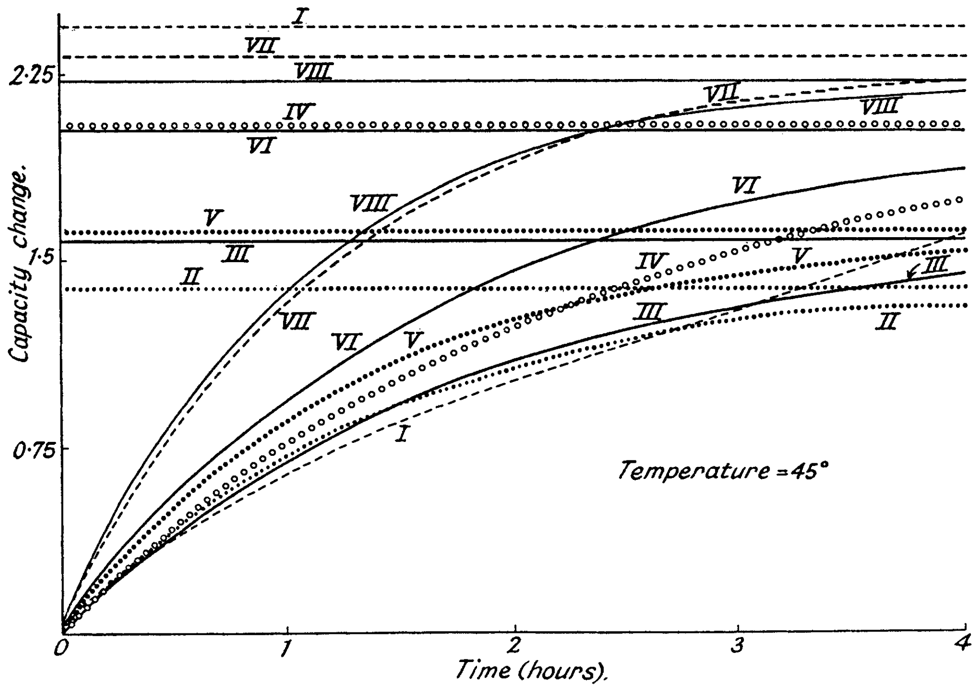
In most cases the densities and refractive indexes, and in some cases the dielectric constants (relative to benzene or chloroform), of these solvents have been checked. The data are assembled in Table VII, together with the molecular volumes, solvent radii, and "Onsager" factors (Q) used previously in this paper.

TABLE VII.

	$\varepsilon_{25°}$.	$[n^2_D]_{25°}$.	$d^{25°}_{4°}$.	$V_{25°}$.	$(r_{solvent}) \times 10^8$.	Q.
*cyclo*Hexanone	18·2	2·1031	0·9411	104·1	3·12	1·33
C_5H_5N	12·4	2·2720	0·9773	80·8	2·87	1·35
o-$Cl_2C_6H_4$	9·82	2·3951	1·2934	113·6	3·21	1·37
C_6H_6	2·27 *	2·2420	0·8738	89·3	2·96	1·15
$CHCl_3$	4·72 †	2·0825	1·4790	80·7	2·87	1·23
CCl_4	2·23	2·1656	1·5855	97·0	3·05	1·15
*cyclo*Hexane	2·04	2·0221	0·7740	108·5	3·16	1·12
C_6H_5Cl	5·61 ‡	2·3180	1·1012	102·1	3·10	1·30

* Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, **123**, 664.
† Ball, *J.*, 1930, 570. ‡ Sugden, *J.*, 1933, 768.

FIG. 6.



Curve No.	Solvent.	Total capacity change.*	Curve No.	Solvent.	Total capacity change.*
I	*cyclo*Hexanone	2·43	V	Carbon tetrachloride	1·60
II	Chloroform	1·38	VI	Benzene	2·02
III	*o*-Dichlorobenzene	1·58	VII	*cyclo*Hexane	2·22
IV	Pyridine	2·04	VIII	Chlorobenzene	2·30

* In arbitrary units of a micrometer drive (see Le Fèvre and Northcott, *loc. cit.*).

Apparatus and Procedure.—The essential modifications to standard practice have already been noted (Le Fèvre and Northcott, *loc. cit.*). The thermostat liquids (paraffin) were in all cases dyed a deep red.

The formal justification for the use of the dielectric constant as an index of the progress of these reactions lies in the fact that, for each of some 16 diazocyanides hitherto examined, this property has had a rectilinear dependence upon concentration, so that, *e.g.*, $\varepsilon_{12} = \varepsilon_2(1 + \alpha\omega_{cis})$ for one form, or $\varepsilon_2(1 + \gamma\omega_{trans})$ for the other. Starting at t(time) = 0 with a weight fraction S of *cis*-isomer, after a given time interval a weight fraction x of the *trans*-isomer has been formed. Then $(\varepsilon_{12})_t = \varepsilon_2 + \alpha\varepsilon_2 S + x\varepsilon_2(\gamma - \alpha)$, *i.e.*, x is linear with ε_{12}. Since changes in the latter are compensated by adjustments of a parallel timing capacity, the rates have been, in fact, plotted as capacity–time curves, from which the times of half change can be read directly. Fig. 6 is reproduced as a specimen of our results.

As examples of the non-dependence of the times of half-change ($t_{\frac{1}{2}}$) upon concentration the following figures for *p*-chlorobenzenediazocyanide at 45° may be quoted :

$10^5 w_1$.	Solvent.	$t_{\frac{1}{2}}$, mins.	$10^5 w_1$.	Solvent.	$t_{\frac{1}{2}}$, mins.	$10^5 w_1$.	Solvent.	$t_{\frac{1}{2}}$, mins.
438	C_6H_6	69	845	C_6H_5Cl	39	1592	C_5H_5N	90
1258		66	1886		42	2380		90
1667		66	2458		42	2967		89

To indicate the extent of the "initial disturbances" (cf. p. 944) we compare below, for typical runs (of the *p*-chloro-derivative at 45°) the *k* values calculated at stated time intervals with those obtained by reading $t_{\frac{1}{2}}$ from a smoothed curve incorporating numerous actual observations :

Time, mins.	*cyclo*-Hexanone.	C_5H_5N.	*o*-$Cl_2C_6H_4$.	Solvent. C_6H_6.	$CHCl_3$.	CCl_4.	*cyclo*-Hexane.	C_6H_5Cl.
5	0·360	0·478	0·597	0·992	0·719	0·778	0·865	0·956
15	0·334	0·483	0·542	0·690	0·730	0·777	0·870	1·02
30	0·309	0·461	0·584	0·636	0·726	0·779	0·881	0·995
60	0·256	0·458	0·585	0·636	0·713	0·772	0·874	0·996
90	0·255	0·462	0·582	0·635	0·732	0·775	0·873	0·994
120	0·255	0·462	0·586	0·632	0·715	0·774	0·875	1·00
190	0·254	0·462	0·577	—	0·734	0·768	0·868	1·00
240	0·258	0·463	0·589	0·634	0·732	0·769	0·873	0·99
360	0·250	—	—	—	—	—	—	—
480	0·248	—	—	—	—	—	—	—
k from $t_{\frac{1}{2}}$	0·25	0·46	0·58	0·63	0·73	0·77	0·87	0·99

Parachors.—Benzene solutions of *p*-chloro- and 2 : 4 : 6-tribromo-benzenediazocyanides at 25° were examined by the procedure of Hammick and Andrew (*J.*, 1929, 754; cf. Sugden, *ibid.*, 1924, **125**, 27). Owing to solubility limitations, concentrations greater than mol.-fraction = 0·004 could not be used and $(P)_{obs.}$ was therefore uncertain; *e.g.*, for the two solutes named, values of (*a*) 347, 356, 358 and (*b*) 453, 461 were recorded respectively. The corresponding calculated figures are 342 and 456. Attempts to estimate the molecular surface areas (from $-\,d\gamma/d\log C$; Gibbs's equation) were unsatisfactory because the results (32—55A^2) did not enable us to check the dimensions used in discussion above (p. 947).

General Note.—In the course of recent discussions on diazocyanides in *Chemistry and Industry* [1948, 158 (Calderbank, Le Fèvre, and Northcott), 270 (Hodgson), 301 (Waters), 732 (Le Fèvre, Northcott, and Wilson), 543 and 782 (Hodgson), 588 (Le Fèvre and Northcott)], Hodgson has questioned the purities of the stable and labile forms actually used in the various investigations with which we are concerned. He says "In my experience, the rate of conversion of many of these *cis*-diazocyanides is very rapid even below 0° . . . " and " . . . if I am right, all Professor Le Fèvre's work refers either to mixtures of *cis*- and *trans*-forms or to *trans*-forms only."

Our answer to these charges is largely based on the measurements now reported in detail for the first time. Pure solutes of sharp m. p. have always been used as starting materials, while the interval for half-change (at ordinary temperatures) of the substances upon which dipole-moment and infra-red observations were made, respectively, in 1938 and 1947, has never been *less* than 8 *hours*. We therefore feel confident that our past data, requiring only *minutes* for their collection, have been correctly ascribed, and that photo-equilibria, or changing mixtures of labile and stable isomers, have not been mistaken for either of the separate forms.

Note, added November 5th, 1948.—The authors are grateful to the Referees for the following further comment. " . . . the experiments made with *cis*-*p*-chlorobenzenediazocyanide in a wide range of solvents, including some like pyridine which would *immediately* combine with free ions (or radicals), give conclusive proof that this isomeric change is wholly intramolecular and does not involve any transient dissociation of the labile isomeride."

The stability of the system, and the quantitative yield of the *trans*-isomeride in all these solvents is also an argument for the rejection of an "*iso*nitrile" formulation.

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