113. *The* cis-*Form of Azobenzene and the Velocity of the Thermal* cis ⟶ trans-*Conversion of Azobenzene and Some Derivatives.*

By G. Spencer Hartley.

Ordinary (*trans-*) azobenzene is partly converted into the *cis*-form on exposure of solutions to light. The pure *cis*-form has been isolated, and its configuration established. Its solutions absorb more light in the blue end of the visible spectrum than those of the *trans*-form, and use is made of this property to determine the concentrations in solution. In the crystalline state the *cis*-form can be kept indefinitely in the dark,

but is converted completely into the *trans*-form in solution. The conversion is a unimolecular reaction, not greatly dependent on the solvent, and the temperature coefficient corresponds to an energy of activation of 23 kg.-cals. per g.-mol.

Solutions of several derivatives of azobenzene become darker on exposure to light. This is proved in some cases, and assumed in the others, to be due to partial conversion into the *cis*-forms. The subsequent thermal *cis* —→ *trans*-conversion of the 4-amino-, 4-dimethylamino-, and 4-hydroxy-azobenzenes is more rapid than that of azobenzene. In the first two it is very sensitive to acid, and in the last to base, catalysis, behaviour which is attributed to very much greater ease of conversion of the ionised compounds. The conversion of azobenzene itself is catalysed by strong acids in aqueous solution but simultaneous chemical reactions occur in this case.

The cis-*Form of Azobenzene.*—The isolation of a second form of azobenzene from solutions exposed to light has already been reported (*Nature*, 1937, **140**, 281). Further facts indicating that this is the missing geometrical isomer, to be expected by analogy with the diazotates, diazocyanides, and azoxy-compounds, have since been established. The evidence may be summarised as follows :

(1) That the new form is converted completely into the ordinary form on heating in a small enclosed space without change of pressure is evidence of the identity in chemical composition of the two forms. (2) Freezing-point determinations on 5% solutions in benzene and acetic acid gave depressions of 1·44° and 1·09° respectively, corresponding to $M = 179$ and 190 (Calc. for $C_{12}H_{10}N_2 : M$, 182), and thus disposing of the remote possibility of the new form being a polymer. (3) The new form has a dipole moment of 3·0 D. in benzene solution, according to measurements by R. J. W. Le Fèvre, whereas that of the normal form is zero (*idem*; and Bergmann *et al., Ber.*, 1930, **63**, 2572). (4) The new form, though differing by only 3° in m. p., is considerably more soluble in polar solvents, particularly in water (6·5 × 10⁻⁴ mol./l. at 25° as compared with 2 × 10⁻⁵), and less soluble in petrol (b. p. 40—60°) at 0° (*ca.* 0·9%; cf. 3·5% for ordinary form). (5) The preparative agent (light) is one which is known to be particularly active in promoting geometrical rearrangement about a double bond, *e.g.*, in fumaric–maleic acids (Warburg, *Ber. Berl. Akad.*, 1919, 960), stilbene (Smakula, *Z. physikal. Chem.*, 1934, *B*, **25**, 90), oximes (Brady and McHugh, J., 1924, **125**, 547), azoxybenzene (Müller, *Annalen*, 1932, **493**, 166), and diazocyanides (present paper).

It may therefore be taken as established that the new form is the *cis*-isomer, the ordinary form being *trans*, as shown by its zero moment (see above) and its crystal structure (Robertson *et al., Proc. Roy. Soc.*, 1936, *A*, **154**, 197, and private communication).

In the crystalline state the *cis*-form appears to be quite stable in the dark at room temperature. It forms small, bright red crystals from petrol. The m. p., determined by quick plunging, is 71·4°; it falls on repeated measurement, owing to rapid conversion in the liquid state at this temperature into the *trans*-form. The course of the m. p.'s on slow repetition was a simple fall to a eutectic at 41°, followed by a rise to that of the pure *trans*-form at 68·0°.

Dilute solutions of the same concentration of either form quickly become identical on exposure to daylight. The equilibrium mixture contains 15—40% of the *cis*-form, depending on the solvent. This concentration is determined, at ordinary temperatures and light intensities, entirely by the relative velocities of the two photochemical reactions, *cis* —→ *trans* and *trans* —→ *cis*. The thermal reaction occurs only in the *cis* —→ *trans* direction, but is too slow to have any influence on the photochemical equilibrium. In the remainder of this paper we are concerned mainly with the thermal reaction. The photochemical reaction is being further investigated in these laboratories.

An approximate measurement of the heat evolved in the *cis* —→ *trans* reaction was made by melting weighed quantities of the two forms on mercury at about 135° in a small Dewar vessel. At this temperature the *cis* —→ *trans* reaction is almost instantaneous. The heats absorbed per g. were : for the process, solid *trans* at 21° —→ liquid *trans* at 135°, 84, 77, and 79 cals. (3 expts.), and for solid *cis* at 21° —→ liquid *trans* at 135°, 15 and 15 cals. (2 expts.). For the process, solid *cis* at 21° —→ solid *trans* at 21°, we obtain, therefore, the surprisingly large value of 65 cals. evolved per g. (12 kg.-cals./g.-mol.).

cis–trans-Isomerism in Derivatives.—It was to be expected that other azo-compounds would pass partly into the *cis*-form on exposure of solutions to light. It was found that 4 : 4'-dimethylazobenzene behaved similarly to azobenzene in that the light absorption increased on exposure of an acetone solution and the solute became in part more resistant to precipitation by water. Isolation of the *cis*-form was not attempted. 4-Methoxyazobenzene showed the same behaviour; isolation was attempted by the same method as for *cis*-azobenzene (see p. 637), but the chloroform extract left behind a viscous red oil which failed to crystallise at − 15°. A dilute solution of the dried oil had a greater light absorption than that of a solution of the same weight concentration of the normal crystalline substance. After exposure of the solutions to light the absorption readings were identical and intermediate between those of the original solutions.

Samples of *cis-* and *trans-p*-bromobenzenediazocyanides, kindly supplied by Mr. H. Vine, were made up in identical concentration in benzene. The former had the greater absorption. After exposure to daylight both reached the same intermediate absorption, found, by calibration with mixtures, to correspond to 20% of the *cis*-form.

The question arose whether the important class of azo-dyes might show the same behaviour. Almost all these substances have hydroxy-, amino-, or substituted aminogroups in the *o-* or the *p*-position to the azo-group. For this reason the behaviour of some 4-amino- and 4-hydroxy-derivatives in various solvents was examined. 2-Substituted isomers would be expected to behave, at least qualitatively, in the same way. The compounds examined were 4-hydroxy-, 4-amino-, 4-dimethylamino-, and 4-methoxyazobenzenes, and the fully methylated quaternary ammonium salt. All showed appreciable darkening in some solvents on exposure to light, reverting to normal at different rates in the dark. With the first three compounds, the thermal reversion to the stable form was much too rapid in hydroxylic solvents to permit the method of isolation used for azobenzene to be applied. The quaternary salt reverts very slowly, but in this case isolation of the *cis*-form would have required a closer study of the solubilities of the salts with various anions than the object in view seemed to justify. That the change in absorption on exposure is, in these compounds also, due to the photochemical production of the *cis*-form is therefore at present an assumption based on analogy.

Method of Analysis.—A photometric method was used to determine the amounts of *cis*- and *trans*-forms of azobenzene in a given solution, since the former has a greater absorbing power for blue light than the latter (between 2 and 3 times as great, depending on solvent). A photoelectric null instrument of a new type, to be described elsewhere, enabled a reading on the sliding scale of a neutral-tinted glass wedge compensator to be obtained for solutions within a certain concentration range (*ca.* 3—8 × 10^{-4} mol./l.) in a Hilger Pyrex cell 2 cm. long. The light used was that from a high-temperature tungsten lamp, passed through a Kodak Wratten filter, No. 47 (transmission band approx. 4000—4800 A). The intensity was insufficient to effect appreciable photochemical change during a measurement. It was assumed in the work previously reported that the scale reading was linear against percentage composition, since it was found to be linear against concentration for the pure *trans*-compound. This assumption was found to be not strictly true. Calibration curves were therefore constructed for acetone as solvent. Experiments in other solvents were carried out at much higher concentrations, so that no effect of solvent on the photometer reading remained after dilution with acetone to the concentration convenient for analysis.

Solutions of known total concentration were diluted quantitatively with acetone, and the percentage of the *cis*-form could then be obtained from the photometer reading by interpolation on the family of calibration curves with an accuracy of 0·5—1·0% (Method 1).

Solutions of the concentration convenient for analysis have, for a given concentration, photometer readings independent of the initial isomeric composition, if they have been exposed to bright daylight (not necessarily sunlight) for a few minutes. This enabled the concentrations of both forms to be determined in cases where quantitative dilution was not convenient. Dilution was continued till a convenient photometer reading was obtained, the diluted solution exposed, and a second reading obtained. The total concentration corresponding to the latter was found from one curve, and the percentage composition of the original solution then obtained from the family as before. This method (Method 2) was necessarily rather less accurate (about 1·0—1·5%). The fully exposed dilute solutions in acetone contained 25% of the *cis*-form,

the higher value of 27% previously reported being due to the inaccurate assumption mentioned above.

In the case of the azobenzene derivatives, the absorption, in the narrow blue region used, was not always increased on exposure. In the dimethylamino-compound, considerable reduction resulted, especially in acetone, but the visual colour increased considerably. The visible band must therefore be considerably displaced, not, as in azobenzene itself, being increased in intensity without displacement (Le Fèvre and Vine, this vol., p. 438).

Conversion Velocity Measurements.—All operations except the illuminations were carried out in a darkened room lit by a carbon-filament 32 c.p. lamp, which was found to cause no appreciable change in a cold *cis*-azobenzene solution in ¼ hour. To prevent photochemical change when the room was more brightly lit for other work, the water of the 25° thermostat tank in which the reaction vessels were placed was stained with methyl-orange, and the solid and the *trans*-solutions were kept in a dark cupboard.

The velocity of the dark reaction in azobenzene was followed in solutions of concentration $8·0 \times 10^{-3}$ mol./l., 1 c.c. being taken at intervals and diluted to 25 c.c. with acetone for analysis. With acetone itself, further measurements were made at the analytical concentration. In experiments at 25°, Method 1 was used. At higher temperatures it was desired to withdraw samples quickly and to run them into cold acetone to stop the reaction. The pipetting was therefore done only approximately, and Method 2 applied. For the pure liquid, samples were withdrawn by dipping in a glass rod and washing it with acetone, Method 2 again being used in the analysis. The constant higher temperatures were obtained by jacketting the reaction vessels with vapour of boiling acetone, carbon tetrachloride or water. The reaction vessels, of about 10 c.c. capacity, had ground glass stoppers and necks; the latter extended beyond the ground part, so that the vapour jacket could extend above the stopper.

In making measurements in water a different procedure was necessitated by the fact that the solubility of the *trans*-form is much below the concentration convenient for accurate photometric measurements. The reactions were therefore carried out in shaken vessels, and solid *trans*-azobenzene was added. The *trans*-form has a negligible tendency to form a supersaturated solution and is removed from the solutions as it is formed. Samples were withdrawn through a micro-filter (Jena glass) and the concentration of the remaining *cis*-form determined photometrically. These measurements were made at 25° only. At temperatures above the eutectic, the *cis*-form would be partly removed in a liquid phase and the method would therefore not be applicable.

The reaction in water is catalysed by hydrogen ions. Measurements were made, by the method used for water, in various concentrations of several strong acids.

Measurements were made of the velocity of conversion in benzene solution of *cis-p*-bromobenzenediazocyanide by the same method as for azobenzene. The results were in good agreement with the measurements of Le Fèvre and Vine (*loc. cit.*) by the dielectric-constant method.

For the measurements on methoxyazobenzene, solutions of the *cis*-rich oil (see p. 635) were used, the photometer being calibrated by mixtures of this solution with one of equal concentration of the ordinary (*trans*-) form. For the quaternary ammonium compound in water and the dimethylamino-compound in acetone, the light-equilibrium solution was the starting material, calibration being effected by mixtures with unexposed solution of equal concentration. In the case of the former, the photometer reading displacement was small, and the results therefore less accurate. That the amount of *cis*-form is in each case unknown by a constant factor is of no consequence, of course, for the calculation of the first-order velocity constant.

The light absorption of exposed solutions of the amino- and hydroxy-compounds in all solvents and of the dimethylamino-compound in petrol and benzene reverted to the normal value in the dark too quickly for calibration of the photometer by mixtures to be possible. The difference of photometer reading from the dark value had therefore to be taken to be proportional to the amount of *cis*-form. The logarithms of these differences plotted against time gave lines which were straight within the large random error due to the difference in these cases being small (corresponding to 5—15% change in mean extinction), to the measurements being of necessity made in the photometer cell which was not thermostatically controlled, and perhaps also to changing catalytic effects. The velocity constants are therefore very crude, the accuracy being perhaps only 10—25%, but they differ so greatly that the figures are nevertheless of considerable significance.

The hydroxy-, amino-, and dimethylamino-compounds were very sensitive to base or acid catalysis. In alcoholic solution no changes of absorption could be detected on exposure,

except slight ones in the last compound. It is unlikely that the absorption curves of *cis-* and *trans-*forms will be identical, and the use of a different light filter again gave no change. The most obvious explanation is that the thermal reaction is too quick to permit the photochemical reaction to be detected. The same applied to the dimethylamino- and the amino-compound in acetone until a trace (*ca.* 10^{-3}N) of piperidine was added to neutralise the acidity due to atmospheric carbon dioxide. A change on exposure was then found, disappearing in the dark at a rate corresponding to a half-life period of no less than 6 hours for the *cis-*form of the first-named. Addition of piperidine to the benzene and the petrol solutions of these compounds enabled more reproducible conversion rates to be obtained. The apparently analogous addition of benzoic acid to the benzene solution of the hydroxy-compound accelerated the reaction. Measurements were made of the conversion velocities of the amino- and the dimethylamino-compound in acetone (with piperidine) with addition of acetic acid and methyl alcohol in increasing concentration. The additions were made quickly *after* exposure of the alkaline solutions. The catalytic influence of acid on the dimethylamino-compound in acetone can readily be demonstrated. If two test-tubes are filled with the same dilute solution (with a trace of piperidine) and one is exposed to sunlight for a few minutes, the latter is obviously more deeply coloured. If now a few drops of acetic acid are added to the first, no change is apparent, but if it is added to the second, the colour is seen to return to normal in a few seconds.

The catalytic effects of piperidine, methyl alcohol, and benzoic acid on the conversion of the exposed solutions of the hydroxy-compound in benzene were similarly examined.

The results are recorded in Table I.

Preparations.—trans-*Azobenzene.* The commercial product is nearly pure *trans.* Only one sample examined contained a detectable amount (less than 2%) of *cis.* Pure *trans-*form was prepared by two methods, *viz.,* (i) recrystallisation of the commercial product from an alcoholic solution boiled for 6 hours in the dark, and (ii) successive partial precipitation by water from acetone solution. M. p.'s and photometer readings were in exact agreement.

trans-4-*Hydroxy-, -4-amino-, and -4-dimethylamino-azobenzenes.* The first was prepared by coupling diazotised aniline with phenol, and the others were commercial products. All were purified by several recrystallisations from water–alcohol and petrol–benzene.

trans-4-*Methoxyazobenzene.* The purified hydroxy-compound was methylated, the product extracted by benzene from alkaline aqueous alcohol, and recrystallised from methyl alcohol.

trans-*Azobenzene-4-trimethylammonium nitrate.* The purified 4-dimethylamino-compound was condensed with methyl sulphate in nitrobenzene at 150°, the cooled solution decanted from tarry by-products, and the methosulphate extracted with water. The extract was made alkaline with sodium carbonate and non-ionised products extracted with benzene; the quaternary nitrate was then precipitated with ammonium nitrate. It recrystallised very well from water.

cis-*Azobenzene.* Experiments showed that even from heavy petrol, in which the ratio of the solubilities of the *cis-* to the *trans-*form would be expected to be a minimum, the latter is the first to crystallise out after exposure to light. A larger preparation of the *cis-*form was therefore carried out by a modification of the method previously described. A saturated solution (*ca.* 10%) of ordinary azobenzene in 500 c.c. of glacial acetic acid (to which 10 c.c. of water were added to stop freezing) was placed in a large, white, enamelled-iron tray with a glass cover in bright light on the roof. Acetic acid was preferred to acetone or alcohol on account of its smaller volatility and of its affording a higher percentage of *cis-*form. After 3—4 hours, the proportion of *cis-*form (determined by Method 2) reached a steady value of 24%. The solution was then diluted in the dark with 450 c.c. of water (an amount found by experiment to precipitate nearly all the *trans* and none of the *cis*) and filtered. The residue was used for further exposures. The filtrate was diluted with a further 500 c.c. of water and extracted with chloroform. The extract was washed with water and evaporated in a vacuum at once, the crude product being then dried, the main essential for an efficient yield being to get the *cis* form in the solid state as soon as possible. The crude products of several exposures were united and crystallised from petrol between room temperature and that of an ice–salt freezing mixture. Crystallisation was stopped as soon as a fraction having an appreciable content of *trans* (Method 2) came out. Purification was carried out by recrystallisation, care being taken to wash each batch of crystals with cold petrol to remove mother-liquor, which always contains a little *trans-*form due to thermal conversion. Identity of m. p.'s and of photometer readings of standard solutions of successive fractions was used as a criterion of purity. The yield of pure *cis-*form was 8 g. per exposure (of 50 g.).

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TABLE I.

*Thermal* cis ⟶ trans-*conversion in azobenzenes.*

Solvent.	Temp.	Half-life period.	Solvent.	Temp.	Half-life period.
(a) 4-Hydroxyazobenzene.					
Petrol (b. p. 40—60°)	19°	3·0 mins.	C$_6$H$_6$ + 0·4% MeOH	19°	0·5 mins.
C$_6$H$_6$	,,	3·3 ,,	,, 5 × 10^{-6}N-C$_5$H$_{11}$N	21	1·6 ,,
,, + 0·5% Ph·CO$_2$H	,,	1·2 ,,	,, 10 ,, ,, ,,	,,	1·0 ,,
,, + 0·1% MeOH	,,	2·1 ,,	COMe$_2$	19	2·9 ,,
,, + 0·25% ,,	,,	0·9 ,,			
(b) 4-Aminoazobenzene.					
Petrol + 3 × 10^{-3}N-C$_5$H$_{11}$N				19	9 ,,
C$_6$H$_6$ + ,, ,,				,,	10 ,,
COMe$_2$ + ,, ,,				18	20 ,,
,, + ,, ,,		+ 2% MeOH		,,	3·8 ,,
,, + ,, ,,		+ 4% ,,		,,	2·5 ,,
,, + ,, ,,		+ 6% ,,		,,	1·8 ,,
,, + ,, ,,		+ 6 × 10^{-3}N-HOAc		21	0·4 ,,
(c) 4-Dimethylaminoazobenzene.					
Petrol + 3 × 10^{-3}N-C$_5$H$_{11}$N				19	5·0 ,,
C$_6$H$_6$ + ,, ,,				,,	21 ,,
COMe$_2$ + ,, ,,				,,	360 ,,
,, + 5 ,, ,,				21	390 ,,
,, + ,, ,,				45·5	26 ,,
,, + ,, ,,		+ 8% MeOH		20	200 ,,
,, + ,, ,,		+ 7·4 × 10^{-3}N-HOAc		18	70 ,,
,, + ,, ,,		+ 13·8 ,, ,,		,,	21 ,,
,, + ,, ,,		+ 27·3 ,, ,,		,,	6·7 ,,
,, + ,, ,,		+ 38·4 ,, ,,		,,	4·0 ,,
,, + ,, ,,		+ 49·4 ,, ,,		,,	2·6 ,,
,, + 2·5 ,, ,,		+ 25·3 ,, ,,		,,	4·8 ,,
(d) 4-Methoxyazobenzene.					
C$_6$H$_6$	25	30 hrs.	50% COMe$_2$-H$_2$O	25	63 hrs.
COMe$_2$	,,	49 ,,			
(e) Azobenzene-4-trimethylammonium ion.					
H$_2$O	75·6	1·6 ,,	H$_2$O	99·5	0·16 ,,
(f) Azobenzene.					
Pure liquid	76·6	19 mins.	COMe$_2$	25	198 hrs.
,,	100	1·8 ,,	H$_2$O	,,	600 ,,
CCl$_4$	25	94 hrs.	,, + 1·0N-NaOH	,,	860 ,,
,,	56·4	2·3 ,,	,, + 1·0N-NaCl	,,	600 ,,
,,	76·6	0·29 ,,	,, + 0·26N-HCl	,,	73 ,,
C$_6$H$_6$	25	119 ,,	,, + 0·56 ,,	,,	35 ,,
,,	56·4	2·5 ,,	,, + 0·96 ,,	,,	16 ,,
,,	76·6	0·35 ,,	,, + 4·16 ,,	,,	(ca. 0·7 ,,)
HOAc	25	186 ,,	,, + 0·23N-HClO$_4$	,,	79 ,,
,,	56·4	4·2 ,,	,, + 0·53 ,,	,,	30 ,,
,,	76·6	0·60 ,,	,, + 0·26N-H$_2$SO$_4$	,,	98 ,,
,, + 50% water	25	360 ,,	,, + 0·54 ,,	,,	61 ,,

RESULTS AND DISCUSSION.

The conversion followed the first-order equation in all cases. The results of all the measurements are recorded in Table I as half-life periods. In Fig. 1, the logarithms (decadic) of the velocity constants (in hours^{-1}) for the non-catalytic conversion are plotted against reciprocal absolute temperature. For azobenzene itself, in two solvents at three temperatures and in the fused state at two, the points lie, as nearly as can be expected for measurements in condensed systems, on parallel straight lines. The slopes give a mean activation energy of 23 kg.-cals./g.-mol. For the diazocyanide we find 22 (Le Fèvre and Vine give 21·5) and for dimethylaminoazobenzene 21 kg.-cals. This slight decrease with increasing ease of conversion of the compound does not require a different mechanism for the reaction in different substances. Although the velocity increases over 10,000-fold

from azobenzene and the quaternary salt in water to hydroxyazobenzene in petrol, there is no clear separation into " fast " and " slow " groups. Moreover, the general influence of solvent, when acid or base catalysis does not occur, is the same whatever the substituent, the velocity decreasing with increasing polarity and polarisability of the solvent. The only apparent exception to this is of doubtful significance—the *cis*-hydroxy-compound is converted appreciably more quickly in acetone than in benzene, but this is probably explained by the very great sensitivity of this compound to the hydroxyl group, which will be present in small amount in the enolic form of the ketone, and by absorption of atmospheric moisture.

FIG. 1.
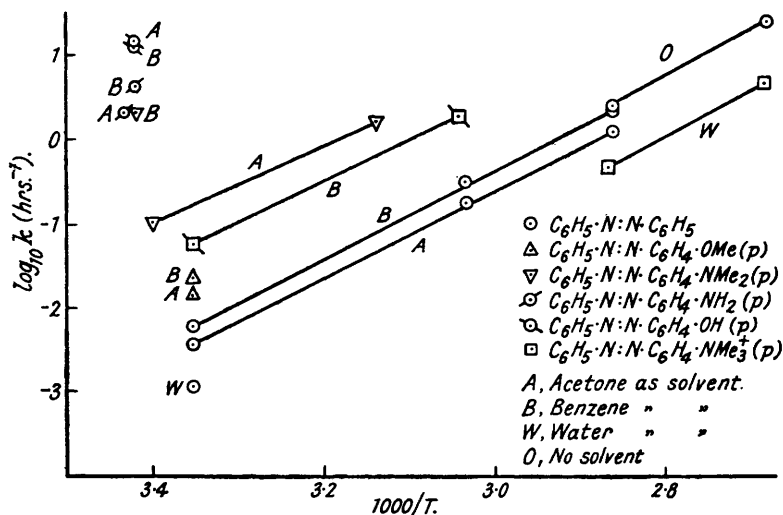
Influence of temperature and of substituents on the non-catalysed conversion.

The classical explanation of the change in absorption spectra on ionisation of amino- or hydroxy-azo-compounds was that the ions had the quinonoid structures (I), in support of which there was the production of compounds identical with the above when synthesis of the phenylhydrazones of benzoquinoneimide or benzoquinone was attempted. We should now say that the relationship between (I) and the azo-structures (II) is that of
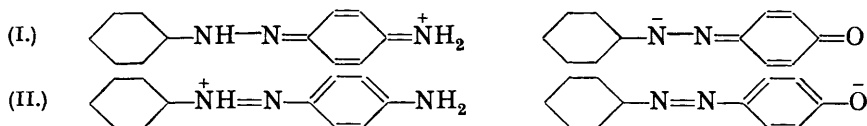
mesomerism, the true structure being intermediate but probably more nearly (I) than (II). The weakness of the N=N double bond in the ion provides an explanation of the acid or base catalysis of the *cis* ⟶ *trans* conversion. Rotation about the N–N axis in the ion will be almost free, and the double bond will therefore re-form to give the stable (*trans*) configuration, when the ion loses or gains a proton to re-form the uncharged molecule.

The uncharged molecule may be considered to be mesomeric between the corresponding structures (III) and (IV), but will be much more nearly (IV) than (III), since the non-

catalysed *cis* ⟶ *trans* reaction is relatively very slow. The effect of substituents on the non-catalysed reaction increases roughly with increase of electron release from the
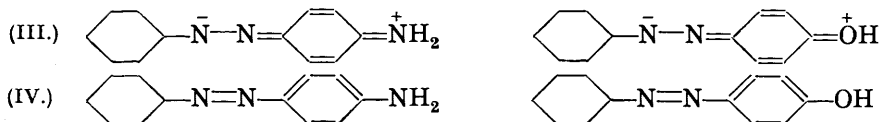
4-substituent, as would be expected for the mechanism proposed, the electron-repelling substituents favouring the quinonoid form. The retarding effect of polar non-hydroxylic solvents is probably best regarded as due to reduction of the repulsion between the –C–N= dipoles. In hydroxylic solvents, a chain of molecules with hydrogen bonds from the amino- or the hydroxyl group to the remoter azo-nitrogen atom could, as it were, close the external circuit and permit resonance between (III) and (IV) without ionisation

Whether or not this last mechanism is operative in pure hydroxylic solvents we have not at present the experimental evidence to decide, but the catalysis by methyl alcohol in dilute solution (see Figs. 2, 3, and 4) requires that there should also be a *uni*molecular reaction with hydroxylic molecules. Most probably the hydroxyl group functions as a base or acid, and is naturally much weaker in these properties than piperidine and acetic acid respectively.

Acid and base catalysis.

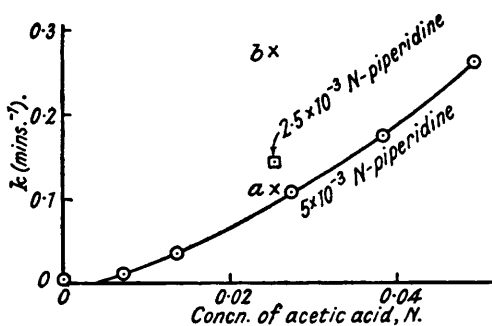FIG. 2.

4-*Dimethylaminoazobenzene in acetone*
(*corrected to* 18°).
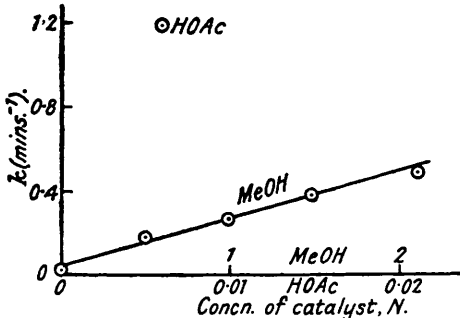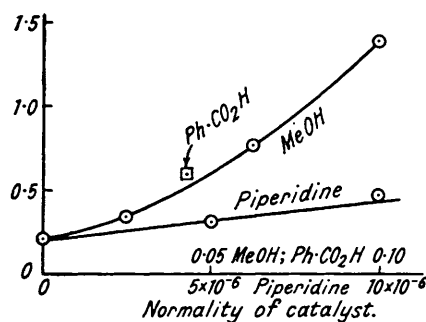
FIG. 4.

4-*Hydroxyazobenzene in benzene*
(*corrected to* 19°).

FIG. 3.

4-*Aminoazobenzene in acetone* (*with* 3 × 10⁻³N-*piperidine*)
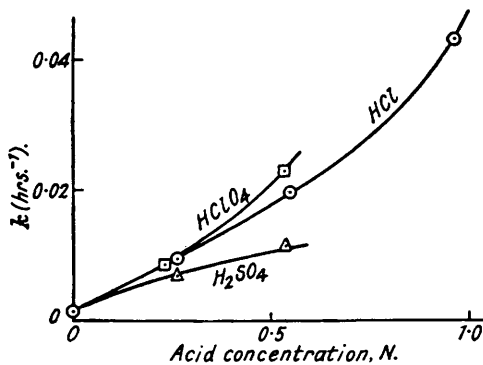(*corrected to* 18°).

FIG. 5.

Azobenzene in aqueous acids at 25°.

It will be seen from Figs. 2 and 3 that the amino- is much more sensitive to acid catalysis than the dimethylamino-compound. The actual concentration of ionised form is in both cases extremely small, as is evident from the fact that a strong acid must be added to acetone solutions before the characteristic pink colour appears. The full curve in Fig. 2 refers to measurements with one concentration of piperidine, and the point ⊡ to half this concentration. The points × give the velocities from the curve, corresponding to (*a*) the same excess concentration of acetic acid over piperidine as obtains at ⊡, and (*b*) the same ratio of excess acetic acid to piperidine, which ratio will determine the "hydrogen ion" ([HO·CMe₂]⁺) concentration in the buffer solution. That the observed velocity is intermediate, indicates that *both* hydrogen ion and undissociated acid are
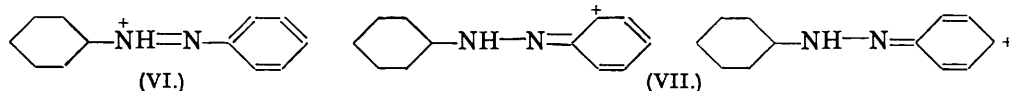
effective. The former is much the more effective, since, when no base is present to produce the buffer action, the much weaker acid, carbon dioxide, is sufficient to promote a very rapid reaction. When base is present, however, the concentration of hydrogen ions will be very low.

The extreme sensitivity of the amino- and the hydroxy-compounds to acid or basic substances makes it at once evident that the *cis*-form will never be produced in appreciable amounts in the ordinary azo-dyes, made and applied as they are in aqueous media. Even when a second diazotisation and coupling have been effected, as in analogues of (V), the

(V.) $\langle\!\!\bigcirc\!\!\rangle$—N=N—$\langle\!\!\bigcirc\!\!\rangle$—N=N—$\langle\!\!\bigcirc\!\!\rangle$—OH
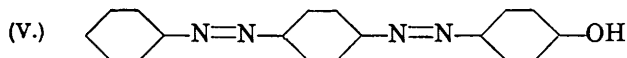
same mechanism can operate right through to the more remote azo-group, so that this also, though less affected, would probably be far too easily reconverted into the *trans*-form thermally to permit the photochemical reaction to build up an appreciable amount of the *cis*-form in aqueous media.

The acid catalysis of the reaction in azobenzene itself is presumably due to the azonitrogen atoms functioning as bases. It is well known that azobenzene behaves as a base, although a very weak one, being somewhat soluble in concentrated mineral acids. The positive charge on the nitrogen atom in the normal form of the ion (VI) will facilitate electron transfer from an *o*- or *p*-carbon atom (VII). The mechanism is therefore the same as in the acid catalysis of the amino-derivatives but of an altogether different order of

$\langle\!\!\bigcirc\!\!\rangle$—$\overset{+}{N}$H=N—$\langle\!\!\bigcirc\!\!\rangle$ $\langle\!\!\bigcirc\!\!\rangle$—NH—N=$\overset{+}{\langle\!\!\bigcirc\!\!\rangle}$ $\langle\!\!\bigcirc\!\!\rangle$—NH—N=$\langle\!\!\bigcirc\!\!\rangle$ +
    (VI.)   (VII.)

magnitude, requiring a considerable concentration of mineral acid to produce an appreciable effect. It was necessary, in the measurement of the reaction in acid and salt solutions, to measure the solubility of the *trans*-form therein. These measurements were extended to the *cis*-form (the solution in this case being saturated with both forms at once, and the photometer reading corrected for the small concentration of *trans*-form present). The results (Table II) give some idea of the concentration of the azobenzene ions. In

TABLE II.

Solubility of azobenzene in acid, alkali, and salt solutions (g.-mols./l.).

Solvent.	trans-.	cis-.	Solvent.	trans-.	cis-.
Water	$2\cdot4 \times 10^{-5}$	$6\cdot45 \times 10^{-4}$	$\frac{1}{2}$N-HCl	$2\cdot3 \times 10^{-5}$	$6\cdot28 \times 10^{-4}$
$\frac{1}{4}$N-NaCl	1·65 ,,	4·64 ,,	N-HCl	2·15 ,,	6·40 ,,
N-NaCl	1·2 ,,	3·68 ,,	N-NaOH	1·3 ,,	—

these relatively low acid concentrations it appears that the formation of ions only just counteracts the ordinary " salting-out " effect. If the hydrochloric acid has the same salting-out effect as sodium chloride, we should conclude that, in N-acid, about half of the azobenzene exists as a cation. The *cis*-form is not much, if at all, more basic than the *trans*. The conversion velocity of the ions must therefore be about 100 times greater than that of the neutral molecules.

Decomposition in Acid Solutions.—The measurements in acid solutions indicated that some side reaction accompanies the *cis* ⟶ *trans*-conversion, because the photometer readings approached asymptotically considerably higher values than for the saturated solutions of pure *trans*-form. The half-life times recorded are calculated from the first part of the log (apparent concentration)–time curves. That, in the N/2- and N/4-acid at least, we are measuring approximately the rate of *cis* ⟶ *trans*-conversion, seems certain. The velocities (Fig. 5) are proportional to the acid concentrations for hydrochloric and perchloric acids, and are smaller for sulphuric acid, as is to be expected from the incomplete second dissociation of the last. The amount of side product, on the other hand, judged by the discrepancy between extrapolated and expected " infinity " readings, is dependent on the nature of the acid. The apparent velocity of conversion in 4N-hydrochloric acid is much more than 4 times that in

1N. A second-order reaction is therefore appearing. This is apparently still mainly a *cis* ⟶ *trans*-reaction, for, although the solid product obtained in this case was certainly not pure *trans*-azobenzene, a considerable yield of substance melting sharply at 68° was obtained by recrystallising it from methyl alcohol. A good yield was obtained by the same method from *cis*-azobenzene dissolved in 4N-perchloric acid and kept for 2 hours. Second-order catalysis presumably requires that the second nitrogen atom can also accept a proton.

There may also occur a decomposition of the type investigated by Jacobson (*Annalen*, 1909, **367**, 304) when hydrogen chloride was passed into a solution of azobenzene in methyl alcohol, and benzidine, chloroanilines, and chlorosemidines were produced with evolution of chlorine. *cis*-Azobenzene causes evolution of chlorine from *aqueous* hydrochloric acid. So does the *trans*-form, but in less degree, probably owing to its smaller solubility. At least one product is formed on treatment of *cis*-azobenzene with concentrated acid which is not produced from the *trans*-form. The solutions are red and remain red, even on heating, and, on dilution and repeated extraction with benzene, a pink compound remains in the aqueous layer. It is strongly adsorbed at the benzene interface, is precipitated in a yellow form on addition of alkali, is then soluble in benzene and can be recovered in the pink form by aqueous acid, behaviour characteristic of an aminoazo-compound of rather high molecular weight. It is formed in 10N-solutions of hydrochloric, perchloric, sulphuric, or nitric acid, in increasing amount in the order given, but is not produced at all from *trans*-azobenzene, even on exposure to sunlight.