124. *The Kinetics of the Reduction of Some Azo-compounds.*

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The kinetics of the reduction of a series of substituted azobenzenes by titanous chloride in aqueous alcohol have been studied. The reaction is of the first order with respect to the azo-compound and to titanous chloride, and the rate varies in a complex way with the concentration of hydrochloric acid. If the same active titanous species is to be postulated for the reduction of azo-, nitro-, and azoxy-compounds in this medium, then the simplest way of analysing the results is to set the concentration of the active titanous species proportional to $[HCl]^{-2}$. The effect of [HCl] on the concentration of the active azo-species is then expressed by a simple power series. These species seem to be singly- and doubly-protonated bodies.

In some examples the two stages of reduction, azo → hydrazo, and hydrazo → amines, are comparable in speed, and in one case the kinetics of the consecutive reactions are worked out.

The influence of substituents is complex, and appears to be the result of opposing effects, on the one hand on the process of electron transfer from the reducing agent, and on the other on the equilibrium between protonated and non-protonated azo-species. There are indications that changes in the former are reflected mainly in the activation energy, and changes in the latter in the non-exponential factor of the Arrhenius equation. This state of affairs results in an absence of additivity in free energies of activation.

THIS work continues the study of the reduction of azo-compounds by titanous chloride begun by Large, Stubbs, and Hinshelwood[1] and the general study of the kinetics of

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[1] Large, Stubbs, and Hinshelwood, *J.*, 1954, 2736.

reductions by that agent.[2] The kinetics of the reaction vary quite considerably from compound to compound and certain cases furnish interesting examples of second-order consecutive reactions, or of autocatalytic effects. The study of the influence of substituent groups on the rate reveals some slightly unusual energy–entropy relations, and the dependence of the rate on the concentration of acid in the medium proves to be of interest.

For purposes of comparison the reduction of azobenzene by stannous chloride has also been studied as part of the attempt to distinguish effects of the acid on the titanous chloride reducing agent from those on the azo-compound.

EXPERIMENTAL

The following reagents were used: a solution of titanous chloride in hydrochloric acid standardised with " AnalaR " ferric ammonium sulphate, in turn standardised against pure potassium dichromate; a solution in hydrochloric acid of stannous chloride, standardised by addition of iodine and titration with sodium thiosulphate solution, potassium iodate being used as a primary standard; azobenzene and 4-hydroxyazobenzene supplied commercially; 2-aminoazobenzene prepared by a slight modification of Witt's method.[3] The other azo-compounds used were kindly given by Imperial Chemical Industries Limited, Dyestuffs Division. The compounds were recrystallised as necessary. The small amounts of the *cis*-isomers taken to be present were removed by Hartley's method,[4] assumed to be generally applicable.

The experimental procedure adopted for the measurement of reaction rates was that described by Large *et al.*[1] It consisted in the spectrophotometric determination of the residual azo-compound. The following modifications in detail were introduced. (i) In the experiments with 2 : 4 : 4′-triaminoazobenzene, 2 : 2′ : 4-trihydroxyazobenzene, and 4-amino-2′ : 4′-dihydroxyazobenzene the reaction was stopped when desired by sufficiently copious dilution of the solution with a suitable acid–alcohol mixture. With 2 : 2′ : 4-trihydroxyazobenzene experiments were carried out both with an acid–alcohol mixture and with ferric alum solution as quenching reagent. (ii) Since 2-aminoazobenzene undergoes spontaneous decomposition in presence of acid, quenching of mixtures containing it was effected by a solution of sodium hydroxide, the precipitate being removed by centrifuge. (iii) No suitable quenching reagent could be found for stannous chloride, and when this was used samples of the reaction mixture were transferred directly to the " Unicam " cells, the times at which the actual readings were made being taken as the reaction times. The experiments were made at 20·0° to ensure that very little change of temperature should occur in the time between sampling and examination. (iv) " End-point " determinations were carried out both with excess of the azo-compound and with excess of the reducing agent.

RESULTS

2 : 4-*Diaminoazobenzene.*—End-point determinations with an excess of titanous chloride indicate that reduction to primary amines is quantitative. With excess of the azo-compound, however, the amount of it consumed is greater than would be expected if it were fully reduced. There is evidently competition for the available titanous chloride between the azo-compound itself and the hydrazo-compound formed in the first stage of its reduction. The two stages of the reaction: azo-compound $\longrightarrow$ hydrazo-compound $\longrightarrow$ products, must therefore proceed at comparable rates. The reduction is autocatalytic, some of the reaction–time curves being S-shaped, and the addition of reaction products causing a large increase in the rate (Table 1). Values of k_1 were therefore calculated from initial rates, a procedure which is valid since the reaction is followed by the decrease in concentration of the azo-body and not by the consumption of titanous chloride.

2-*Aminoazobenzene.*—End-point determinations indicate that reduction is quantitative. The reaction is autocatalytic. Some decomposition of the azo-compound occurs in acid solution. The methods used for the calculation of rate constants are discussed later.

2 : 4 : 4′-*Triaminoazobenzene.*—End-point determinations again indicate that the two stages of the reduction are of comparable speed, and the reaction is found to be autocatalytic. Rate constants were therefore calculated from initial rates.

4-*Hydroxyazobenzene.*—End-point determinations indicate quantitative reduction, and the course of the reaction with time is found to follow the second-order law. Rate constants were therefore calculated in the usual way.

[2] Newton, Stubbs, and Hinshelwood, *J.*, 1953, 3384; Stephen and Hinshelwood, *J.*, 1955, 1393.
[3] Witt, *Ber.*, 1912, **45**, 2380.
[4] Hartley, *J.*, 1938, 633.

2 : 2′ : 4-*Trihydroxyazobenzene.*—The rates of the two stages of the reduction are comparable, and although for high acid concentrations satisfactory bimolecular rate constants can be calculated, for low acid concentrations the problem of consecutive second-order reactions has had to be solved by a method which is discussed later.

4-*Amino*-2′ : 4′-*dihydroxyazobenzene.*—The reduction to the primary amines is quantitative and satisfactory second-order rate constants can be calculated.

Order of Reaction.—The order of reaction was investigated for several of the compounds studied, and for each the rate was found to be proportional to the concentration of titanous chloride and to that of the azo-compound, as was found for the reduction of azobenzene and 4-aminoazobenzene.[1] Typical results for one of the compounds (2 : 4-diaminoazobenzene) are given in Table 1.

TABLE 1. *Reduction of* 2 : 4-*diaminoazobenzene* : *order of reaction.*

[HCl] = 3·293N. Temperature 25·0°.

10^4 [Azo] (mole l.$^{-1}$)	7·73	7·73	7·73	7·73	5·80	3·86	1·93	3·8 *	3·8 *	3·8 *
10^4 [$TiCl_3$] (mole l.$^{-1}$)	30·9	23·2	15·5	7·73	30·9	30·9	30·9	15·0	15·0	15·0
10^6 Initial rate (mole l.$^{-1}$ min.$^{-1}$)	4·20	3·15	2·25	1·10	3·40	1·95	1·00	3·00	3·20	2·36
$10^2 k_1$ (sec.$^{-1}$ l. mole^{-1})	2·92	2·92	3·13	3·06	3·15	2·71	2·78	8·77	9·36	6·90

* In these experiments the products from an " infinity " run were added to the other reagents, the values given for the various concentrations being the concentrations in the resulting reaction mixture.

Effect of Acid Concentration.—The effect of acid concentration on the rate for various compounds is shown in Table 2. Its effect on the rate of reduction of azobenzene by stannous chloride was also studied, and the results are included in Fig. 2.

TABLE 2. *Effect of acid concentration.*

2 : 4-Diaminoazobenzene

[HCl] (mole l.$^{-1}$) ...	0·128	0·257	0·367	0·515	0·701	0·905	1·326	1·805	2·310	2·835	3·293
$10^3 k_1$ (sec.$^{-1}$ l. mole^{-1})	10·8	6·26	5·91	6·26	8·00	8·00	11·5	12·2	17·4	24·1	29·3

2-Aminoazobenzene

[HCl] (mole l.$^{-1}$)	0·099	0·257	0·515	0·937	1·335	2·310	3·121	3·263
k_1 (Method I)	0·970	0·960	0·523	0·462	0·510	0·420	0·472	0·502
k_1 (Method II)	0·938	0·870	0·545	0·440	0·498	0·378	0·423	0·490

4-Hydroxyazobenzene

[HCl] (mole l.$^{-1}$]	0·122	0·257	0·405	0·515	0·677	0·937	1·335	1·783	2·310	3·221	3·263
k_1	1·23	0·90	0·81	0·77	0·79	0·91	1·03	1·12	1·45	2·49	3·17

Activation Energies.—These were determined for 2 : 4-diaminoazobenzene, 4-hydroxyazobenzene, and 2 : 2′ : 4-trihydroxyazobenzene, and are given in Table 4 together with the values for azobenzene and 4-aminoazobenzene.

Kinetics of Consecutive Second-order Reactions.

In several examples, end-point determinations made with excess of each reagent in turn indicate that the rates of the two stages of the reduction are comparable. The kinetics of the reaction are therefore complicated by the finite accumulation of the hydrazo-compound formed in the first stage. If the amount of this intermediate present at any time is small, the rate of disappearance of the azo-compound itself is not much affected and the calculation of second-order rate constants by the usual formula is possible. When, however (as in the reduction of 2 : 2′ : 4-trihydroxyazobenzene at low acid concentrations), the concentration of the hydrazo-compound becomes considerable, the kinetics of consecutive second-order reactions have to be worked out before the complete course of the reaction–time curves can be expressed.

The initial stage of the reduction, that is to the hydrazo-compound, is of the first order with respect to the azo-compound and to the titanous chloride. If the reduction of the hydrazo-compound itself is assumed to be similarly of the first order with respect to each reagent, the equations for the rate of reaction may be formulated in the following way :

At time, t, [azo-compound] = A, [hydrazo-compound] = B, [$TiCl_3$] = T, and

$$\left.\begin{aligned} dA/dt &= -k_1AT \\ \text{and}\qquad dB/dt &= k_1AT - k_2BT \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k_1 and k_2 are the second-order rate constants for the first and the second stage of the reduction respectively.

Therefore $$\mathrm{d}B/\mathrm{d}A = k_2B/k_1A - 1$$

From this expression by integration

$$B = (A_0^{1-k}A^k - A)/(1 - k) \qquad (2)$$

where $$k = k_2/k_1$$

When B reaches its maximum, $\mathrm{d}B/\mathrm{d}A = 0$ and $k = A_m/B_m$, where A_m and B_m are the values of A and B at this time.

Since each stage of the reduction requires two moles of titanous chloride for each mole of substrate, the concentrations of titanous chloride, azo-compound, and hydrazo-compound are related by

$$T_0 - T = 2B + 4(A_0 - A - B) \qquad (3)$$

If the initial concentration of titanous chloride is chosen so as to be just sufficient to ensure quantitative reduction of the azo-compound to primary amines, then

$$T_0 = 4A_0 \qquad (4)$$

Hence

$$-\frac{\mathrm{d}A}{\mathrm{d}t} = k_1A\left\{4A_0 - 4A_0 + 4A + 2\frac{(A_0^{1-k}\mathrm{A}^k - A)}{1 - k}\right\}$$

$$= k_1A\left\{\left(4 + \frac{2}{k - 1}\right)A - \frac{2A_0^{1-k}A^k}{k - 1}\right\}$$

$$= k_1A^2(4 + l - lA_0^{1-k}A^{k-1}), \text{ where } l = 2/(k - 1)$$

Therefore $$-k_1 \,.\, \mathrm{d}t = \mathrm{d}A/A^2(4 + l - lA_0^{1-k}A^{k-1})$$

This expression cannot be integrated directly, but can be expanded as a power series, which may then be integrated term by term:

$$\frac{\mathrm{d}A}{A^2(4 + l - lA_0^{1-k}A^{k-1})} = \frac{\mathrm{d}A}{A^2(4 + l)}\left\{1 + \frac{lA_0^{1-k}}{(4 + l)}A^{k-1} + \frac{l^2A_0^{2(1-k)}}{(4 + l)^2}A^{2(k-1)} + \ldots\right\}$$

which on integration gives

$$-k_1t = \sum_{n=0}^{n=\infty}\frac{l^n}{(4 + l)^{n+1}(nk - n - 1)}\left\{A_0^{n(1-k)}A^{(nk-n-1)} - A_0^{-1}\right\}$$

This forms a convergent series and it is therefore possible to evaluate k_1 from a limited number of terms. (For certain values of k the series becomes indeterminate, and other methods of integration have to be employed.)

The above formula was applied to the example of 2 : 2′ : 4-trihydroxyazobenzene as follows. One experiment was carried out with an acid–alcohol mixture as quenching agent, the values of A at various times being determined spectrophotometrically. In a second experiment ferric alum was added to the quenching reagent, so that, on standing, the hydrazo-compound present was completely reoxidised to the azo-compound. In this experiment the finally measured trihydroxyazobenzene concentration was then equal to $A + B$. The values of B calculated from these results are shown in Fig. 1. From this graph it was found that $\mathrm{d}B/\mathrm{d}t = 0$ when $t = 3{\cdot}0$, and at this point $A/B = 1{\cdot}42 = k$. Values of k_1 were then calculated from the first nine terms of the above expression for a series of values of A and t taken from the reaction–time curve (Fig. 1), and are given in Table 3. The error due to this approximation is well below 1%.

TABLE 3. *Reduction of* 2 : 2′ : 4-*trihydroxyazobenzene.*

$[\mathrm{TiCl_3}] = 0{\cdot}00062$M. [Azo] $= 0{\cdot}000155$M. [HCl] $= 0{\cdot}257$N.
Temperature 25·0°.

t (min.)	1	2	3	4	5	6	7	8	9
10^4[Azo] (mole $\mathrm{l.}^{-1}$)	1·006	0·745	0·567	0·446	0·366	0·322	0·286	0·256	0·226
k_1	13·1	12·3	12·5	12·8	12·9	12·4	12·1	11·9	12·1

As a check on the accuracy of the method, and on the correctness of the above interpretation of the experimental results, the reaction–time curve and the curve representing the formation of the hydrazo-compound were reconstructed by a method which did not involve the approximations used in the calculation of k_1. From a series of values of A the corresponding values of B were calculated by equation (2), and values of T were then obtained by equations (3) and (4). By the use of equation (1) in the form

$$-\,\mathrm{d}t/\mathrm{d}A = 1/k_1AT$$

a graph of $\mathrm{d}t/\mathrm{d}A$ against A was constructed. Integration of the equation gives $t_1 = \int_{A_0}^{A_1} \frac{\mathrm{d}t}{\mathrm{d}A}\,\mathrm{d}A$, and values of t were therefore obtainable by graphical integration. The reconstructed curves are shown in Fig. 1.

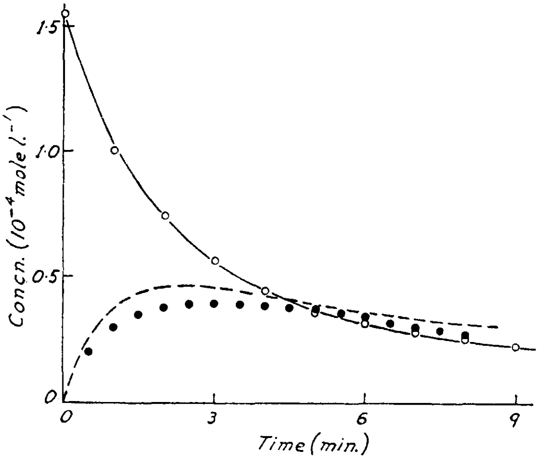


FIG. 1. *Reduction of* 2 : 2′ : 4-*trihydroxyazobenzene at low acid concentration.*

Consumption of azo-compound :
○ Experimental values.
—— Calculated curve.

Formation of hydrazo-compound :
● Experimental values.
- - - - Calculated curve.

Spontaneous reaction of 2-*aminoazobenzene.*

In acid solution 2-aminoazobenzene undergoes a spontaneous reaction, probably a decomposition, and this has to be taken into account in the calculation of rate constants for the reduction by titanous chloride. Two methods were used.

Method I.—A series of values were calculated at various stages of the reduction for the expression $x/4ta(a - x)$, where a is the initial concentration of the azo-compound and $(a - x)$ the concentration at time t, the initial concentrations of 2-aminoazobenzene and titanous chloride being experimentally equivalent. These values were then extrapolated to zero reaction to give the apparent second-order rate constant k'. The decomposition reaction was assumed to be of the first order with respect to the azo-compound, so that if k_1 and k_0 are the rate constants for the reduction and decomposition respectively,

$$\mathrm{d}x/\mathrm{d}t = 4k_1(a - x)^2 + k_0)(a - x)$$

and hence $$k' = k_1 + k_0/4a$$

The values of k_0 obtained experimentally by following the disappearance of the azo-colour in the absence of titanous chloride were plotted against acid concentrations and the values of k' were then corrected by the use of values of k_0 read off this curve to give the values of k_1.

Method II.—Initial rates of change of the azo-compound were measured both in the presence and in the absence of titanous chloride, and from these the initial rates of the reduction were calculated. The values of the rate constant were obtained from these initial rates.

A comparison of the results obtained by the two methods is given in Table 2.

Autocatalytic effects.

With some of the azo-compounds used the phenomenon of autocatalysis is observed. Each of the compounds in question has an *o*-amino-substituent, so that one of the products must be an *o*-phenylenediamine, and it is therefore possible that a reactive complex is formed between the diamine and one of the reagents. Titanous salts are known to possess weak powers of complex formation, and with an *o*-diamine might well give rise to complexes the reducing action of which would differ from that of the titanous chloride in its usual state. A possible alternative explanation is that the transient odd-electron intermediate, which is presumably formed as the first step in the reduction of the hydrazo-compound, is able to promote the reduction of the azo-compound, being itself re-oxidised to the hydrazo-compound.

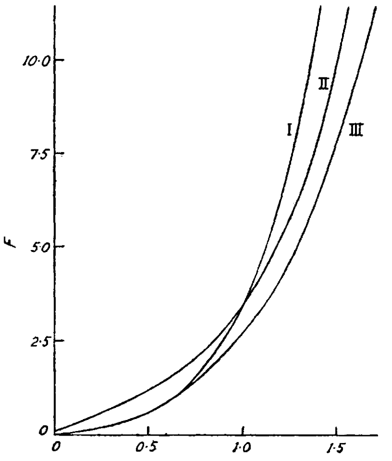
DISCUSSION

Reaction Mechanism.—In a previous discussion [1] of the mechanism of reduction of azobenzene and 4-aminoazobenzene by titanous chloride it was suggested that the complete rate-equation is of the form

$$\text{Rate} = C^{-n}(\alpha C^2 + \beta C^4 + \gamma C^8 + \ldots\ldots)$$

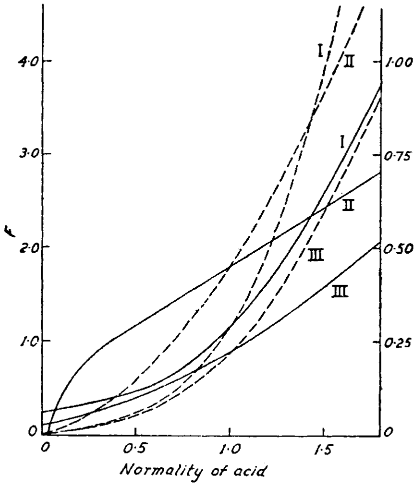
where C is the analytical concentration of hydrochloric acid. The term C^{-n} represents the effect of acid concentration on the reactive titanous species, and the rest of the expression the effect on the reactive azo-species.

FIG. 2. *Reduction of azobenzene by titanous chloride and by stannous chloride: functional relation to acid concentration.*



I. $F = 100k_1[\text{HCl}]^2$ for TiCl_3.
II. $F = 100k_1[\text{HCl}]$ for TiCl_3.
III. $F = k_1$ for SnCl_2.

FIG. 3. *Values of k_1[HCl] and k_1[HCl]^2 for various azo-compounds.*



Left-hand scale: 4-aminoazobenzene (I), 4-hydroxyazobenzene (III).
Right-hand scale: 2-aminoazobenzene (II).

The function F in the various cases is as follows:

	I	II	III
Continuous lines	$10k_1[\text{HCl}]$	$k_1[\text{HCl}]$	$k_1[\text{HCl}]$
Broken lines	$10k_1[\text{HCl}]^2$	$k_1[\text{HCl}]^2$	$k_1[\text{HCl}]^2$

The rate of reduction of nitrobenzene is inversely proportional to the square of the acid concentration, and this can be accounted for by the assumption that the reactive species are $\text{Ph·NO}_2\text{H}^+$ and TiO(OH),[2] or, alternatively, Ph·NO_2 and Ti(OH)_2^+. On the latter assumption the first step would be the transfer of an electron to the nitrobenzene molecule, the resultant ion then taking up a proton. In the reduction of azoxybenzene the rate is inversely proportional to the first power of the acid concentration, and this fact indicates that the reactive species are either Ph·NO:NPh and Ti(OH)^{2+} or $\text{Ph·NO}^+\text{H:NPh}$ and Ti(OH)_2^+. The medium used in each case was the same as that used in the present work for the reduction of azo-compounds. If the reactive titanous species is assumed to be the same in each case it will most probably be Ti(OH)_2^+. Accordingly, $n = 2$, from the equation $[\text{Ti(OH)}_2^+] = K[\text{Ti}^{3+}]/[\text{H}^+]^2$. This view receives some support from a consideration of the graphs of k_1[HCl] and of k_1[HCl]^2 against [HCl] for the reduction of azobenzene by titanous chloride (Fig. 2). The second, on the whole, has the appearance of a more probable relation between the active azo-species and the acid concentration than the first, especially when values of these functions for several of the azo-compounds are compared (Fig. 3). It can be seen that while the graphs of $k_1[\mathrm{HCl}]^2$ against [HCl] are all of a similar form, those of $k_1[\mathrm{HCl}]$ against [HCl] vary considerably, and usually do not seem to correspond to any very likely function.

Over a considerable range the graph of $k_1[\mathrm{HCl}]^2$ for the reduction of azobenzene by titanous chloride closely resembles that of k_1 for the reduction by stannous chloride (Fig. 2). This shows at any rate that the existence of a minimum in the curve of k_1 for the titanous reduction is not to be ascribed to variations in the titanous species alone, since the subsequent rapid increase is found with the stannous chloride reaction also. If the concentration of the active titanous species is assumed to be inversely proportional to the square of the acid concentration, then over the corresponding range the stannous species would be independent of the acid concentration and might be $SnCl_3(OH)^{2-}$. The species $SnCl_3^-$, which sometimes plays a part in the reactions of aqueous stannous chloride, could easily become important at higher acid concentrations. The above scheme depends upon the assumptions that the predominant titanous species in the solution is Ti^{3+} and that the reactive titanous species is the same throughout. Neither is certain, so that only general probabilities can be inferred.

Effect of Substituents.—Table 4 gives the values of the activation energy and of the free energy of activation calculated from the formula $\Delta F = -\boldsymbol{R}T \ln k_1$. Values of $\log_{10} A$ are calculated from the expression $k_1 = A\mathrm{e}^{-E/\boldsymbol{R}T}$. The introduction of a single substituent lowers the activation energy, and the change is very nearly the same for hydroxyl and amino-groups. The introduction of extra amino- or hydroxyl groups has very little further effect on the activation energy. The decrease in the value of $\log_{10} A$ produced by two amino-groups is nearly twice that produced by one. On the other hand, the introduction of hydroxyl groups into 4-hydroxyazobenzene causes an increase in $\log_{10} A$, while the introduction of a single hydroxyl group into azobenzene results in a decrease.

TABLE 4. *Effect of substituents.* (Temperature 25°).

	[HCl] = 0·257N				[HCl] = 2·310N			
	10^3k_1	ΔF (kcal. mole^{-1})	E (kcal. mole^{-1})	$\log_{10} A$	10^3k_1	ΔF (kcal. mole^{-1})	E (kcal. mole^{-1})	$\log_{10} A$
Azobenzene	22·4	2·250	16·0	10·09	190	0·983	15·7	10·80
2-Aminoazobenzene	810	0·125	—	—	385	0·565	—	—
4-Aminoazobenzene	125	1·232	12·6	8·34	375	0·581	12·7	8·89
2 : 4-Diaminoazobenzene	6·3	3·001	12·6	7·04	16	2·448	13·2	7·89
2 : 4 : 4′-Triaminoazobenzene	10	2·727	—	—	12·1	2·614	—	—
4-Hydroxyazobenzene	904	0·0596	—	—	1,453	−0·221	12·3	9·18
2 : 2′ : 4-Trihydroxyazobenzene	12,500	−1·495	—	—	1,310	−0·160	14·1	10·46
4′-Amino-2 : 4-dihydroxyazobenzene	3,180	−0·684	—	—	4,700	−0·916	—	—

It seems likely that the reduction of azobenzene involves the setting up of equilibria between azobenzene and the ions $Ph{\cdot}N^+H{:}NPh$ and $Ph{\cdot}N^+H{:}N^+HPh$ followed by the transfer of an electron, and that these processes are the rate-determining ones.[1] Hydroxyl and amino-groups, by their inductive effects, should facilitate the electron transfer but reduce the equilibrium concentration of the protonated azo-species. The electromeric effect of hydroxyl will not assist the ease of electron transfer, but will facilitate the addition of protons. From a consideration of the results as a whole it appears that the activation energy, which is almost independent of the acid concentration, may well be mainly correlated with the electron-transfer process, while the probability factor may be determined mainly by the equilibria governing the concentrations of the protonated azo-species. The introduction of a single amino- or hydroxyl substituent seems to facilitate the electron transfer and reduces the activation energy to a limiting value, after which further substitution has little effect. The inductive effect of amino- and hydroxyl groups reduces the value of $\log_{10} A$, but where more than one hydroxyl group is introduced, the electromeric effect, by making electrons available at the reaction centre, can more or less offset the reduction brought about by the inductive effect.

The pattern which emerges is one in which, clearly, there are superposed and conflicting effects at work. There is, it would seem in consequence of this, a conspicuous lack of the additivity in the energies or free energies of activation, which has sometimes been found. Such additivity appears to be characteristic of a mechanism in which a single step determined the rate. Where a number of simultaneous processes are of comparable importance and each plays some part in determining the rate, this additivity is evidently not to be found.

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