The Kinetics of the Reduction by Titanous Chloride of Azobenzene and 4-Aminoazobenzene.

By N. R. LARGE, F. J. STUBBS, and SIR CYRIL HINSHELWOOD.

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The reduction of *trans*-azobenzene or of *trans*-4-aminoazobenzene by titanous chloride in aqueous-alcoholic solution is of the first order with respect to each component, the rate-determining step being the transfer of an electron from a titanous species to the azo-compound which has taken up protons. (The *cis*-compounds are reduced with very great rapidity and the *trans*-compounds must be freed from them for satisfactory measurements.) The 4-amino-compound yields aniline and *p*-phenylenediamine, but the unsubstituted azo-compound gives hydrazobenzene, 84% of which is very rapidly transformed into benzidine (or isomers), the remainder suffering reduction or disproportionation.

The most remarkable characteristic of the reductions is their dependence on the concentration of hydrochloric acid (Figs. 1 and 2) and of chloride ions, which follows a complicated power series, the curves becoming extremely steep at higher acid concentrations.

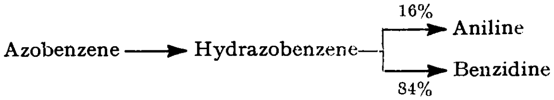
The simplest interpretation is that at higher acid concentrations the electrons from the titanous chloride are transferred to species of the type $\mathrm{Ph\overset{+}{N}H{:}\overset{+}{N}HPh}$, the formation of which is facilitated by the screening action of oppositely charged chloride ions. The active titanous species appears to be a partially hydrolysed form, the concentration of which varies as an inverse power of the acid concentration.

Analogous assumptions about proton addition to azo- or hydrazo-compounds are useful in explaining the benzidine transformation and the disproportionation or reduction reactions (schemes I, II, III, p. 2743).

THIS work continues the general study of the kinetics of reduction by titanous chloride begun by Newton, Stubbs, and Hinshelwood (*J.*, 1953, 3384) with nitrobenzene and its substitution products. The kinetics of the reactions of titanous chloride with azobenzene, and with 4-aminoazobenzene have now been examined.

At the outset a complication appeared in that normally purified specimens of azobenzene showed an initial burst of very rapid reduction followed by a much slower reaction. This was traced to the fact that the *cis*-azobenzene present in most preparations is reduced very many times more rapidly than the predominant *trans*-form. Nearly pure *trans*-azobenzene was then prepared by Hartley's method (*J.*, 1938, 633) and used with precautions against its conversion into the *cis*-form by light. The small residual amounts of the *cis*-form, if present, were allowed for by a change in the origin of the reaction–time curves to a point beyond the initial rapid stage.

The stoicheiometry of the reaction indicated that only 16% of the azobenzene was reduced to aniline, the remainder being converted into benzidine (or isomers) by the isomerization of the hydrazobenzene, thus, formally :



The proportion of aniline was nearly independent of the titanous chloride concentration over a considerable range, and its formation was probably not by a direct action of titanous chloride on hydrazobenzene, as will be shown below.

When stoicheiometrically equivalent concentrations of azobenzene (in aqueous alcohol) and titanous chloride were employed the reaction–time curves followed the usual equation of the second order throughout their course, and separate variation of the concentrations showed the rate to be proportional to the azobenzene and the titanous concentrations severally. It appears therefore that the rate-determining step is the primary attack of the titanous species on the azobenzene.

With the 4-amino-derivative of azobenzene the results were generally similar except that the reduction proceeded completely to the corresponding substituted aniline.

One of the most interesting aspects of the kinetics is the influence of acid concentration (which is shown in Figs. 1 and 2). With nitrobenzene the reduction rate had been found to be approximately proportional to the inverse square of the acid concentration, an effect explained by the variation in the concentration of the partially hydrolysed titanous complex assumed to be the active species. A rather similar influence is observable with the 4-aminoazo-compound in the lower acid range, but in the higher acid range the inverse dependence gives place to a very remarkable increase in rate with the concentration. A very similar increase is found with the azobenzene itself, while in the lower range the rate becomes nearly constant. This constancy, however, is seen by comparison of the results for nitrobenzene with those for 4-aminoazobenzene to be almost certainly due to a compensation of two opposing effects. In the lower acid range the rate falls because of a change in the concentration of the active titanous species, while in the higher ranges it rises (in the case of the azo-compounds only, but not of nitrobenzene) in proportion to a high and increasing power of the concentration of hydrochloric acid.

FIG. 1. *Effect of acid concentration on the rate of reduction of azobenzine at 25°.*

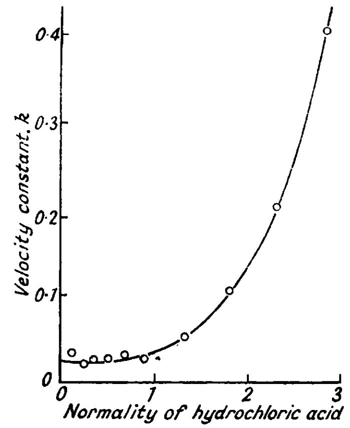
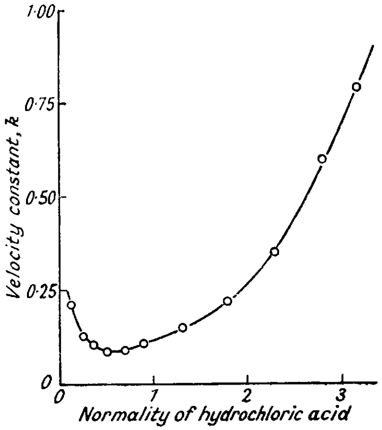


FIG. 2. *Effect of acid concentration on the rate of reduction of 4-aminoazobenzene at 25°.*



The proportion of benzidine formed is nearly independent of the acid concentration. Thus the rate of isomerization of the hydrazobenzene, and the rate of formation of aniline, seem to follow similar laws. Carlin, Nelb, and Odioso (*J. Amer. Chem. Soc.*, 1951, **73**, 1002) state that the rate of the benzidine transformation is proportional to $[H^+]^2$, a law which, over a limited range, would agree with what has been found in the present experiments for the rate-determining step in the reduction of azobenzene. All these effects are rather unexpected.

When the rate is found to vary with the analytical concentration of hydrochloric acid this could indicate proportionality to $[H^+]$ $[Cl^-]$ as much as to $[H^+]^2$, and in certain ranges added chloride ions were in fact found to have nearly as great an influence as hydrogen ions in accelerating the reduction of the azo-compounds.

It is significant that the dependence on a high power of the hydrochloric acid concentration seems to be characteristic of the binuclear bodies and of reactions where the simultaneous addition of two protons may be necessary for effective completion of the change. Azobenzene needs two protons (and two electrons from the reducing agent) for conversion into hydrazobenzene. The transformation of hydrazobenzene into benzidine formally requires none, but considerations of reaction entropy render it almost impossible that the two protons appearing in the amino-groups should be the two which leave the *para*-positions. Thus here also the addition from the medium of two protons appears to be necessary (though no completion of the process by electrons from the reducing agent is required).

The addition of two protons to the same molecule cannot be expected to be easy, but will be much facilitated if the added ions are screened by ions of the opposite sign. Such screening can take place in various ways. Two H^+Cl^- ion pairs at the distance of the two reaction centres will repel one another less than two H^+ ions. Two quadrupoles, $\begin{pmatrix} H^+Cl^- \\ Cl^-H^+ \end{pmatrix}$, will do so even less, though the occurrence of the more highly screened structures becomes less and less probable. To a very rough approximation the probability of simultaneous addition might be set proportional to $a[H^+]^2 + b\{[H^+][Cl^-]\}^2 + c\{[H^+][Cl^-]\}^4$ or, if C is the analytical concentration of hydrochloric acid, to $\alpha C^2 + \beta C^4 + \gamma C^8$. The inaccuracy of each individual term of this expression will hardly be likely to invalidate the result that the rate is proportional to a series of increasing powers of C, as indeed appears to be found. (If in the benzidine transformation *para*-hydrogen atoms have to be removed as protons before the internal electron shifts permit the two nuclei to join—as a model shows they may—the negative ions may well have an additional function as receptors.)

The dependence of reduction rate on acid concentration is further complicated by the inverse proportionality of the more active titanous species to a power of the acid concentration (Newton *et al.*, *loc. cit.*), and this accounts for the flattening of the curve at low acid concentration or the existence of a minimum. The complete equation will be of the form :

$$\text{Rate} = C^{-n}(\alpha C^2 + \beta C^4 + \gamma C^8 \ldots) \qquad \ldots\ldots \qquad (1)$$

where n in part of the range may be 2 or 3, but is itself probably variable.

In view of the fact that the influence of acid on the rate is represented by so complicated a series, and that the allowance for the change in the concentration of the active titanous species is not quite certain, the possibility cannot be ruled out that at the lower acid concentrations there is a contribution from the species $\mathrm{Ph\overset{+}{N}H{:}NPh}$ as well as from the doubly charged form. What is important, however, is that at higher acid concentrations there is a still greater contribution from the species with the two protons. Otherwise there seems to be no clear explanation of the very steep dependence on $[H^+]$ and $[Cl^-]$.

The activation energy is independent of the acid concentration at least over a considerable range. This fact is of some importance in the consideration of the conditions under which valid comparisons between azobenzene and substituted derivatives can be made.

EXPERIMENTAL

Methods.—The solvent was a mixture of equal volumes of ethyl alcohol and water (42·5% of alcohol by weight).

The small amounts of the *cis*-isomers present in the azo-compounds were removed by Hartley's method (*loc. cit.*) and the purified compounds were stored in the dark to prevent isomerisation. A sample of *cis*-azobenzene prepared by Hartley and kindly given by Imperial Chemical Industries Limited, Dyestuffs Division, was used in some of the preliminary experiments. The azo-compounds were dissolved in absolute alcohol, and the titanous chloride in aqueous hydrochloric acid. In the calculation of the initial concentration of the reactants corrections were made for the contraction on mixing. The acid concentration of the titanous solutions was determined by potentiometric titration.

The course of the reaction was followed by determination of the residual azo-compound. Samples were pipetted into an excess of ferric alum solution and examined in a " Unicam " SP 600 Spectrophotometer at 440 mμ (for azobenzene) or 500 mμ (for 4-aminoazobenzene), calibration curves being prepared for each set of experimental conditions. End-points were determined by titration of the excess of ferric alum with titanous chloride.

All reaction flasks were blackened as a precaution against the isomerisation of the azo-compound by light, and were kept filled with carbon dioxide from a cylinder. Pipettes were flushed out with carbon dioxide before use.

The concentration of benzidine in the products was determined by addition of 5 ml. of the reaction mixture (from which the excess of titanous chloride had been removed by atmospheric oxidation) to 5 ml. of 0·1M-potassium chlorate and 10 ml. of 0·012N-titanous chloride. An orange-red colour developed and reached a maximum intensity in about 15 min., after which the absorption at 550 mμ was measured in the spectrophotometer. Calibration curves were prepared with solutions of benzidine under the experimental conditions.

End-points.—Determination of end-points indicated that the amount of titanous chloride consumed was 116% of that required for the formation of hydrazobenzene (2·32 and 2·33 equiv. of $TiCl_3$ per mole of azobenzene in two experiments). The concentration of benzidine in the reaction products accounted for approx. 84% of the hydrazobenzene (83·6, 84·4, and 83·5% in direct benzidine determinations) and hence it was concluded that the remaining 16% was reduced to aniline. As a result of this preliminary investigation the experimentally determined equivalent concentrations of the reagents were used in later experiments. With 4-aminoazobenzene the consumption of titanous chloride corresponded to complete reduction of the azo-compound to the corresponding amine (3·96 and 4·09 equiv. of $TiCl_3$ per mole of 4-aminoazobenzene in two experiments, the theoretical amount being 4·0 equiv.).

Behaviour of the cis-*Isomer.*—In the early experiments in which a sample of azobenzene recrystallised from alcohol was used, a very rapid initial reaction was observed. Experiments on *cis*-azobenzene showed that the rate of reduction was very great and it was concluded that the anomalous reaction–time curves observed with ordinary azobenzene were due to the *cis*-azobenzene present in the recrystallised sample.

Methods of determining Velocity Constants.—Nearly pure *trans*-azobenzene was prepared and appeared to contain only a trace of the *cis*-isomer, but even this, owing to the very great difference in the rates of reduction of the isomers, had an appreciable effect on the reaction–time curve in the first moments. The remaining trace of the *cis*-isomer could be removed by mixing the azobenzene solution with a fairly concentrated hydrochloric acid solution for some time before the start of an experiment, and when this initial treatment was practicable satisfactory second-order rate constants were found. Where, however, a low acid concentration was needed in the experiment this procedure was impossible. In these cases satisfactory rate constants were obtained by displacement of the origin of the reaction–time curves to a point beyond the initial very rapidly-curving section.

In most experiments for the determination of velocity constants analytically equivalent concentrations of titanous chloride and azobenzene were used, 2·32 moles of $TiCl_3$ being known to be required for one mole of azobenzene. Thus $dx/dt = k(a - x)(b - 2{\cdot}32x)$ where b is usually $2{\cdot}32a$, so that $dx/dt = 2{\cdot}32k(a - x)^2 = k'(a - x)^2$. It should be noted that what is recorded in the Tables is in fact k, the true velocity constant of the initial rate-determining step, in sec.$^{-1}$ l. mole^{-1}. In the case of 4-aminoazobenzene b is usually $4{\cdot}0a$ since complete reduction to the amines occurs.

Order of Reaction.—The variation of the rate of reduction with the concentrations of titanous chloride and of azobenzene was determined from the initial rates which in each case were found to be proportional to the separate concentrations (Table 1).

TABLE 1. *Reduction of azobenzene : order of reaction.*

Rate is in mole of azobenzene consumed per l. per sec. [HCl] = 0·515N. 25·0°.

[$TiCl_3$], mole/l.	0·0062	0·0062	0·0062	0·0046	0·0031	0·00155	0·0031
[PhN:NPh], mole/l.	0·0031	0·0023	0·00155	0·0031	0·0031	0·0031	0·00155
10^7 × Rate	9·3	7·2	5·0	7·0	4·8	2·3	2·5
Rate/[$TiCl_3$][PhN:NPh]	0·048	0·050	0·052	0·049	0·050	0·048	0·052

At high acid concentrations the curve of a second-order reaction was obtained provided that the acid and the azo-compound were mixed for some time before the start of the experiment. Typical second-order rate constants are shown in Table 2.

TABLE 2. *Velocity constants at high acid concentrations.*

[$TiCl_3$] = 0·0031 mole/l. [PhN:NPh] = 0·00133 mole/l. [HCl] = 2·310N.

10^4 × Azobenzene consumed (mole/l.)	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0
$10k$ at 20·0°	1·25	1·27	1·23	1·20	1·16	1·13	1·11	1·09	1·12
$10k$ at 40·0°	6·84	6·19	6·08	6·09	6·25	6·32	6·52	6·65	6·89

[$TiCl_3$] = 0·0031 mole/l. [4-Aminoazobenzene] = 0·000773 mole/l. [HCl] = 2·310N.

10^4 × 4-Aminoazobenzene consumed (mole/l.)	1·0	2·0	3·0	4·0	5·0
$10k$ at 10·0°	1·29	1·20	1·14	1·13	1·25

Table 3 shows the rate constants obtained at low acid concentrations compared with those obtained by displacement of the origin of the reaction–time curve to eliminate the rapid initial reaction of the traces of the *cis*-form.

TABLE 3. *Velocity constants at low acid concentrations.*

[TiCl$_3$] = 0·0031 mole/l. [PhN:NPh] = 0·00133 mole/l. [HCl] = 0·257N. 30·0°.

10^4 × Azobenzene consumed (mole/l.)	1·0	2·0	3·0	4·0	5·0	6·0	7·0
100*k*	8·26	4·86	4·06	3·67	3·52	3·53	3·66
100*k* *	—	3·60	3·39	3·25	3·22	3·31	3·51

[TiCl$_3$] = 0·0031 mole/l. [4-Aminoazobenzene] = 0·000773 mole/l. [HCl] = 0·257N. 20·0°.

10^4 × 4-Aminoazobenzene consumed (mole/l.)	1·0	2·0	3·0	4·0	5·0
100*k*	14·3	11·0	9·31	8·69	8·97
100*k* *	—	9·39	8·42	8·18	8·72

* Origin changed to "azobenzene consumed = 1·0 × 10^{-4} mole/l."

With 4-aminoazobenzene the order of reaction was verified by determination of rate constants for varying initial concentrations, as shown in Table 4.

TABLE 4. *Reduction of 4-aminoazobenzene : order of reaction.*

[HCl] = 2·310N. 25·0°.

10^3[TiCl$_3$] (mole/l.)	3·1	1·55	3·1
10^4[4-Aminoazobenzene] (mole/l.)	7·73	7·73	3·86
k	0·355	0·42	0·36

Effect of Acid Concentration.—The effect of acid concentration on the reaction rate was investigated over a wide range. Fig. 1 shows the results obtained with azobenzene. At low acid concentrations the rate is nearly constant, but above 0·8N the curve closely follows a law which is not far from exponential in form. The curve obtained with 4-aminoazobenzene (Fig. 2) is closely similar at the higher acid concentrations, but at lower acid concentrations shows a well-defined minimum.

Salt Effects.—The effect of added chloride on the reaction rate is shown in Table 5 and also the effect of replacing some of the chloride ions by sulphate ions. The effect of chloride ions appears to be approximately the same as that of an equal concentration of hydrogen ions, while sulphate (or bisulphate) ions retard the reaction slightly.

TABLE 5. *Effect of chloride and sulphate ions.*

	Azobenzene				4-Aminobenzene		
[H$_2$SO$_4$]	—	—	2·053	2·053	2·053	—	—
[HCl]	2·310	0·826	0·257	0·257	0·257	2·291	2·256
[NaCl]	0·400	—	—	0·400	—	—	—
[NH$_4$Cl]	—	1·000	—	—	—	0·500	—
[NH$_4$·HSO$_4$]	—	—	—	—	—	—	1·000
[H$^+$]	2·310	0·826	1·298	1·298	1·298	2·291	2·260
[Cl$^-$]	2·710	1·826	0·257	0·657	0·257	2·791	2·256
([H$^+$] + [Cl$^-$])/2	2·51	1·33	0·78	1·11	0·78	2·54	2·26
k (experimental)	0·264	0·057	0·026	0·029	0·115	0·49	0·30
k *	0·261	0·050	0·028	0·039	0·099	0·45	0·34

* *k* is the value of the rate constant for the hydrochloric acid concentration *x*, where *x* = ([H$^+$] + [Cl$^-$])/2 (Figs. 1 and 2).

Ionic concentrations are the nominal values corresponding to complete dissociation.

Activation Energy.—The activation energies for the reduction of azobenzene and of 4-aminoazobenzene respectively were each measured at two different values of the acid concentration, of which they were found to be almost independent. The activation energy is considerably lower for the amino-derivative than for azobenzene itself (Table 6.)

TABLE 6. *Activation energies.*

	[HCl]	Values of 100*k*								Activation energy
Temp. (°c)		5·0°	10·0°	15·0°	20·0°	25·0°	30·0°	35·0°	40·0°	(kcal./mole)
Azobenzene	0·257N	—	—	0·901	1·54	2·05	3·41	5·62	8·44	16·0
	2·310N	2·84	4·48	7·80	11·8	17·2	29·0	48·7	65·1	15·7
4-Aminoazobenzene	0·257N	—	4·0	6·95	8·65	10·9	18·0	23·7	38·7	12·6
	2·310N	—	11·9	19·1	25·1	35·5	49·8	81·7	—	12·7

Hydrazobenzene.—The hydrazo-compound appears to be the primary product of the reduction and the final products from azobenzene are aniline, benzidine, and isomers of benzidine. The behaviour of hydrazobenzene itself was therefore investigated, the amount of benzidine formed being estimated by the method described above, the probable amount of aniline formed being calculated from the concentration of the residual titanous chloride. In the absence of titanous chloride, hydrazobenzene when treated with acid yields a small quantity of azobenzene, the concentration of which could be estimated colorimetrically. The results of these experiments are shown in Table 7.

TABLE 7. *Products from hydrazobenzene.*

Compn. of reaction mixture.			Percentage of hydrazobenzene converted into		
[HCl] (N)	10^4[Hydrazobenzene] (mole/l.)	10^3[$TiCl_3$] (mole/l.)	benzidine	aniline	azobenzene
2·310	7·7	—	79·1	—	5·2
0·905	7·7	—	79·3	—	5·3
0·257	7·7	—	84·1	—	7·3
2·310	7·7	3·09	87·2	16·7	—
0·905	7·7	3·09	89·5	19·8	—
0·257	7·7	3·09	93·8	19·8	—
2·310	3·8	—	84·0	—	8·2

Approximate estimates of the speed of the benzidine transformation under the experimental conditions showed it to be so rapid in comparison with the initial reduction of the azo-compound that its rate would not influence the kinetics of the reduction.

DISCUSSION

The reduction of *trans*-azobenzene (and of *trans*-4-aminoazobenzene) by titanous chloride is a reaction of the second order. The products from azobenzene are benzidine and aniline, the benzidine transformation being very much more rapid under the experimental conditions than the initial reduction to the hydrazo-compound, which is thus the rate-determining step.

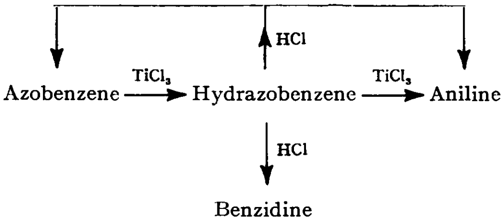
The proportions of the products formed from hydrazobenzene itself are not much affected by the acid concentration, and thus it seems that the mechanisms by which aniline and benzidine are formed involve similar or identical intermediates. The proportion of benzidine is actually increased by the presence of titanous chloride, and this appears imcompatible with conversion of hydrazobenzene into aniline by direct reduction alone.

The disproportion of some of the hydrazobenzene into aniline and azobenene has been reported by Ingold and Kidd (*J.*, 1933, 984) and by Dewar (*J.*, 1946, 777), and this reaction is probably responsible for the formation of aniline in the present case. Given the percentage of benzidine formed in the absence of titanous chloride it should be possible to calculate the amounts of azobenzene and aniline produced and also the percentages of benzidine and aniline formed in its presence, when the azobenzene will be reduced again to hydrazobenzene. In Table 8 the experimentally determined values from Table 7 are compared with the calculated values, and good agreement is obtained for the benzidine formation, but for aniline and azobenzene the comparison is less satisfactory. This may be due in some measure to the difficulty in determining the residual titanous chloride with sufficient accuracy, but the low values of observed azobenzene formation tend to suggest other pos-

TABLE 8. *Products from hydrazobenzene; comparison of observed and calculated values.*

Percentage of hydrazobenzene converted into					
Benzidine		Aniline		Azobenzene	
obs.	calc.	obs.	calc.	obs.	calc.
79·1	—	—	—	5·2	10·4
79·3	—	—	—	5·3	10·3
84·1	—	—	—	7·3	7·9
87·2	88·3	16·7	12·8	—	—
89·5	88·5	19·8	10·5	—	—
93·8	91·4	19·8	6·2	—	—
84·0	—	—	—	8·2	8·0

sible reactions. The disproportionation reaction and a direct reduction may both play some part in the formation of aniline, according to the scheme :



Uncertainty about the exact fate of the hydrazobenzene does not, however, affect the main conclusion, namely, that the rate-determining step is the reduction of the azo-compound to the hydrazo-compound, or vitiate measurements of the rate of this reaction.

With 4-aminoazobenzene, there is no evidence of a benzidine change, the final products being aniline and *p*-phenylenediamine. The absence of a benzidine derivative may be attributed to the blocking effect of the *para*-substituent, the product formed being a semidine which is further reduced to the primary amines.

The acid concentration has little effect on the activation energy, but a remarkable one on the rate (Figs. 1 and 2). A rapid increase in the order of reaction with respect to acid concentration is found at concentrations above about 0·8N. A comparable effect is produced by chloride ions, but sulphate or bisulphate ions simply cause a slight retardation.

These effects are in marked contrast with what is found in the reduction of nitrobenzene, where the rate over a certain range is inversely proportional to the square of the acid concentration, and only slightly affected by chloride ions (Newton *et al.*, *loc. cit.*). The reduction of azoxybenzene in these respects resembles that of nitrobenzene (M. J. Stephen, unpublished work). The inverse relationship is almost certainly a function of the titanous species, and the rapid increase in order at higher acid concentrations in the present case is a function of the azobenzene species.

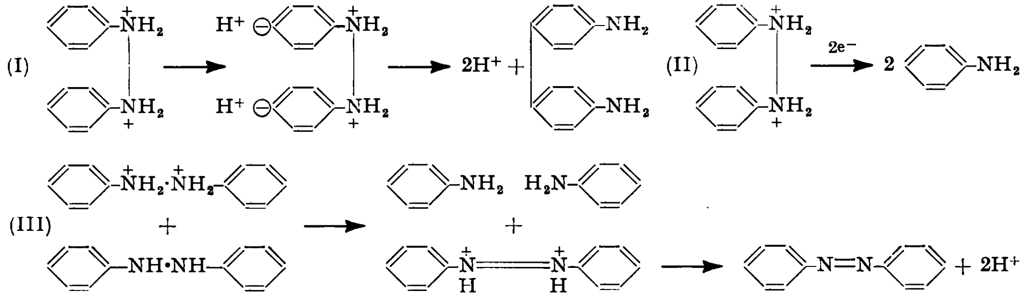
The more or less exponential increase in rate suggests that the relationship may be in fact a power series of the general form suggested by equation (1), an interpretation of which has already been discussed. With azobenzene a logarithmic plot of the results in Fig. 1 indicated that the power of the acid concentration to which the rate is proportional rises from zero to roughly 7 in the range 0·5N to 3·5N. With 4-aminoazobenzene the course is generally similar.

The earlier investigations with nitrobenzene did not include the high acid concentrations used in the present work, so that no very accurate estimate of the way in which the active titanous species varies can be made. Apart from this, more than one such species may participate, and the complicated interionic effects cannot be allowed for quantitatively. For this reason it is hard to say whether at lower acid concentrations $\mathrm{Ph\overset{+}{N}H{:}NPh}$ is a reactive species or not. But there seems little doubt about the increasing importance of $\mathrm{Ph\overset{+}{N}H{:}\overset{+}{N}HPh}$ over most of the range in Fig. 1.

In the lower acid range there is a difference in behaviour between azobenzene and its amino-derivative which follows a relation similar to that found with nitrobenzene. The apparent independence of acid concentration found with azobenzene in this same range must be due to the compensating variations of concentration of the reactive species ($\mathrm{Ph\overset{+}{N}H{:}\overset{+}{N}HPh}$) on the one hand and of the active titanous species on the other. In acid solution the 4-amino-compound must exist mainly in the form $\mathrm{PhN{:}N{\cdot}C_6H_4{\cdot}\overset{+}{N}H_3}$, and since the positive charge reduces the probability of addition of two further protons to the azo-group, the dependence on acid concentration is shifted relatively to that of azobenzene. Over the lower acid range the predominating influence is now that of the variation of the concentration of the active titanous species, which is known from the work on nitrobenzene to depend upon $[\mathrm{HCl}]^{-2}$ or $[\mathrm{HCl}]^{-3}$.

It seems therefore that one of the most important reacting species in the reduction of the azo-compounds is the one with the two positive charges on the azo-group (suitably screened), $\mathrm{Ph}\overset{+}{\mathrm{N}}\mathrm{H}{:}\overset{+}{\mathrm{N}}\mathrm{HPh}$, to which, in the rate-determining step, an electron is transferred from the titanous species. This step will be followed by the rapid transfer of a second electron from the reducing agent.

This view that the electron transfer is in fact the rate-determining step is consistent with the fact that the activation energy for 4-aminoazobenzene is lower than that for azobenzene itself, the positive charge conferred on the molecule by the $\cdot\overset{+}{\mathrm{N}}\mathrm{H}_3$ group facilitating the transfer. (The substituent influences are being further investigated.)



As suggested earlier, the law found by Carlin, Nelb, and Odioso (*loc. cit.*) for the effect of acid on the rate of the benzidine transformation may probably be regarded as similar to that found in the present work for the reduction of the azo-compounds. Moreover, the relative amounts of benzidine and of aniline formed from azobenzene are nearly independent of the acid concentration. There is thus the interesting possibility that the participation of a common intermediate explains all these observations, the various reactions being formulated according to the annexed scheme.

PHYSICAL CHEMISTRY LABORATORY, OXFORD UNIVERSITY. [*Received, March* 17*th*, 1954.]