The Kinetics of the Reduction of Azoxybenzene (and Some Derivatives) by Titanous Chloride.

By M. J. STEPHEN and SIR CYRIL HINSHELWOOD.

[Reprint Order No. 5959.]

It is concluded that the reduction of azoxybenzene by titanous chloride in aqueous alcohol proceeds as follows: (*a*) azoxybenzene ⟶ aniline; (*b*) azoxybenzene ⟶ azobenzene ⟶ hydrazobenzene ⟶ benzidine + aniline. About 20% of the total follows (*a*) which is believed to depend upon dissociation of the binuclear compound after a first (rate-determining) stage of reduction. In (*b*) the velocity constants of the first and the second stage are of comparable magnitude, and the azobenzene concentration passes through a maximum.

The initial rate of reduction of the azoxybenzene is proportional to $[TiCl_3]$, and to $[Ph{\cdot}NO{:}NPh]$, and the whole system is an example of second-order consecutive reactions, the kinetics of which have been worked out. The initial rate is approximately proportional to $1/[H^+]$.

The influence of substituent groups on the rate is in the few examples tested considerably smaller than in the reduction of substituted nitrobenzenes.

There are large differences (which are discussed) in the effects of acid concentration on the titanous chloride reduction of nitrobenzene, azoxybenzene, and azobenzene.

THE present study of the reduction by titanous chloride of azoxybenzene and some derivatives continues previous work on the reaction of nitrobenzene and azobenzene and their derivatives (Newton, Stubbs, and Hinshelwood, *J.*, 1953, 3384; Large, Stubbs, and Hinshelwood, *J.*, 1954, 5211). It proves less suitable for the investigation of energy–entropy relations and of additive effects in series of substituted compounds, the influence of the substituent groups being rather small. The reaction of titanous chloride with the azoxy-compound presents, however, certain interesting contrasts with that with the nitro- and azo-compounds, and incidentally furnishes a good example of second-order consecutive reactions.

EXPERIMENTAL

The following reagents were used: titanous chloride, a solution in hydrochloric acid standardised with "AnalaR" ferric ammonium sulphate; azoxybenzene, recrystallised from alcohol, m. p. 35—36°; *pp'*-azoxyanisole, prepared according to Vorländer (*Ber.*, 1907, **40**, 1423), m. p. 116°; *mm'*-azoxyanisole, prepared according to Rotarski (*Ber.*, 1908, **41**, 865), m. p. 50°; *mm'*-azoxyaniline, prepared according to Andrews (*J.*, 1896, **69**, 8), m. p. 146—148°; *pp'*-azoxyaniline, prepared according to Mixter (*J. Amer. Chem. Soc.*, 1883, **5**, 2), m. p. 184°.

The method of studying the rate of reduction of the azoxy-compounds by titanous chloride consisted in the addition of samples of the reaction mixture to excess of ferric alum and back-titration with titanous chloride, the disappearance of the red colour from 0·5 ml. of 10% aqueous ammonium thiocyanate indicating the end-point. It was found convenient to have two titanous chloride solutions, one exactly 0·2M and the other exactly 0·05M, the first for making up the reaction mixtures and the second for the titrations. The hydrochloric acid concentration of both solutions was adjusted and controlled by titration with standard sodium hydroxide in conjunction with a pH-meter, the titanous hydroxide precipitate making acid–base indicators useless. The titanous chloride solutions were stored in reservoir burette systems in an atmosphere of hydrogen. The reaction mixture itself was made from equal volumes of alcohol and aqueous hydrochloric acid, titanous chloride in hydrochloric acid being mixed with the azoxy-compound in alcohol at zero time, in an Erlenmeyer flask placed in a thermostat. A non-oxidising atmosphere above the mixture was maintained by a stream of carbon dioxide saturated with alcohol. At the time of mixing both reagents were at the temperature of the bath. The titanous chloride was added by a pipette, so calibrated that the volume introduced would be 50 ml. at 18°.

At intervals of time, samples (normally 10 ml.) of the reaction mixture were pipetted into a measured excess of ferric alum, each pipette being first well flushed with carbon dioxide. The residual ferric alum was back-titrated with titanous chloride as in the standardisation. Two corrections had to be applied, one for the contraction in volume on mixture of alcohol and water, the second for thermal expansion at the higher temperature. The total correction varied between 1·5 and 3%, the calculated values being verified by tests with solutions of titanous chloride and alcohol.

From such measurements curves were plotted showing percentage reaction against time. The initial rate obtained from the tangent to the curve at zero time can be expressed in moles of $TiCl_3$ $l.^{-1}$ $sec.^{-1}$ and if the reaction is of the second order can be written in the form :

$$\text{initial rate (above units)} = k_0[\mathrm{TiCl_3}][\text{azoxybenzene}]$$

where k_0 is the specific rate constant and the reactant concentrations expressed in moles $l.^{-1}$ are those initially present. When the initial rate is required in terms of moles of azoxybenzene $l.^{-1}$ $sec.^{-1}$, the appropriate stoicheiometric factor must be introduced, and k_0 is replaced by another constant.

From experiments with an excess of titanous chloride left until all the azoxybenzene had been reduced, it was found that 1 mole of azoxybenzene is equivalent to 4·65 moles of titanous chloride, and not to 6 moles as would have been expected if azoxybenzene were reduced completely to aniline. These " infinity " runs were carried out in flasks having greased ground-glass stoppers and first well flushed out with carbon dioxide. This procedure was necessary because even a gentle current of carbon dioxide caused appreciable evaporation over a long period of time. These tests usually lasted at least two days, after which carbon dioxide was again passed, and samples were run into an excess of ferric alum and back-titrated as usual. Blank tests were also made with titanous chloride alone.

Azoxybenzene was found to yield partly benzidine and partly aniline. The benzidine produced was estimated as follows. The solution, after the axoxybenzene had been completely reduced, was made alkaline with sodium hydroxide and then extracted with ether which removed the aniline and benzidine. The ether was extracted with 0·25N-hydrochloric acid and to the extract 2 ml. of M-sulphuric acid were then added. The solution was left in ice water for 30 min. to ensure the complete precipitation of benzidine sulphate, which was filtered off at the pump and well washed with ice-cold water saturated with benzidine sulphate, and finally with a little cold aqueous alcohol. The precipitate was transferred to a flask and titrated with standard sodium hydroxide. Towards the end of the titration the solution was boiled. This method was tested on a standard benzidine solution and shown to be satisfactory. It was found that 67·5% of the azoxybenzene is reduced to benzidine. Moderate changes in concentration of titanous chloride or hydrochloric acid do not appreciably affect the degree of conversion.

In an attempt to identify intermediate products in the reaction, absorption spectra of samples at different times were determined, and compared with those of azoxy- and azobenzene. Azobenzene was thus shown to be an intermediate. The amount was determined at a series of times from the absorption of samples at 430 and 450 μ, where the absorption due to azoxybenzene, aniline, and benzidine is negligible. A calibration curve under the conditions prevailing was constructed by use of a standard solution of azobenzene.

The second phase of the investigation involved the determination of activation energies for azoxybenzene and substituted derivatives, with some of which the sparing solubility necessitated lower working concentrations. The titanous equivalent of each azoxy-compound had to be determined, as the presence of substituents affected the final benzidine : aniline ratio. The temperature range extended from 10° to 40°, and at least 5 temperatures were used for activation-energy determination. The thermostats operating between room temperature and 40° were electrically heated water-baths. That for work below room temperature was an insulated methyl alcohol–water bath with a set of internal coils through which a cooling liquid was pumped from a refrigerator.

The energies of activation were determined by plotting the logarithm of the time for 10% reaction, 20% reaction, and so on against the reciprocal of the absolute temperature and finding the slope of each line by the method of least squares. The calculated values of E for various percentage reactions could if necessary be extrapolated to zero reaction to give the initial activation energy.

RESULTS

Products of Reduction.—The amounts of titanous chloride consumed at the end of the reaction are shown in Table 1. The mean titanous chloride equivalent of azoxybenzene is 4·65 moles.

TABLE 1. *Stoicheiometric ratios.*

Initial [azoxybenzene], 42·7 × 10^{-4} mole $l.^{-1}$; oxidation time, 3 days.

Initial [$TiCl_3$] (10^{-4} mole $l.^{-1}$)	515	515	643	643
Final [$TiCl_3$] (10^{-4} mole $l.^{-1}$)	315	317	445	448
$TiCl_3$/azoxybenzene (moles)	4·69	4·65	4·65	4·59

There are two products of reduction, aniline and benzidine. Estimation of the benzidine produced showed that 67·5% of the azoxybenzene is reduced to benzidine. This is consistent with the figure of 4·65 for the titanous equivalent.

Order of Reaction.—Reaction–time curves for the reduction of azoxybenzene by titanous chloride at 25° were plotted to determine the dependence of the rate on the initial concentrations of azoxybenzene, titanous chloride, and acid severally. The initial rates of reaction expressed as moles of titanous chloride $l.^{-1}$ $min.^{-1}$ were read off from the curves. A linear relation was found when the initial rate was plotted against the initial concentration of azoxybenzene or of titanous chloride, indicating the first order of reaction with respect to each. These results are shown in Tables 2 and 3. A linear relation was also found when the initial rate was plotted against the reciprocal of the acid concentration. The line did not, however, pass through the origin and the rate was found to be expressed closely by the equation $[H^+](\text{Rate} - 0{\cdot}6) = \text{const.}$ (Table 4).

TABLE 2. *Variation in concentration of azoxybenzene.*

25°; [$TiCl_3$] = 515 × 10^{-4} mole $l.^{-1}$; [HCl] = 515 × 10^{-3} mole $l.^{-1}$.

Initial rate (10^{-4} mole of $TiCl_3$ $l.^{-1}$ $min.^{-1}$)	22·8	20·0	16·9	14·3	8·6	5·9
Initial [azoxybenzene] (10^{-4} mole $l.^{-1}$)	137·6	120·0	103·0	86·0	51·6	34·4
Rate/concn.	0·166	0·167	0·164	0·166	0·167	0·171

(Note: The drawing of tangents to curves is inevitably somewhat arbitrary, but for any given series a consistent convention was adopted so that the relative values are considered reliable, though they may differ from the true absolute values.)

TABLE 3. *Variation in concentration of titanous chloride.*

25°; [Azoxybenzene] = 86 × 10^{-4} mole $l.^{-1}$; [HCl] = 515 × 10^{-3} mole $l.^{-1}$.

Initial rate (10^{-4} mole of $TiCl_3$ $l.^{-1}$ $min.^{-1}$)	19·8	16·5	14·0	9·5	7·0	4·5
Initial [$TiCl_3$] (10^{-4} mole $l.^{-1}$)	825	722	618	412	309	206
Rate/concn.	0·0240	0·0228	0·0227	0·0231	0·0227	0·0218

TABLE 4. *Variation in concentration of acid.*

25°; [Azoxybenzene] = 110 × 10^{-4} mole $l.^{-1}$; [$TiCl_3$] = 515 × 10^{-4} mole $l.^{-1}$.

Initial rate (10^{-4} mole of $TiCl_3$ $l.^{-1}$ $min.^{-1}$)	29·0	19·0	10·5	8·0	6·0	4·5	3·5
[HCl] (mole $l.^{-1}$)	0·258	0·368	0·703	0·906	1·33	1·75	2·31
10^4 [HCl] (Rate − 0·6)	7·33	6·77	6·96	6·72	7·18	6·82	6·69

A closer study of the entire titanous chloride–azoxybenzene reaction–time curve showed, however, that a second-order equation was not satisfactorily followed (Table 5). k_0 is calculated from the expression: $k_0 = x/at(a - x)$ where a is initial concentration of reactants (stoicheiometrically equivalent) expressed, as moles of $TiCl_3$ $l.^{-1}$, and x is the amount which reacted in time t.

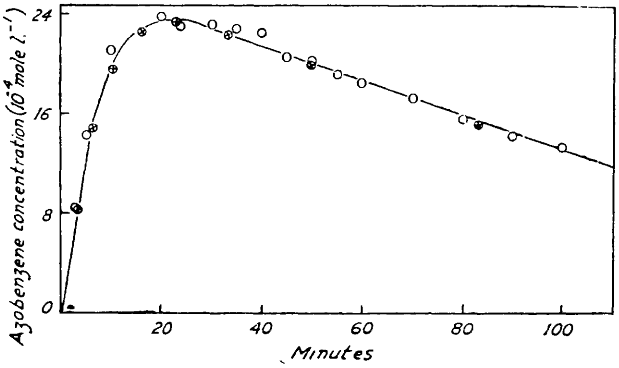
TABLE 5. *Variation of velocity constant.*

25°; Initial [azoxybenzene] = 110 × 10^{-4} $mole^{-1}$.
Initial [$TiCl_3$] = 515 × 10^{-4} mole $l.^{-1}$.

Reaction (%)	5	10	15	20	25	30	35	40	45
Time (min.)	1·6	4·0	7·1	10·8	15·1	20·0	25·2	31·8	40·6
k_0 {$sec.^{-1}$ l. (mole of $TiCl_3$)$^{-1}$} × 10^2	1·07	0·90	0·80	0·75	0·72	0·70	0·70	0·68	0·65

To account for the decrease in k_0, intermediate products in the reaction were looked for. The absorption spectra of samples after different times of reaction were compared with those of azo- and azoxy-benzene, and azobenzene was found to be an intermediate. A curve showing the amount of azobenzene present at various times during the reaction is shown in Fig. 1. The form of this curve together with that for the variation in initial reactants is dealt with theoretically in the Discussion section, but it should be mentioned here that k_0 of Table 5 is only a conventional value since in the full treatment special conversions by the appropriate stoicheiometric factors are necessary.

FIG. 1. *Formation of azobenzene during reduction of azoxybenzene.*



O, Experimental; ⊗, calculated.

The effect, on the rate, of chloride ions (in the form of sodium chloride added initially to the reaction mixture) is shown in Table 6.

TABLE 6. *Effect of sodium chloride.*

[Azoxybenzene] = 110 × 10^{-4} mole l.$^{-1}$; [TiCl$_3$] = 515 × 10^{-4} mole l.$^{-1}$; [HCl] = 515 × 10^{-3} mole l.$^{-1}$.

[NaCl] (mole l.$^{-1}$)	0	0·223	0·333	0·444	0·555
Initial rate (mole of TiCl$_3$ l.$^{-1}$ min.$^{-1}$)	18·0	18·0	18·4	18·6	18·9

Activation Energy.—For the reduction of azoxybenzene, reaction-time curves between 10° and 40° and for acid concentrations of 0·256, 0·515, and 2·84N were determined. From these curves Table 7 was prepared.

TABLE 7. *Temperature coefficients for azoxybenzene.*

	Time (min.) for given % reaction at							Activation energy (kcal./mole)
	10°	15°	20°	25°	30°	35°	40°	
[HCl] = 0·256N; [Azoxybenzene] = 110 × 10^{-4} mole l.$^{-1}$; [TiCl$_3$] = 515 × 10^{-4} mole l.$^{-1}$.								
10%	6·6	4·3	2·7	1·9	1·3	—	—	16·8
20%	18·2	12·1	6·1	4·2	2·8	—	—	16·6
30%	27·7	17·1	11·0	7·1	4·8	—	—	17·3
40%	—	33·2	18·6	11·7	7·7	—	—	17·0
								Mean 16·9
[HCl] = 0·515N; [Azoxybenzene] and [TiCl$_3$] as above.								
10%	—	13·0	8·3	4·8	3·2	2·1	1·4	15·8
20%	—	31·0	17·7	10·2	7·0	4·5	3·0	16·3
30%	—	—	33·5	19·1	12·0	7·5	5·1	16·5
40%	—	—	—	28·8	17·8	11·1	7·6	17·2
								Mean 16·4
[HCl] = 2·84N; [Azoxybenzene] and [TiCl$_3$] as above.								
10%	—	—	30·2	19·3	12·0	7·7	5·0	16·3
20%	—	—	64·6	41·2	25·7	16·2	10·6	15·9
30%	—	—	107	67·8	42·5	27·5	17·1	16·5
								Mean 16·2

General mean E = 16·5 kcal./mole.

For the substituted azoxybenzenes similar results are given in Table 8.

TABLE 8. *Temperature coefficients for substituted azoxybenzenes.*

	Time (min.) for given % reaction at					Activation energy (kcal./mole)
	20°	25°	30°	35°	40°	
			pp'-*Azoxyanisole.*			
10%	63	43	33	21	13·5	15·0
20%	151	110	74	48	35	14·7
					Mean	14·8
			mm'-*Azoxyanisole.*			
10%	3·5	2·7	1·6	1·2	0·8	13·3
20%	11·0	7·9	5·1	3·8	2·1	14·1
30%	24·5	17·4	10·1	7·6	5·0	14·0
					Mean	13·8
			pp'-*Azoxyaniline.*			
10%	5·0	4·0	3·3	2·7	2·3	15·2
20%	10·4	8·5	6·9	5·7	4·7	15·2
30%	16·8	13·7	11·3	9·2	7·6	15·2
					Mean	15·2
			mm'-*Azoxyaniline.*			
10%	4·0	2·5	1·6	1·0	0·7	15·3
20%	10·0	5·9	3·9	2·6	1·7	15·2
30%	—	14·5	8·4	6·2	3·9	15·4
					Mean	15·3

DISCUSSION

Kinetics.—The reduction of azoxybenzene to benzidine and aniline by titanous chloride in acid solution takes place according to the equations :

$$\text{Ph·NO:N·Ph} + 4\text{H} \longrightarrow \text{NH}_2\text{·C}_6\text{H}_4\text{·C}_6\text{H}_4\text{·NH}_2 \quad \ldots\ldots \quad 68\%$$

$$\text{Ph·NO:N·Ph} + 6\text{H} \longrightarrow 2\text{Ph·NH}_2 \quad \ldots\ldots\ldots \quad 32\%$$

Large, Stubbs, and Hinshelwood (*J.*, 1954, 2736) showed that azobenzene in acid solution is reduced as follows by titanous chloride

$$\text{Ph·N:N·Ph} + 2\text{H} \longrightarrow \text{NH}_2\text{·C}_6\text{H}_4\text{·C}_6\text{H}_4\text{·NH}_2 \quad \ldots\ldots \quad 84\%$$

$$\text{Ph·N:N·Ph} + 4\text{H} \longrightarrow 2\text{Ph·NH}_2 \quad \ldots\ldots\ldots\ldots \quad 16\%$$

Since only 68% of the azoxybenzene reduced is converted into benzidine compared with 84% of azobenzene it appears that approximately 20% of the azoxybenzene may be reduced directly to aniline without passing through the azobenzene stage, possibly by a dissociation of the binuclear compound after the first electron transfer on reduction. Both phenylhydroxylamine and nitrosobenzene are rapidly reduced to aniline by titanous chloride, and any intermediate stages between them will be still more unstable.

The initial reduction of azoxybenzene by titanous chloride is of the first order with respect to both azoxybenzene and titanous chloride. The reduction of azobenzene is similar in this respect. The equations for the rate of reduction may thus be formulated in the following way :

If at time t, [azoxybenzene] $= A$, [azobenzene] $= B$, [TiCl$_3$] $= T$, then

$$\mathrm{d}A/\mathrm{d}t = -k_1'AT - k'AT = -k_1AT \quad \ldots\ldots \quad (1)$$

where k_1' measures the rate of reaction to azobenzene, and k' that direct to aniline.

$$\mathrm{d}B/\mathrm{d}t = k_1'AT - k_2BT \quad \ldots\ldots\ldots \quad (2)$$

whence

$$\frac{\mathrm{d}B}{\mathrm{d}A} = -\frac{k_1'}{k_1} + \frac{k_2B}{k_1A}$$

Integration gives

$$B = \frac{k_1'}{k_1}\left[\frac{A_0^{1-k}A^k - A}{1-k}\right] \quad \ldots\ldots\ldots \quad (3)$$

where $k = k_2/k_1$ and A_0 is the initial value of A. Let the amount of titanous chloride used in converting 1 mole of azoxybenzene into end products be β and that used in converting 1 mole of azoxybenzene into azobenzene be α. ($\alpha = 2$ and $\beta = 4{\cdot}7$.)

At time t the titanous chloride which has reacted is given by

$$T_0 - T = \alpha B + \beta(A_0 - A - B) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Under conditions where stoicheiometrically equivalent proportions of azoxybenzene and titanous chloride are used, $\beta A_0 = T_0$. Substitution of (4) into (1) gives

$$-\mathrm{d}A/\mathrm{d}t = k_1 A[(\beta + l)A - lA_0^{1-k}A^k] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

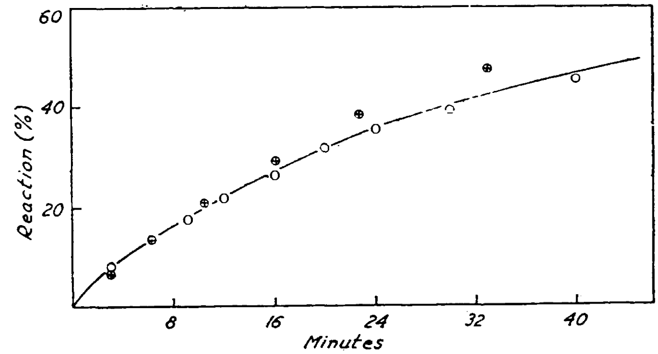
where $l = k_1'(\beta - \alpha)/k_1(k - 1)$.

Before (5) can be resolved the value of k must be known. The [azobenzene]-time curve (Fig. 1) shows a maximum, the condition for which is $\mathrm{d}B/\mathrm{d}t = 0$. Equation (2) gives at this point $k_2/k_1' = A_\mathrm{m}/B_\mathrm{m}$, where A_m and B_m are the values of [azoxybenzene] and [azobenzene] at the time corresponding to the maximum :

$$\beta A_\mathrm{m} = T_\mathrm{m} - (\beta - 2)B_\mathrm{m}$$

Substitution of the numerical values of T_m and B_m from graphs gives $k_2/k_1' = 2{\cdot}5$.

FIG. 2. *Reaction-time curve for azoxybenzene and titanous chloride in equivalent quantities.*



○, Experimental; ⊗, calculated.

From the comparison between the amounts of benzidine formed from azobenzene and azoxybenzene respectively it has been concluded that k_1'/k_1 = fraction of reaction *via* azobenzene = 0·80.

Hence
$$k = \frac{k_2}{k_1} = \frac{k_2}{k_1'} \cdot \frac{k_1'}{k_1} = 2{\cdot}5 \times 0{\cdot}80 = 2{\cdot}0$$

Equation (5) must normally be integrated as a series which becomes indeterminate for the special value $k = 2$, but for this value it so happens that the equation becomes directly integrable and yields

$$t = \frac{1}{\rho}\left(\frac{1}{A} - \frac{1}{A_0}\right) - \frac{\varepsilon}{\rho^2}\ln\frac{A(\rho - \varepsilon A_0)}{A_0(\rho - \varepsilon A)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\rho = k_1\beta + k_1'(\beta - \alpha)$ and $\varepsilon = k_1'(\beta - \alpha)/A_0$.

If now k_1, the rate constant for azoxybenzene, is taken to be $1{\cdot}26 \times 10^{-2}$ (with time in sec. and all concentrations in mole l.$^{-1}$), k_2 is found to be $2{\cdot}52 \times 10^{-2}$ sec.$^{-1}$ l. mole^{-1}, and the curve shown in Fig. 1 for the formation of azobenzene can be calculated. It is seen to agree satisfactorily with experiment. The value of k_2 compares with the figure found by Large *et al.* of $2{\cdot}5 \times 10^{-2}$ for experiments on the direct reduction of azobenzene. From equation (6), [azoxybenzene] and [$TiCl_3$], as well as [azobenzene], were calculated as functions of time. Typical results for the consumption of titanous chloride are shown in Fig. 2.

The value $1{\cdot}26 \times 10^{-2}$ for k_1 required by Fig. 1 can be compared with a direct value obtained approximately in a different way. From the tangent at the origin to a curve of titanous chloride consumed against time, the initial rate of disappearance of $TiCl_3$ can be found. Azobenzene is formed, and in an interval Δt after the start of the reaction has an average concentration B. The amount of titanous chloride used by the azo-compound in this interval $= M = k_2BT_0\Delta t \times 2{\cdot}32$ according to the stoicheiometric figure of Large *et al.* The total amount of titanous chloride reacting in this interval is $T_0 - T$, and of this $(T_0 - T - M)$ reacts with azoxybenzene. 80% of the azoxybenzene yields azobenzene, 20% giving aniline which requires 6 mols. of $TiCl_3$. Thus the average $TiCl_3$: azoxybenzene equivalence is $(0{\cdot}80 \times 2) + (0{\cdot}20 \times 6) = 2{\cdot}8$. Thus the amount of azoxybenzene reacting is $(T_0 - T - M)/2{\cdot}8$ and this is $k_1A_0T_0$. As $\Delta t \longrightarrow 0$, $B \longrightarrow 0$, and $k_1A_0T_0 \longrightarrow (\mathrm{d}T/\mathrm{d}t)_0/2{\cdot}8$. The curvature changes rather rapidly near the origin but $(\mathrm{d}T/\mathrm{d}t)$ is within the range $1{\cdot}8 \times 10^{-5}$ to $2{\cdot}3 \times 10^{-5}$ where $A_0 = 110 \times 10^{-4}$ mole l.$^{-1}$ and $T_0 = 515 \times 10^{-4}$ mole l.$^{-1}$. Thus k_1 is in the range $1{\cdot}1 \times 10^{-2}$ to $1{\cdot}5 \times 10^{-2}$ which includes the value previously obtained.

From Table 4 the initial rate is seen to be nearly proportional to $1/[H^+]$. In view of the considerable hydrolysis of titanous chloride in solution it seems probable that the predominant reducing species is here $Ti(OH)^{2+}$, as was found by Yost and Zabaro (*J. Amer. Chem. Soc.*, 1926, **48**, 1181) in their study of the kinetics of the oxidation of tervalent titanium by iodine, and by Mackenzie and Tompkins (*Trans. Faraday Soc.*, 1942, **38**, 465) in a study of the autoxidation of titanous chloride. The equilibrium involved is :

$$\mathrm{Ti^{3+} + H_2O \rightleftharpoons Ti(OH)^{2+} + H^+}$$

with
$$[\mathrm{Ti(OH)^{2+}}] = K[\mathrm{Ti^{3+}}]/[\mathrm{H^+}]$$

so that the initial rate of reaction of this species with azoxybenzene may be expressed by :

$$\text{Rate} = k[\text{Azoxybenzene}][\mathrm{Ti(OH)^{2+}}] = k_1[\text{Azoxybenzene}][\mathrm{Ti^{3+}}]/[\mathrm{H^+}]$$

Influence of Substituents.—Although the range of substituents investigated is not large, it seems clear that the influence is a good deal less than that observed in the reduction of nitrobenzene. Table 9 shows the rates relative to that for the unsubstituted compound for some of the derivatives in the two series.

TABLE 9. *Influence of substituents.*

Substituent	Relative rates	
	Nitrobenzene series	Azoxybenzene series
H	1	1
p(*p*′)-OMe	0·21	0·48
m(*m*′)-OMe	1·15	1·51
p(*p*′)-NH_2	2·32	1·38
m(*m*′)-NH_2	5·49	1·43

With the azoxy-compounds the range of variation is too narrow for the effective examination of energy–entropy relations, and the number of compounds examined is too small for the testing of additive relations in the free energies of activation. Nevertheless the relative insensitiveness to the effect of the substituent is itself of interest, and may be connected with the influence of hydrion concentration just referred to. With nitrobenzene the reduction rate is proportional nearly to $1/[H^+]^2$ and with azoxybenzene to $1/[H^+]$. Thus, if it is assumed (which of course is not absolutely necessary) that the reducing species is the same in each case, then in the expression for the reaction rate of the azoxy-compound an extra term $[H^+]$ occurs. This might indicate that an extra proton must be present in the transition state. If so, the attachment of this proton would be antagonised by a recession of electrons from the reaction centre, an effect which would tend to neutralise the correspondingly easier transfer of electrons from the reducing agent. Such compensating influences may explain the small total change in rate caused by the substituent groups.

It is also of interest to note that, for comparable conditions of acidity, the azoxy-compounds have lower activation energies than the corresponding nitro-compounds although they are usually reduced more slowly. The entropy of activation is lower. This may be because the transfer of electrons from the titanium to the reaction centre is easier, but that the presence of suitably placed protons to provide the hydrogen for reduction has, with the binuclear compound, become a more critical need. In the discussion of azobenzene reduction it has already been tentatively suggested that the appropriate proton supply is a very important factor. Such a conclusion rests upon the observation that the rate of reaction depends in a quite remarkable way on the acidity. The activation energy, on the other hand, is even lower than for the azoxy-compounds. The following numbers illustrate these relations ($k = Ae^{-E/RT}$).

	E	$\log_{10} A$ for reaction in 0·5N-acid
Nitrobenzene	17,700	12·9
Azoxybenzene	16,500	10·2
Azobenzene	15,800	10·1
p-Aminonitrobenzene	16,500	11·6
pp'-Diaminoazoxybenzene	15,200	9·5
p-Aminoazobenzene	12,700	8·4

Note on Reduction of Nitrobenzene.—The fact that the reduction of azoxybenzene by titanous chloride yields a considerable proportion of benzidine re-opens a question about the course of reduction of nitrobenzene. Newton, Stubbs, and Hinshelwood (*J.*, **1953**, 3384) found that the second-order rate constants for this reduction fell as the reaction proceeded, and attributed the fall to the known possibility of interaction between the intermediates nitrosobenzene and phenylhydroxylamine to give azoxybenzene, which they showed in fact to be reduced at about the rate required to account for the later part of the nitrobenzene reduction. No further consequences depended upon this assumption since the definitive results were expressed in terms of initial rates of reaction. It needs some revision, however, since nitrobenzene yields aniline quantitatively, and, at any rate with a moderate excess of titanous chloride present, no benzidine at all is found. Fresh experiments to elucidate this point have shown :

(*a*) that under actual conditions of the reaction the condensation of nitrosobenzene and phenylhydroxylamine is not rapid enough to divert a serious amount of the nitrobenzene through the azoxybenzene route (the curves of titanous chloride consumption which seemed in the previous work to indicate the contrary can be explained by the fact that phenylhydroxylamine is easily re-oxidised by ferric alum) ;

(*b*) that phenylhydroxylamine and titanous chloride give a reaction which remains of the second order over most of its course (the corresponding reduction of nitrosobenzene being too fast to measure) ; and

(*c*) that over the greater part of the reaction course nitrobenzene (determined by extraction and photometry) and titanous chloride are removed from the system in very nearly the stoicheiometric ratio corresponding to aniline formation.

The fall in the second-order constants with time in the course of the nitrobenzene reduction is now attributed to a combination of several factors, including, first, the not strictly linear proportionality of the active titanous species to the total concentration, and, secondly, small diversion of the reaction through more difficultly reduced intermediate products, or formation of aminophenol towards the end of the reduction (though this does not occur when the titanous chloride is in excess and is in any case less than was supposed). Although the reaction products added to a fresh reacting mixture have been shown to have no retarding effect, it remains a possibility that they cause slow changes in the state of co-ordination of the reducing titanous species and so impair its activity in some degree.

PHYSICAL CHEMISTRY LABORATORY, OXFORD UNIVERSITY. [*Received, December 14th*, 1954.]