Summary

The rate of the reaction between osmium tetroxide, hydrogen ion and bromide ion at 100° in acid concentrations from 1.2 to 3.5 *M* has been studied and the reaction in the rate determining step has been found to be of the first order with respect to each of the reacting constituents.

On the basis of this study and an earlier investigation of the equilibrium between octavalent osmium, hydrogen ion, bromide ion, reduced osmium and tribromide ion a mechanism has been suggested indicating the steps in the initial stages of the reaction. In all the acid solutions the first and rate determining step is a reduction of the osmium to the hexavalent state. In solutions of low acid and high bromine concentration, rapid follow reactions carry the osmium to the heptavalent state, but in solution of high acid and low bromine concentration the tendency is toward the quadrivalent form.

In the expression

$$k = -\frac{d(\mathrm{OsO_4})}{dt} \times \frac{1}{(\mathrm{Os_8})(\mathrm{H^+})(\mathrm{Br^-})(\gamma\pm)^2}$$

the value of k has been found to be approximately 0.28 when the time is expressed in hours.

LOS ANGELES, CALIF. RECEIVED OCTOBER 19, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, THE UNIVERSITY OF MINNESOTA]

Electrochemical Properties of Diphenylbenzidine Sulfonic Acid

BY L. A. SARVER AND I. M. KOLTHOFF

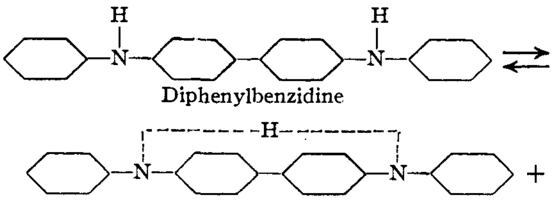
It has been mentioned in previous work[1] that upon oxidation of a substituted aromatic diamine such as diphenylbenzidine there is first formed a green insoluble intermediate product, and then a more soluble violet quinoid compound of high coloring power.

The intermediate product was assumed to be a meriquinone, or double molecular compound composed of one molecule of the diphenylbenzidine itself and one molecule of the oxidized quinoid form; but no proof has ever been presented as to the correctness of this view, and from the recent work of Michaelis[2] it was thought possible that the green substance might be a semiquinone, or compound derived from diphenylbenzidine by the transfer of one electron instead of two.

It has been proved in a number of cases by electrochemical means that the intermediate oxidation products of diamines are really semiquinones and not meriquinones, but this has never been achieved for a compound of the benzidine series because of the insolubility and instability of the oxidation products. The green product from diphenylbenzidine itself is extremely insoluble, while that from diphenylbenzidine disulfonic acid is only slightly soluble. However, a polysulfonic acid of diphenylbenzidine has been obtained recently[3] which gives a fairly soluble and stable green oxidation product, and it appeared that with this substance it might be possible to decide whether or not semiquinones are formed by compounds of the benzidine series.

Since the only function of the sulfonic acid groups is to increase the solubility of the reagent and its oxidation products, let us consider the mechanism for the oxidation of diphenylbenzidine itself. We shall call the first and second oxidation products diphenylbenzidine green and diphenylbenzidine violet, respectively.

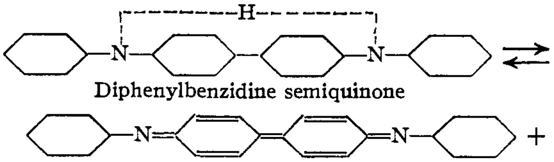
According to the semiquinone theory, the first stage of the oxidation should be:



Diphenylbenzidine

Diphenylbenzidine semiquinone $\mathrm{H^+} + e$ (1)

where e represents an electron transferred; the second stage would then be



Diphenylbenzidine semiquinone

Diphenylbenzidine violet $\mathrm{H^+} + e$ (2)

According to the meriquinone theory, on the other hand the first stage of the reaction would be

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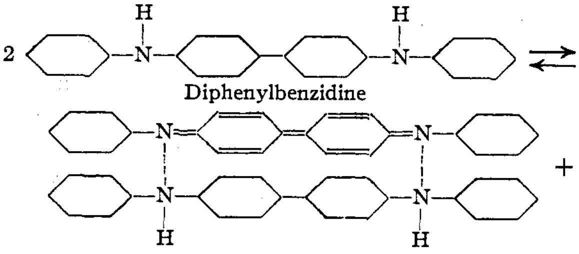
[1] I. M. Kolthoff and L. A. Sarver, THIS JOURNAL, **52**, 4179 (1930).

[2] See L. Michaelis, *Chem. Rev.*, **16**, 243 (1935), where references to earlier work may be found.

[3] L. A. Sarver and Wm. Von Fischer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 271 (1935).



Diphenylbenzidine meriquinone $2H^+ + 2e$ (3)

and the second stage would be

$$\text{Diphenylbenzidine meriquinone} \rightleftarrows 2 \text{ diphenylbenzidine violet} + 2H^+ + 2e \quad (4)$$

If the number of moles of diphenylbenzidine taken for titration is represented by a, and the number of moles oxidized at any time by x, the potentials during the first stage of the reaction should be given by

$$E = E_0 + \frac{RT}{F} \log \frac{x}{a - x}, \text{ at constant } pH \quad (5)$$

if the green compound is a semiquinone, and by

$$E = E_0 + \frac{RT}{2F} \log \frac{[\text{M. Q.}]}{[\text{D. B.}]^2}, \text{ at constant } pH \quad (6)$$

if it is meriquinone.

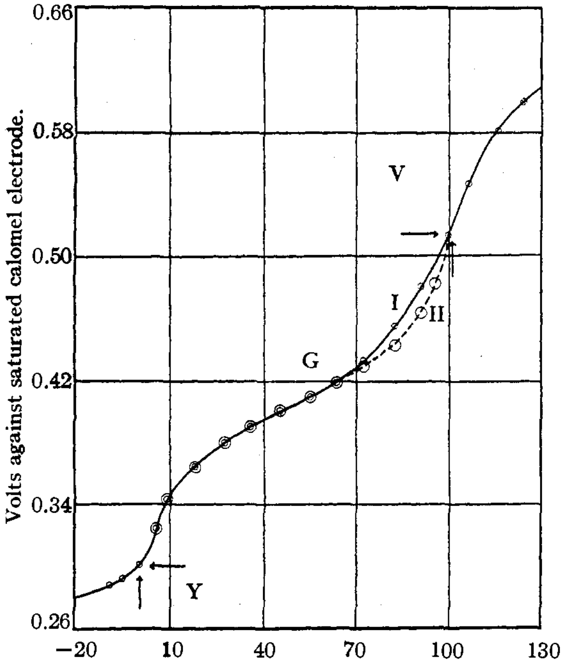


Fig. 1.—I, potentials observed; II, potentials calculated as semiquinone; $E = 0.405 + 0.06 \log([\text{D. B. semiquinone}]/[\text{D. B.}])$; V, violet; G, green; Y, yellow.

Similar equations apply to the second stage of the reaction.

By a comparison of the shapes of the experimental titration curves with those calculated on the basis of the formation of semiquinones and meriquinones, respectively, it should be possible to decide which theory is correct in this case.

Experimental

The diphenylbenzidine sulfonic acid used was prepared and purified by the method of Sarver and von Fischer,[3] and a microscopical examination revealed no appreciable amount of sodium sulfate to be present. Upon ignition, an amount of sodium sulfate corresponding to 52.7% of the sample was obtained; a compound with ten sulfonic acid groups should give 52.1%. Stock solutions in water were prepared which contained 1 g. of the yellow sodium salt per liter, and suitable quantities of sulfuric acid were added in each experiment just before titration.

The reduction potential of ferrous iron in sulfuric acid solution was not sufficiently low to effect complete reduction of the green compound, but in the presence of fluoride the change from green to yellow, indicating complete reduction of the green, occurred at approximately 0.30 v., against the saturated calomel electrode (or at 0.55 v., against the normal hydrogen electrode), in 1.0 N sulfuric acid solution.

Attempts were made to titrate portions of the diphenylbenzidine sulfonic acid with bromine in a buffered solution at a pH of 4, but the oxidation products decomposed so rapidly that no steady potentials could be obtained. However, when the titrations were performed in 1.0 N sulfuric acid, using standard solutions of potassium dichromate and ferrous iron in the same concentrations of sulfuric acid, potentials were obtained which were subject to very little drift, at least during the first stage of the oxidation. The best results were obtained by adding a slight excess of dichromate over that theoretically required for the oxidation of all the diphenylbenzidine sulfonic acid to the corresponding green, allowing the system to come to equilibrium, then adding some hydrofluoric acid to lower the potential of the ferrous–ferric iron system, and back-titrating with standard ferrous solution.

In this way, some very good titration curves were obtained (Fig. 1), which showed distinct breaks at the disappearance of the violet and green, respectively. In a large number of experiments, 1.7 ml. of 0.01 N dichromate was used up in the first stage of the oxidation of 20 ml. of the stock indicator solution, whereas the amount of ferrous solution necessary for the back titration of the green was equivalent to only 1.1 ml., and the quantity theoretically required upon the assumption that the reagent was pure diphenylbenzidine decasulfonic acid was 1.48 ml. The volume of dichromate consumed varied somewhat in the series of experiments, but the amount of ferrous solution required for the reduction of the green remained remarkably constant. Indeed, a portion still needed 1.1 ml. of ferrous solution for back titration after standing for one month in the normal sulfuric acid solution. It would appear that part of the diphenylbenzidine sulfonic acid was oxidized in an irreversible way, but that the green intermediate product itself was very stable.

The potentials observed during a typical titration of this sort are given in Table I, in comparison with the calculated values which should be obtained according to the semiquinone and meriquinone theories, respectively (see also

Fig. 1). In each experiment, 20 ml. of the 0.1% water solution of diphenylbenzidine sulfonic acid was treated with 50 ml. of 1.5 *N* sulfuric acid and 2.0 ml. of 0.01 *N* potassium dichromate in 1.0 *N* sulfuric acid. The potential of the mixture rose gradually during the establishment of equilibrium over a period of twenty to thirty minutes, at the end of which time 5.0 ml. of C. P. 48% hydrofluoric acid was added, and the back titration begun with 0.01 *N* ferrous solution in 1.0 *N* sulfuric acid. Thus the sulfuric acid concentration was approximately 1.0 *N* and constant throughout the titration. The system was allowed to come to equilibrium after the addition of each drop of reducing solution, the whole experiment requiring several hours.

It will be seen from an examination of the data in Table I that the experimental values agree quite well with those calculated on the assumption that the green compound is a semiquinone; they disagree with those calculated for a meriquinone. In the upper part of the curves, the observed values are higher than the calculated ones for a semiquinone, which is what we would expect if there were some overlapping of the first and second stages of the oxidation. Hence, the evidence points quite definitely to the existence of a semiquinone as an intermediate product in the oxidation of benzidine derivatives, rather than to a meriquinone.

TABLE I

(1.47×10^{-5} mole of diphenylbenzidine sulfonic acid in 70 ml. of 1.0 *N* sulfuric acid, and 2 ml. of 0.01 *N* $K_2Cr_2O_7$ in 1.0 *N* sulfuric acid; 5 ml. of 48% C. P. hydrofluoric acid added after thirty minutes, and back titration begun with 0.01 *N* ferrous solution in 1.0 *N* sulfuric acid; potentials referred to satd. calomel electrode.)

% oxidized	Volume, ml.	E. m. f., v. Obsd.	Calcd. as meriquinone	Calcd. as semiquinone
18.2	78.2	0.3649	0.3793	0.3658
27.3	78.1	.3793	.3876	.3794
36.4	78.0	.3905	.3948	.3904
45.5	77.9	.4005	.4017	.4003
54.6	77.8	.4093	.4088	.4097
63.6	77.7	.4195	.4166	.4196
72.7	77.6	.4331	.4258	.4306
81.8	77.5	.4555	.4379	.4442

$E_{\text{S. Q.}} = 0.405 + 0.06 \log (X/(100 - X))$, where X equals percentage of D. B. oxidized. $E_{\text{M. Q.}} = 0.294 + 0.03 \log [\text{M. Q.}]/[\text{D. B.}]^2$.

As regards the second stage of the oxidation (from green to violet), the experimental results were much less satisfactory. First, the oxidation potential of the potassium dichromate was not high enough to ensure complete conversion of the green intermediate product to the violet holoquinoid form, and, second, more energetic oxidizing agents caused a marked decomposition of the latter, accompanied by drifting potentials. The result was that the quantity of the violet form found varied from experiment to experiment, and only rarely approximated to that consistently found for the green. However, even though the experimental conditions were so unfavorable, the observed potentials always lay closer to the values calculated on the basis of the semiquinone theory than to those required by the semiquinone theory.

Summary

Diphenylbenzidine decasulfonic acid has been oxidized to the corresponding green and violet forms, and the subsequent reduction studied electrometrically. The green form was very stable, the violet considerably less so, and both were reasonably soluble in water and dilute acid solutions. The form of the titration curves indicated that the green intermediate product was a semiquinone, not a meriquinone.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 13, 1936

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON, AND THE GEORGE WASHINGTON UNIVERSITY]

The Apparent Volumes and Thermal Expansions of Certain Salts in Aqueous Solution between 20 and 40°[1]

BY R. E. GIBSON AND JOHN F. KINCAID

In the course of a study of the correlation of the compressions with other thermodynamic properties of solutions we found it necessary to obtain reliable values of the thermal expansions. For a few aqueous salt solutions these quantities could be computed from measurements already published but the general result of a careful survey was the discovery of an almost complete absence of reliable systematic data. Interest in thermal expansions is enhanced by the researches of Gucker,[2] who found that when the apparent molal expansibilities of electrolytes in aqueous solutions are plotted against the square root of the volume concentration straight lines are obtained, but that the slopes of these lines depend markedly on the individual characters of the salts and are negative instead of positive as an extrapolation of the interionic attraction theory would require. It seemed desirable, therefore, to determine some expansions

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(1) Part of this work is taken from a thesis presented by John F. Kincaid to the George Washington University in partial fulfilment of the requirements for the degree of Master of Arts.

(2) F. T. Gucker, Jr., THIS JOURNAL, **56**, 1017 (1934).