ences in chemical properties of covalent and ionic azides and nitrates can be correlated with differences in structure. The use of the adjacent charge rule is illustrated by its application in the discussion of the structures of nitrogen pentoxide, nitrogen tetroxide, and the oxygen acids of heavier atoms.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Reaction between Osmium Tetroxide and Hydrobromic Acid. II. Rate Study

BY H. DARWIN KIRSCHMAN AND WILLIAM R. CROWELL[1]

In a previous article on a study of the equilibrium between osmium tetroxide, hydrogen ion and bromide ion at 100°, it was suggested that at low acid and high bromine concentrations the reaction might be of the type[2]

$$OsO_4 + H^+ + {}^5/_2Br^- \rightleftharpoons Os(OH)O_3^-Br + {}^1/_2Br_3^- \quad (1)$$

The purpose of the present work was to carry out a study of the rate of the reaction between osmium tetroxide, hydrogen ion and bromide ion with a view of learning more of its nature and to determine, if possible, the validity of certain assumptions made in the earlier investigation.

The general plan of the work consisted of the analysis for bromine of the contents of the reaction tubes at various time intervals in experiments conducted in a manner similar to that employed in the equilibrium problem. From the results obtained an attempt was made to determine the order of the reaction with respect to octavalent osmium, hydrogen ion and bromide ion.

The general form of the rate expression can be stated as

$$-\frac{d(OsO_4)}{dt} = k(Os_8)^a\,(H^+)^b\,(Br^-)^c\,\frac{(f_1)^a\,(f_2)^b\,(f_3)^c}{f_4}$$

In the present instance $k = k_0K$ where k_0 is the specific reaction rate constant and K the equilibrium constant of the intermediate complex. f_1, f_2, f_3 and f_4 are the activity coefficients of octavalent osmium, hydrogen ion, bromide ion and the intermediate complex, respectively.

In the first series of experiments, the initial concentration of all the reacting constituents was kept constant except that of the osmium, which was changed about twofold. A second series of runs was made at different concentrations of hydrobromic acid but at a fixed initial concentration of osmium. A third series of runs was made at approximately constant ionic strength and at the same initial concentration of octavalent osmium. Some of these runs were carried out at different concentrations of bromide ion but at a fixed concentration of hydrogen ion. In other runs the bromide ion concentration remained constant while the hydrogen ion concentration was changed. The purpose of the experiments at constant ionic strength was to determine the orders with respect to hydrogen and bromide ion, and to see if the sum of these orders was approximately equal to the order with respect to hydrobromic acid found in the second series of runs. Finally, using the rate data thus obtained, a series of rate constants was calculated.

Experimental

The apparatus was that employed in the equilibrium experiments.[2] The potassium hydroxide solution of osmium tetroxide was prepared as described in our previous article on the determination of octavalent osmium.[3] The hydrobromic acid was prepared from red phosphorus and bromine by the well known method. The middle fraction of the distillate was redistilled until a water white product was obtained.

The experimental procedure was essentially the same as that used in the equilibrium experiments with one modification in the case of the solutions 1.2 and 1.6 M in hydrobromic acid. In these solutions there was a tendency for the bromine formed to react with the reduced osmium when the tubes were broken in the chilled water in the titration beaker. To overcome this difficulty, sufficient hydrobromic acid was added to the water in the titration beaker to make the acid concentration after the addition of the contents of the reaction tube about 0.1 N.

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[1] The authors were assisted in the experimental work by Messrs. Glen Seaborg and Robert Brinton, students in the Chemistry Department at the University of California at Los Angeles.

[2] Kirschman and Crowell, THIS JOURNAL, **55**, 488 (1933).

[3] Crowell and Kirschman, *ibid.*, **51**, 175 (1929).

TABLE I

CONCENTRATION OF REDUCED OSMIUM AT VARIOUS TIME INTERVALS AT 100°

In moles per 1000 grams of water × 10^3

	Concn. in moles per 1000 g. of water				Reaction time in hours										
Runs	$OsO_4 \times 10^3$	HBr	KBr	KCl	1/24	1/12	1/6	1/4	1/3	1/2	1	2	4	8	24
1	4.30	1.24	..	..	..	...	...	0.210	..	0.355	0.670	1.05	1.61	2.04	2.31
2	4.28	1.66	..	..	..	...	...	.479	..	1.12	1.92	2.28	2.48	2.59	2.61
3	4.36	2.10	..	..	..	...	0.840	...	1.68	2.24	2.66	2.70	2.62	2.72	
4	4.34	2.55	..	..	..	0.806	1.88	2.67	3.08	3.31	3.38				
5	2.04	2.55	..	..	..	.408	0.816	1.10	..	1.59	1.69	1.69			
6	4.48	3.50	..	..	1.76	3.54	4.32	4.32							
7	2.07	3.50	..	..	0.880	1.80	2.01	2.01							
	Runs at Approximately Constant Ionic Strength														
8	4.15	1.31	..	2.18	..	...	...	0.95	..	1.90	2.64	2.90	2.90		
9	4.15	1.31	1.31	0.88	0.33	0.91	1.84	2.34	..	2.84	3.06				
10	4.15	1.31	2.18	..	.43	.93	2.04	2.68	..	3.01					
11	4.15	1.75	..	1.75	..	.66	...	1.88	..	2.79	2.93	3.06	3.18		
12	4.15	1.75	1.75	..	..	1.39	2.80	3.22	..	3.35	3.37				
13	4.15	2.62	..	0.88	.85	1.96	3.53	3.83							
14	4.15	2.62	0.88	..	..	2.54	4.00	4.00							

Results of the Rate Experiments

Table I shows results of rate experiments at 100°. All concentrations of reduced osmium are expressed in moles per 1000 g. of water. Runs 1–7 inclusive are at different concentrations of octavalent osmium and of hydrobromic acid, while runs 8–14 inclusive are at the same osmium concentration and approximately at the same ionic strength as the hydrobromic acid run at 3.50 *M*. In order to keep the solutions at the same ionic strength for different concentrations of hydrogen ion and bromide ion, potassium bromide and potassium chloride were used in addition to the hydrobromic acid. While these salts, particularly potassium chloride, may influence the nature of the reduced osmium complexes, they should not affect markedly the initial rates.

The initial rates were obtained by plotting the data in Table I and obtaining the slopes of the curves by well-known graphical methods. The values for the individual runs are shown in column 2 of Table II. The order of the reaction n_r with respect to any reactant was calculated from the expression

$$n_r = \frac{\text{Log rate ratio}}{\text{Log activity ratio}}$$

By comparing run 4 with run 5, and run 6 with run 7, the effect of doubling the osmium concentration in a fixed concentration of hydrobromic acid was determined. The average of the two values of n_{OsO_4} was 0.98.

In runs 1, 2, 3, 4 and 6 the concentration of osmium was approximately the same while the concentration of acid was changed in steps from 1.24 to 3.50 *M*. The runs compared were 1 and 2, 1 and 3, 1 and 4, 1 and 6, 2 and 3, 2 and 4, and 2 and 6, 3 and 4, 3 and 6, and 4 and 6. To calculate the activity of the hydrobromic acid, the activity coefficients shown in Table II column 5 were used. It was assumed that the ratio of the activity coefficients of the octavalent osmium and the intermediate complex was constant. The calculated order with respect to hydrobromic acid varied from 2.5 to 1.9. For the most part the higher values were obtained when comparing the lower acid concentrations. The average of the series of ten values was 2.17.

TABLE II

INITIAL RATES AND RATE CONSTANTS

Runs	Ionic strength moles per 1000 g. H_2O	$-(OsO_4)/dt$ moles per 1000 g. H_2O per hr. × 10^3	Specific rate $k' \times 10$	$\gamma\pm$ at 100°	Rate constant $k \times 10$
1	1.24	0.84	1.30	0.88	1.7
2	1.66	2.14	1.80	.99	1.8
3	2.10	5.04	2.66	1.14	2.0
4	2.55	10.9	3.87	1.33	2.2
5	2.55	4.92	3.72	1.33	2.1
6	3.50	43.2	7.86	1.94	2.1
7	3.50	21.6	8.55	1.94	2.3
8	3.50	3.79	5.46	1.26	3.4
9	3.50	10.9	7.52	1.26	4.7
10	3.50	12.2	6.50	1.26	4.1
11	3.50	8.2	6.50	1.37	3.5
12	3.50	16.8	6.50	1.37	3.5
13	3.50	23.4	8.20	1.63	3.1
14	3.50	30.4	7.90	1.63	3.0

In runs 8 to 14, inclusive, in which the ionic strength was kept constant, the order with respect to bromide ion was calculated by comparing runs 8 and 9, 8 and 10, 11 and 12 and 13 and 14. While it is realized that the activity coefficient of hydrobromic acid in the solutions used is not exactly constant at constant ionic strength, this fact does not prevent fair estimates of the order being made. The average value of n_{Br^-} was 1.18. The order with respect to hydrogen ion was obtained by comparing runs 6 and 10, 6 and 12, 9 and 13 and 10 and 14. In this case the average value of n_{H^+} was 1.22. Although the general tendency is for the orders in both series to run somewhat above unity, this is presumably due to the fact that the activity effects are not the same in all of the solutions. It seems reasonable to suppose that the order with respect to both bromide and hydrogen ion is one, and this checks fairly well with the results obtained with hydrobromic acid solutions containing no salt. These results indicate that the assumption that the intermediate complex is neutral in character is justified.

In the light of the results described, the rate expression can take the form

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

whence

$$k = -\frac{\mathrm{d}(\mathrm{OsO_4})}{\mathrm{d}t} \times \frac{1}{(\mathrm{Os_8})(\mathrm{H^+})(\mathrm{Br^-})(\gamma\pm)^2} = \frac{k'}{(\gamma\pm)^2}$$

where $\gamma\pm$ represents the mean ion activity coefficient of the hydrobromic acid.

Table II shows results of calculations of k' and k made in accordance with the above expressions. The activity coefficients were calculated from recent data of Harned[4] obtained from measurements made on solutions of hydrobromic acid and mixtures of hydrobromic acid and potassium bromide. In this calculation it was necessary to make a small extrapolation from 3.0 to 3.5 *M*, and also to correct the values to 100° by use of thermal data given in the "International Critical Tables."[5,6]

Attention is called to the fact that the constants for experiments 1–7 inclusive are in very fair agreement and the same is true for experiments 8–14 inclusive. The value of k for the latter group is definitely higher than that for the former group. The reason for this is not evident, but may be due to uncertainties in the values of γ_{HBr} in these solutions. It is a curious fact that the assumption that γ_{HBr} is equal for all solutions of ionic strength 3.5 *M* leads to better constancy of k for experiments 8–14 as well as to a much better agreement between the k's of both series of experiments.

Conclusions

Since the results indicate that the reaction in the rate determining step is first order with respect to octavalent osmium, hydrogen ion and bromide ion, the mechanism that is suggested for the initial stages of the reaction is as follows.

$$\mathrm{H_2OsO_5} + \mathrm{H^+} + \mathrm{Br^-} \longrightarrow \mathrm{H_2OsO_4} + \mathrm{HBrO} \qquad (2)$$

(Rate determining step)

$$\mathrm{HBrO} + \mathrm{H^+} + \mathrm{Br^-} \longrightarrow \mathrm{Br_2} + \mathrm{H_2O} \qquad (3)$$

(Rapid follow reaction)

$$\mathrm{Br_2} + \mathrm{Br^-} \longrightarrow \mathrm{Br_3^-} \qquad (4)$$

(Rapid follow reaction)

$$\mathrm{H_2OsO_4} + {}^1/_2\mathrm{Br_3^-} \longrightarrow \mathrm{HOsO_4} + \mathrm{H^+} + {}^3/_2\mathrm{Br^-} \qquad (5)$$

(Rapid follow reaction)

$$\mathrm{HOsO_4} + \mathrm{Br^-} \longrightarrow \mathrm{Os[(OH)O_3Br]^-} \qquad (6)$$

(Rapid follow reaction)

The sum is (1).

The formation of hexavalent and heptavalent forms other than those shown is, of course, quite possible.

In the previous work on the equilibrium study the statement was made that the equilibrium constants indicated that the tendency was for the octavalent osmium to be reduced to the heptavalent state in solutions of low acid and high bromine concentration and that at high acid and low bromine concentration the tendency was toward reduction to the quadrivalent state. The present work seems to show that in all the solutions, 1.2 *M* as well as 3.5 *M* in hydrobromic acid with or without potassium bromide or chloride, the first step of the reaction is a reduction of $\mathrm{OsO_4}$ to the hexavalent state. In solutions of low acid concentration the hexavalent osmium is oxidized to the heptavalent form by rapid follow reactions. With increasing acid concentration some of the rapid follow reactions lead more and more to a reduction to the quadrivalent form with the setting up of more or less complicated equilibria. In all the solutions in which the bromine is not confined in the reaction tubes, the net effect is a reduction to the quadrivalent form.

In conclusion we wish to express our appreciation to Dr. Don M. Yost for his valuable assistance in this work.

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(4) Harned, This Journal, 57, 1865 (1935).

(5) "International Critical Tables," Vol. V, p. 177.

(6) It should be noted that in the equilibrium study described in a former paper[3] the application of these new values of $\gamma\pm$ will change the absolute values of the equilibrium constant quite radically. The relative values, however, will still be in sufficient accord to justify the conclusions then drawn.

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

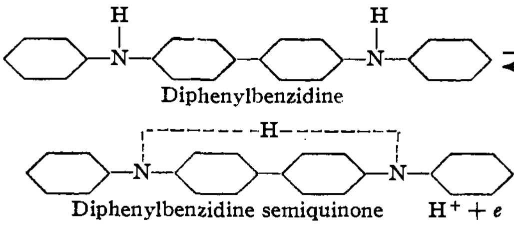
It has been mentioned in previous work[1] that upon oxidation of a substituted aromatic diamine such as diphenylbenzidine there is first formed a green insoluble intermediate product, and then a more soluble violet quinoid compound of high coloring power.

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.

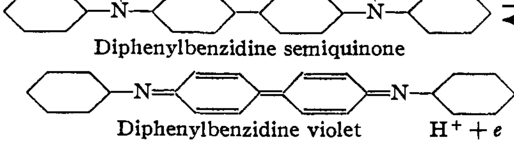
Since the only function of the sulfonic acid groups is to increase the solubility of the reagent and its oxidation products, let us consider the mechanism for the oxidation of diphenylbenzidine itself. We shall call the first and second oxidation products diphenylbenzidine green and diphenylbenzidine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

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



(1)

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



(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).