rium with nitric acid at 20° are the hexahydrate, tetrahydrate, dihydrate, sesquihydrate, monohydrate and hemihydrate.

Anhydrous manganous nitrate was prepared by dehydration at room temperature.

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

The Catalytic Effect of Osmium Compounds on the Reduction of Perchloric Acid by Hydrobromic Acid

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In a previous communication it was shown that the reduction of perchloric acid by hydrobromic acid was catalyzed by trivalent ruthenium salts, and a mechanism for the catalyzed reaction was proposed.[1] Because of the similarity of the oxidation states of ruthenium and osmium it was thought that osmium compounds might behave in a similar manner. Preliminary experiments showed that the reaction is catalyzed by osmium tetroxide, $K_2OsO_4 \cdot 2H_2O$, K_2OsBr_6 and K_3OsBr_6, although the effect is much less than in the case of ruthenium.

Equilibrium and rate studies of the reaction between osmium tetroxide and hydrobromic acid carried out in these laboratories have been helpful in shedding some light on the probable mechanism of the osmium-catalyzed reactions.[2,3] It has been shown that the rate-determining step in the former reaction is a reduction of the osmium to the hexavalent state. Rapid follow reactions which then take place depend upon the acid and bromine concentrations. At high acid and low bromine concentrations the tendency is toward reduction to the quadrivalent state. At low acid and high bromine concentrations the tendency is toward formation of the heptavalent form. At equilibrium several oxidation states of osmium are present together and Kirschman and Crowell were forced to assume as a result of their measurements that the equilibrium concentration of heptavalent osmium predominated at high bromine and low acid concentrations. This assumption does not seem to be in accord with the known instability of perosmates, but the results of the equilibrium measurements are not easily explained on any other basis. Latimer has suggested the possibility of the presence of osmyl, OsO_2^{++}, derivatives in these solutions.[4]

The purpose of the present investigation was to study the rate of the osmium-catalyzed reaction between perchloric and hydrobromic acids at 100° and at different concentrations of the reacting constituents. The solutions were maintained at approximately constant ionic strength, in order to determine the order of the reaction with respect to each constituent involved. With the aid of these data and the information regarding the osmium tetroxide–hydrobromic acid reaction, it is possible to propose a mechanism for the catalyzed reaction.

Experimental

Reagents.—The compounds used consisted of osmium tetroxide, potassium osmate, potassium bromoosmate, potassium bromoperosmite, hydrobromic acid, perchloric acid, sodium perchlorate and sodium chloride. In these experiments the osmium compounds must be prepared with special care to eliminate ruthenium, which has a catalytic effect. The best obtainable osmium metal was fused with potassium hydroxide and potassium nitrate. The water extract was then heated with 6 *N* nitric acid and the osmium tetroxide produced was distilled into 1 *N* potassium hydroxide. The resulting hydroxide solution was treated with ethyl alcohol to precipitate the violet crystals of $K_2OsO_4 \cdot 2H_2O$ and these were washed with alcohol. To the potassium osmate was added a solution of nitric acid and the tetroxide again distilled into 1 *N* potassium hydroxide. Again the osmium was recovered from the alkali solution as potassium osmate. One portion of the osmate was then heated with a solution of dichromic acid and the osmium tetroxide distilled into 1 *N* potassium hydroxide. This last solution was the source of the tetroxide used in the experiments. A second portion of the osmate was used as the source of the hexavalent compound, samples of which were weighed out and added directly to the reaction tubes. A third portion of the osmate was treated with dichromic acid and the tetroxide distilled into an ice-cold solution of concentrated hydrobromic acid which was then refluxed for about two hours. This solution was partially evapo-

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[1] Crowell, Yost and Carter, THIS JOURNAL, **51**, 786 (1929).

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

[3] Kirschman and Crowell, *ibid.*, **59**, 20 (1937).

[4] Latimer, "Oxidation Potentials," Prentice-Hall, New York, p. 217.

TABLE I

EFFECT OF PERCHLORATE, BROMOOSMATE, BROMIDE, AND HYDROGEN ION ON THE REACTION RATE AT 100°

Experiment number	1	2	3	4	5
	Initial concn. (ion mol./l.) of				
Perchlorate	0.50	1.00	0.50	0.50	0.50
Bromoosmate $\times 10^{-3}$	3.8	3.8	3.8	3.8	7.6
Bromide	1.2	1.2	2.4	1.2	1.2
Hydrogen	2.9	2.9	2.9	1.45	2.9
	Bromine formed (millieq./l.) in				
15 min.	2.3	4.8	2.4	0.90	4.4
30 min.	4.0	7.7	5.0	1.8	7.6
1 hour	7.1	14.2	9.6	2.6	13.2
2 hrs.	11.6	22.7	19.1	4.3	21.3
4 hrs.	23.4	38.8	34.0	7.2	35.6
8 hrs.	33.4	61.6	62.7	12.3	58.1
24 hrs.	68.0	108	127	23.2	105
48 hrs.	99.6	151	179		
96 hrs.	140	192	240		

rated on the steam-bath and the potassium bromoosmate precipitated by the addition of potassium bromide. The red crystals of K_2OsBr_6 were separated and washed with alcohol and then subjected to a second crystallization from hydrobromic acid. The solution of bromoosmate was obtained by dissolving the red crystals in dilute hydrobromic acid and adding enough concentrated hydrobromic acid to make the acid concentration 3 *N*. The K_3OsBr_6 was prepared from the hydrobromic acid solution of the bromoosmate by electrolytic reduction according to the method recently described by one of the authors.[5]

The hydrobromic acid was prepared from recrystallized potassium bromide by distillation with sulfuric acid, redistillation of the resulting acid and retention of the middle fraction.

Experimental Procedure.—Solutions of the compounds used were prepared with concentrations of such values that the proper volumes could be pipetted into test-tubes and the concentrations desired could be obtained in a total volume of 10.0 cc.

The tubes were sealed, heated at 100° in a water-bath for the desired periods of time and then removed and immersed in an ice-bath. The bromine evolved was determined by breaking the tubes in about 250 cc. of ice cold 0.10 *N* hydrobromic acid solution and conducting a potentiometric titration with approximately 0.01 *N* hydrazine sulfate.[3]

To compare the catalytic effects of the tetroxide, potassium osmate, bromoosmate and bromoperosmite, tubes were prepared 0.0038 *M* in the osmium compound, 2.9 *M* in hydrogen ion, 1.2 *M* in bromide ion, 0.50 *M* in perchlorate ion and 1.2 *M* in chloride ion. These were heated at 100° for twenty-four hours and then analyzed for the bromine liberated. The quantities of bromine formed in the four cases were substantially the same and amounted to about 68–70 milliequivalents per liter.

Since the catalytic effects of the four forms of osmium were essentially the same, it was decided that the quadrivalent salt, K_2OsBr_6, would be the most convenient form to use in the rate experiments. Further reasons for selecting this will be discussed later.

Since the oxidation of quadrivalent osmium by bromine was found to be a factor in the catalyzed reaction, experiments were also carried out with solutions of K_2OsBr_6, hydrobromic acid, and bromine under conditions parallel to those in the rate runs when the bromine concentration was about four times that of the osmium compound. Results indicated that while the initial rate of oxidation of the osmium to the hexavalent state was somewhat faster than the catalyzed reaction, it was not far from the same order of magnitude.

Experimental Results.—Table I presents the results of representative rate experiments in which may be noted the effects of a two-fold change in the concentrations of perchlorate, bromoosmate, bromide and hydrogen ion. In order to work at approximately constant ionic strength, the sum of the concentrations of all compounds present in all experiments was kept at 2.9 *M*. In all runs except no. 4 this was accomplished by use of perchloric, hydrobromic and hydrochloric acids. In no. 4 perchloric acid, hydrobromic acid, sodium perchlorate and sodium chloride were used. The amount of bromine formed is expressed as milliequivalents per liter.

By comparing runs 1 and 2 it will be seen that a doubling of the concentration of perchlorate, the concentrations of the other reacting constituents remaining the same, approximately doubles the amount of bromine formed. Comparing runs 1 and 5 in the same manner shows that the reaction is first order with respect to osmium. A comparison of runs 1 and 3 shows that doubling the initial bromide concentration does not affect the rate, but, as the reaction progresses, the order with respect to bromide increases and at the later stages approaches unity. In run 4 the hydrogen ion concentration is one-half that in run 1, and

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[5] Crowell, Brinton and Evenson, THIS JOURNAL, **60**, 1105 (1938).

the experimental data indicate that the order is about 1.5 with respect to this ion.

Mechanism of the Catalyzed Reaction

The results indicate that the rate determining step is initially of zero order with respect to bromide and of the first order with respect to perchlorate, osmium, and hydrogen ion, and that a secondary reaction takes place of the first order with respect to each of the four constituents. To explain this behavior the following mechanism is suggested.

$$\mathrm{OsBr_6^{=} + H^+ + ClO_4^- \longrightarrow OsBr_6OH^- + ClO_3^-} \quad (1)$$

(Rate determining step)

$$\mathrm{OsBr_6OH^- + 2Br^- \longrightarrow OsBr_5OH^{=} + Br_3^-} \quad (2)$$

(Rapid follow reaction. Reverse reaction slow)

$$\mathrm{ClO_3^- + 6H^+ + 9Br^- \longrightarrow 3Br_3^- + Cl^- + 3H_2O} \quad (3)$$

(Rapid follow reaction)

$$\mathrm{OsBr_6OH^- + 1/2Br_3^- + 3H_2O \rightleftarrows Os(OH)O_3Br^- + 6H^+ + 13/2Br^-} \quad (4)$$

(Moderately rapid at high bromine concentrations)

$$\mathrm{Os(OH)O_3Br^- + 1/2Br_3^- \rightleftarrows OsO_4 + H^+ + 5/2Br^-} \quad (5)$$

(Moderately slow at high bromine concentrations).

That (3) is a rapid step was shown by a separate experiment in which a solution 1.5 *M* in hydrobromic acid and 0.25 *M* in potassium chlorate when heated to 100 degrees in a closed tube almost immediately liberated copious amounts of bromine.

In the secondary reaction probably $\mathrm{OsBr_5OH^{=}}$ becomes the catalyst and hexavalent bromide complexes are formed similar in structure to that shown. As the bromine accumulates in the tubes the reverse of reaction (2), and those of that type speed up, and because of this as well as the effect of such equilibria as those shown in (4) and (5) the influence of bromide on the rate increases. However, (4) and (5) also cause more and more osmium to be removed from catalytic action, hence a falling off in the rate as the reaction proceeds. Previous experiments on the reaction between hydrobromic acid and osmium tetroxide would indicate that the rate should fall off more rapidly than it does at the higher bromine concentrations (2), (3). That this is not the case may be because other osmium complexes are formed in these solutions which are reduced more rapidly by bromide in reactions of the type shown in (2).

The fact that the ratio of the rate in run no. 1 to that in run no. 4 is greater than two is possibly due to the circumstance that the concentration of quadrivalent osmium in no. 4 is considerably decreased in the more dilute acid to form osmium tetroxide according to the equilibrium reactions (4) and (5).

The same catalytic effect is obtained with osmium tetroxide as with bromoosmate, probably because at the early stages of the reaction quadrivalent osmium is produced as a result of the reduction of the tetroxide by hydrobromic acid, and at a given bromine concentration the concentration of quadrivalent osmium is approximately the same in both tubes. The effect is the same when potassium osmate is used because the osmate is also reduced to the quadrivalent form soon after the solution is heated. This conclusion was verified by noting that a solution of the osmate in hydrobromic acid decomposed only slowly in the cold but on heating changed in color from yellowish-brown to deep red, and a determination of the amount of bromine liberated showed that the osmium was reduced to the quadrivalent state. That the effect was the same in solutions of bromoperosmite is probably due to the fact that under the conditions of the experiment trivalent osmium is rapidly changed to the quadrivalent form in the presence of bromine. Since in the three cases described the catalyzed reaction is accompanied by other reactions at the beginning of the runs, it will be seen that the initial rate can be best observed by use of quadrivalent osmium solutions.

Summary

The reaction between perchloric and hydrobromic acids with the formation of bromine is shown to be catalyzed by quadrivalent osmium compounds. Rate experiments with bromoosmate show that the rate is proportional to the concentrations of osmium compound, perchlorate and hydrogen ion, and at the later stages of bromide ion. A reaction mechanism is suggested in which the osmium is first slowly oxidized to the hexavalent state and then quickly reduced by bromide to the quadrivalent state. As the bromine accumulates in the reaction tubes complicated equilibria cause the reaction to slow down gradually due to the removal of the quadrivalent osmium by the production of heptavalent and octavalent forms.

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