would indicate that the mercury plays a very important part in the formation of the peroxide.

Summary

Under the ordinary conditions of analysis no hydrogen peroxide is formed in a Jones reductor. It has been proved that the entrance of air does not vitiate results. Hydrogen peroxide solutions introduced into reduced iron solutions cannot then react with permanganate solutions.

STANFORD UNIVERSITY, CALIFORNIA

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THE KINETICS OF THE OXIDATION OF TRIVALENT TITANIUM BY IODINE

BY DON M. YOST AND SIDNEY ZABARO

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Introduction

The oxidation-reduction reactions involving iodine admit of the following rough but useful classification: (1) those in which iodide ion is oxidized to iodine by an oxygen acid; (2) those in which iodide ion is oxidized to iodine by an oxidizing agent not containing oxygen; (3) those in which iodine is reduced by a reducing agent which takes up oxygen; (4) those in which iodine is reduced by a reducing agent which loses an electron but does not add oxygen to form an oxygen acid.

The reactions of Class 1 were studied by Bray,[1] who showed that their mechanism consists in the slow formation of hypo-iodous acid which then reacts with iodide ion to give iodine; for example, $HBrO_3 + HI = HIO + HBrO_2$, followed by $HIO + HI = I_2 + H_2O$.

The reactions of Class 2 do not conform to this mechanism, but in their case the slow step consists in direct oxidation (or, according to the ideas of Brönsted,[2] it consists in the formation of an addition product whose charge is the algebraic sum of the two reacting ions); the reaction $Fe^{+++} + I^- = Fe^{++} + \frac{1}{2}I_2$ is the best example of this class.

The various reactions of Class 3 differ from one another in their mechanisms. Thus the rate of the reaction, $I_2 + H_3AsO_3 + H_2O = 2HI + H_3AsO_4$, has been shown by Roebuck[3] to depend on the concentration of hypo-iodous acid which arises from the hydrolysis of iodine.[4] On the other hand, the reaction between phosphorous acid and iodine does not admit of

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[1] Bray, *Z. physik. Chem.*, **54**, 463 (1906).

[2] Brönsted, *ibid.*, **102**, 169 (1922).

[3] Roebuck, *J. Phys. Chem.*, **6**, 365 (1902).

[4] Noyes, *Z. physik. Chem.*, **47**, 121 (1904).

a hypo-iodite mechanism but has been shown by Mitchell[5] to depend upon the presence of two forms of phosphorous acid.

The reactions of Class 4 are the reverse of those of Class 2 and, like it, may well include reactions in which the rate is determined by the simple interaction of the oxidizing and reducing substances. It may, however, include cases involving the hypo-iodite mechanism. The reaction, $2Fe^{++} + I_2 = 2Fe^{+++} + 2I^-$ is the best example of this class, but it was not studied[6] with the object of determining its mechanism.

In the present paper are described the results of a research made on the rate and mechanism of another reaction of Class 4—the oxidation of trivalent titanium to the quadrivalent state by iodine which, without respect to the different states in which the ions exist, may be expressed by the equation

$$2Ti^{+++} + I_2 + 2H_2O = 2TiO^{++} + 2I^- + 4H^+ \qquad (1)$$

We are indebted to Professors A. A. Noyes and W. C. Bray for helpful advice and criticisms, and to the Carnegie Institution of Washington for financial assistance furnished through Professor A. A. Noyes.

Method of Analysis

All of the efforts made to devise a method for stopping the reaction at any time during its course were unsuccessful. That is to say, no reagent was found which would oxidize the titanium without affecting the iodide or iodine, or which would change the state of the iodide or iodine without affecting the titanium. Some substances which affected only one constituent when present alone were found to affect more than one when present together. Thus hydroxylamine oxidizes trivalent titanium, but does not affect iodide in acid solution; but when a mixture of iodide and trivalent titanium is treated with hydroxylamine, both quadrivalent titanium and iodine are formed.

It was finally found necessary to determine the iodine directly in the reacting mixture with standard thiosulfate solution. Since, as mentioned above, both acid and iodide ion do influence the rate of reaction in question, and since an increase in the concentration of either of them decreases the rate, it was found possible, by adjusting their concentrations, to obtain a mixture which could be titrated with thiosulfate without much error. It was found that by diluting a sample of the reacting mixture with a solution of hydrochloric acid and potassium iodide of such a strength that the final concentrations of iodide and acid were 0.07 N and 0.4 N, respectively, the iodine could be determined with an error not greater than 0.6%. The analytical method used was as follows: 25 cc. of the reaction mixture was pipetted into 65 cc. of a solution containing 1 g. of potassium iodide, 6.5

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[5] Mitchell, *J. Chem. Soc.*, **117**, 1322 (1920); **123**, 2241 (1923).

[6] Banerji and Dhar, *Z. anorg. allgem. Chem.*, **134**, 178 (1924).

cc. of 6 N hydrochloric acid, and 1 cc. of starch solution; and a small excess of thiosulfate was run into the mixture from a buret. The excess of thiosulfate was then titrated back with 0.03 N iodine solution. The total time required for the whole procedure was about one minute.

Preparation of the Solutions

The commercial 20% solution of titanous chloride was diluted, and the solution, which was about 0.3 N, was kept under carbon dioxide. It was standardized daily by running a known volume into a ferric chloride solution and titrating the ferrous iron formed with dichromate solution. The acid concentration was determined by adding an excess of sodium hydroxide to a known volume, filtering off the precipitated titanous hydroxide and titrating the excess of alkali in the filtrate with standard acid, allowance being made for the alkali required for the known amount of titanium present.

Stock solutions of potassium iodide, potassium triiodide, potassium chloride and hydrochloric acid were made up with boiled water and kept under an atmosphere of carbon dioxide. This last step is necessary, since trivalent titanium is readily oxidized by oxygen. In fact, when its solutions are vigorously stirred in the presence of oxygen, all of the titanium is oxidized in a few minutes with the formation of the quadrivalent salt and hydrogen peroxide, the presence of the latter being shown by the orange color of the final mixture.

The volumetric solutions were standardized against potassium permanganate which was standardized by means of sodium oxalate from the Bureau of Standards.

Procedure for the Reaction-Rate Measurements

Definite volumes of the stock solutions and water were mixed in a flask which had been previously swept free from air by carbon dioxide. The titanium solution, which was kept in the thermostat, was added after the contents of the flask had reached its temperature, and the time was counted from the addition; 25cc. samples were withdrawn from time to time and analyzed for iodine as described above.

Since the initial concentrations of the substances in the reaction mixture were known, it is evident that the results of the analyses furnish sufficient data for determining all other concentrations except that of acid and iodide ion. The latter, however, may be calculated from the known equilibrium constant for the reaction, $I^- + I_2 = I_3^-$. The former is uncertain, however, because of our lack of knowledge concerning the extent to which Ti^{+++} and TiO^{++} hydrolyzes. Various reasonable estimates of these quantities were used in the final calculations. It was found that the form of the rate equation was not seriously affected by them, since the amount of acid added was always considerably greater than that formed by hydrolysis.

Formulation of the Reaction Rate

Preliminary experiments established the fact that the rate of the reaction between trivalent titanium and iodine was increased by increasing the concentrations of titanous salts and iodine (or triiodide ion) and was decreased by increasing the concentrations of acid and iodide ion. Moreover, the effects were found to be such that the rate equation could be written in the form

$$\frac{-d\,(I_3^-)}{dt} = k\,\frac{(Ti^{+++})^m\,(I_3^-)^p}{(H^+)^n\,(I^-)^q} \tag{2}$$

Here m, n, p and q should be positive integers if the ions obey the laws of ideal solutions.

The values of m, n, p and q were determined by noting the effect of changes in the initial concentrations of the various substances upon the rate of the reaction. The accurate evaluation of k was accomplished by taking tangents from the experimental concentration-time curve and substituting in Equation 2.

The Reaction-Rate Measurements

A summary of the experimental results is presented in Tables I and II. The columns headed by substances give the initial concentrations in each case in equivalents per liter of solution. The notations $(H^+)'$ and $(H^+)''$ refer to the concentration of hydrogen ion as hydrochloric acid, calculated on the assumptions that the hydrolysis of the trivalent titanium is zero and 50%, respectively. For Expts. 1–7 (Table I) the total initial concentrations of iodine and iodide were 0.0224 and 0.149 equivalent per liter, respectively, in each case.

The values of (I_3^-) and (I^-) were calculated from the total iodide and total iodine by the use of the equilibrium expression $(I_2)(I^-)/(I_3^-) = K$. In the solutions used the constant K was given values between 0.002 and 0.003, according to the ionic strength.[7] As this correction does not exceed 10%, an accurate value of K is not necessary. In the last two columns of Table I are given the mean values of k_1' and k_1'' as defined by the following expressions:

$$k_1' = \frac{-d\,(I_3^-)}{dt}\,\frac{(H^+)'\,(I^-)}{(Ti^{+++})\,(I_3^-)} \quad (3); \qquad k_1'' = \frac{-d\,(I_3^-)}{dt}\,\frac{(H^+)''\,(I^-)}{(Ti^{+++})\,(I_3^-)} \quad (4)$$

In the last column of Table II are given the mean values of

$$k_2 = \frac{-d\,(I_3^-)}{dt}\,\frac{(H^+)'\,(I^-)^2}{(Ti^{+++})\,(I_3^-)} \tag{5}$$

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[7] Washburn and Strachan [THIS JOURNAL, **35**, 691 (1913)] give 0.0013 for K in 0.15 N HI. Brönsted and Pedersen [*Z. physik. Chem.*, **103**, 307 (1922)] give 0.0061 in 1.65 N KCl. The values here used were obtained by assuming that the change in the constant is proportional to the change in ionic strength.

The constants during the course of any one experiment showed no marked trend, but varied about the mean value.

TABLE I

REACTION RATES WITH VARIOUS CONCENTRATIONS OF TITANIUM AND ACID

	Molal concentrations				
Expt.	(Ti^{+++})	$(H^+)'$	$(H^+)''$	$10^3 k_1'$	$10^3 k_1''$
1	0.0288	0.367	0.410	12.6	14.1
2	.0115	.147	.167	14.3	16.0
3	.0115	.275	.282	16.0	16.4
4	.0114	.460	.478	12.0	12.5
5	.0284	.563	.606	10.4	11.2
6	.0113	.147	.164	14.4	16.1
7	.0113	.460	.478	13.5	14.0

TABLE II

REACTION RATES WITH VARIOUS CONCENTRATIONS OF IODINE AND IODIDE

	Molal concentrations					
Expt.	$\Sigma(I_2)$	$\Sigma(I^-)$	(Ti^{+++})	$(H^+)'$	$10^3 k_1'$	$10^3 k_2$
8	0.0224	0.287	0.0113	0.147	16.4	4.1
9	.0045	.0253	.0112	.275	53	1.31
10	.0045	.0564	.0112	.275	26	1.47
11	.0045	.0253	.0112	.275	58	1.47
12	.0045	.108	.0112	.275	15.6	1.67
13	.0045	.108	.0111	.275	15.0	1.62
14	.0111	.0633	.0112	.275	20.2	1.44
15	.0112	.084	.0111	.275	17.2	1.47
16	.0112	.271	.0111	.275	14.0	3.7
17[a]	.0112	.0617	.0101	.275	16.8	1.06
18[b]	.0112	.263	.0101	.275	14.4	3.8

[a] KCl = 0.600 *N*.

[b] KCl = 0.400 *N*.

No corrections for the change in acid concentration with the time were made in calculating the values of the rate constants. This procedure is justified by the facts that the initial concentration of acid is large and that its relative increase is small.

The Mechanism of the Reaction

The values of the constants k_1' and k_1'' in Expts. 1–7, in which the initial concentrations of iodide and iodine were the same, show satisfactory agreement. There is no doubt, therefore, that the values of m and n in Equation 2 are both unity. There is a slight decrease in k_1' with an increase in acid, but this is probably due to variation of the activations of the other ions present.

Expts. 8–16 show that there is not much choice between k_1' and k_2, so that one cannot decide whether the value of q is one or two. The values of k_1' increase with a decrease in the concentration of I^-, while the effect on k_2 is in the opposite direction. The results indicate that, in accordance with the theory proposed by Brönsted,[2] the variations in the values of

k_1' and k_2 may be due to lack of proportionality between the activities of the ions and their concentration. In such cases Brönsted has suggested that the experiments be carried out in solutions of constant ionic strength. Expts. 17 and 18 were carried out in this manner, potassium chloride being added for the purpose. It is evident that the mean values of k_1' resulting from these two experiments with widely different initial concentrations of iodide ion agree much more closely than do those of k_2. It may, therefore, be concluded that the reaction-rate equation is

$$-\frac{d\,(\mathrm{I_3^-})}{dt} = k\,\frac{(\mathrm{Ti^{+++}})\,(\mathrm{I_3^-})}{(\mathrm{H^+})\,(\mathrm{I^-})} \tag{6}$$

If now this experimentally determined equation be simplified by means of the mass-action expression $(\mathrm{I_2})\,(\mathrm{I^-}) = K(\mathrm{I_3^-})$, it reduces to

$$-\frac{d\,(\mathrm{I_3^-})}{dt} = \frac{k_1'}{K}\,\frac{(\mathrm{Ti^{+++}})\,(\mathrm{I_2})}{(\mathrm{H^+})} \tag{7}$$

If, further, the hydrolysis of $\mathrm{Ti^{+++}}$ be assumed to take place in accordance with the mass-action equation $(\mathrm{Ti^{+++}}) = K_\mathrm{H}(\mathrm{H^+})(\mathrm{TiOH^{++}})$ and this expression for $(\mathrm{Ti^{+++}})$ be substituted in (7), there results

$$-\frac{d\,(\mathrm{I_3^-})}{dt} = \frac{k_1'\,K_\mathrm{H}}{K}\,(\mathrm{TiOH^{++}})\,(\mathrm{I_2}) \tag{8}$$

If an addition compound were to be assumed, as proposed in such cases by Brönsted, this equation would represent the rate of the slow bimolecular reaction, $\mathrm{Ti(OH)^{++}} = \mathrm{I_2} = \mathrm{Ti(OH)^{++}.I_2}$. This would then be followed by the rapid reaction, $\mathrm{TiOH^{++}.I_2} + \mathrm{Ti(OH)^{++}} = 2\mathrm{TiO^{++}} + 2\mathrm{H^+} + 2\mathrm{I^-}$.

It is also of interest to consider the form of the rate equation that would be obtained if the mechanism of the reaction involved the presence of hypo-iodous acid. If we assume that the reaction determining the rate is $\mathrm{Ti^{+++}} + \mathrm{HIO} = \mathrm{TiO^{++}} + \frac{1}{2}\mathrm{I_2} + \mathrm{H^+}$, the rate equation would be $-\frac{d\,(\mathrm{I_3^-})}{dt} = k(\mathrm{Ti^{+++}})(\mathrm{HIO})$. If now the mass-action expressions for the hydrolysis of iodine and the formation of $\mathrm{I_3^-}$ from $\mathrm{I_2}$ and $\mathrm{I^-}$ are substituted in this equation, it becomes $-\frac{d\,(\mathrm{I_3^-})}{dt} = k_2\,\frac{(\mathrm{Ti^{+++}})\,(\mathrm{I_3^-})}{(\mathrm{H^+})\,(\mathrm{I^-})^2}$. This equation differs from equation (6), which actually expresses the rate, only in the exponent of $(\mathrm{I^-})$; but it was shown that this is unity when the rate is determined in solutions of the same ionic strength. Hence, it is evident that this reaction, which belongs to Class 4, does not involve a hypo-iodous acid mechanism.

It may be mentioned that Bredig and Michel[8] found that the rate of the reaction, $8\mathrm{Ti^{+++}} + \mathrm{ClO_4^-} + 4\mathrm{H_2O} = 8\mathrm{TiO^{++}} + \mathrm{Cl^-} + 8\mathrm{H^+}$, is directly proportional to the concentrations of titanium and perchloric acid, which they explained by assuming that the first slow step is the formation of

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[8] Bredig and Michel, *Z. physik. Chem.*, **100**, 124 (1922).

$TiClO_4^{++}$ and that this is followed by a rapid reaction between the addition compound and trivalent titanium. It may be noted that the results of the present research, as well as those of Bredig and Michel, could be interpreted by assuming the slow production of quinquivalent titanium to be the first stage in the reaction. There is no independent experimental evidence either for the addition compounds referred to above or for the existence of quinquivalent titanium. The fact, however, that ionic reactions of metathesis and of addition are usually rapid makes it more probable that the slow step in ionic reactions is commonly due to valence changes.

Summary

The rate of the reaction between iodine and trivalent titanium has been measured and found to be directly proportional to the concentrations of trivalent titanium and triiodide ion and inversely proportional to the concentrations of hydrogen ion and iodide ion. Taking into account the triiodide-iodine equilibrium and the probable hydrolysis of trivalent titanium salts, this is shown to correspond to a slow reaction between iodine and $TiOH^{++}$. This fact is not in agreement with the formation of hypo-iodous acid as an intermediate compound. The results could be explained by assuming the slow formation from $Ti(OH)^{++}$ and iodine of an addition product which in turn reacts rapidly with more $Ti(OH)^{++}$ to give the final products of the reaction. A mechanism is also suggested which involves the existence of quinquevalent titanium.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RATE OF THE REACTION BETWEEN ETHYLENE AND CHLORINE

BY T. D. STEWART AND R. D. FOWLER

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Previous Work

The rate of the reaction between gaseous ethylene and gaseous bromine, diluted with air, was determined by Stewart and Edlund.[1] They found a second-order reaction taking place exclusively on the walls of the glass vessel containing the gaseous mixture and showed that the pressure of water vapor had a marked effect on the rate of the reaction. Norrish[2] studied the same reaction in a glass vessel and in glass vessels coated with paraffin wax, stearic acid and cetyl alcohol. The relative rates of the four reactions were approximately as follows: paraffin 1, cetyl alcohol 9,

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[1] Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923).

[2] Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).