

THE MECHANISMS AND RATES OF CERTAIN OXIDATION  
REDUCTION REACTIONS IN AQUEOUS SOLUTION. THE  
EXISTENCE OF TRIVALENT SILVER.

Thesis

by

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## CATALYSIS BY SILVER ION OF THE OXIDATION OF CHROMIC SALTS BY PEROXYSULFURIC ACID. THE EXISTENCE OF TRIVALENT SILVER COMPOUNDS

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In the course of his researches Marshall<sup>2</sup> found that aqueous solutions of peroxysulfuric acid<sup>3</sup> ( $\text{H}_2\text{S}_2\text{O}_8$ ) have very strong oxidizing actions, but that in most cases the reactions were slow at ordinary temperatures. He also found that silver acted as a catalyst in the slow reactions, and presented the results of several qualitative experiments and a rough quantitative one to show this fact. Qualitatively, he found that trivalent chromium is oxidized much more rapidly in the presence of silver ion than in its absence; in fact, unless the silver ion was present, no appreciable oxidation took place at 50° even after 20 hours. Quantitatively, he found that ammonia is oxidized to nitrogen only when silver ion is present, and further that the rate seemed to be proportional to the concentration of peroxy-sulfate ion,  $\text{S}_2\text{O}_8^{2-}$ . Dittrich and Bollenbach<sup>4</sup> found that chloride, bromide, and iodide ions could be oxidized to chlorate, bromate and iodate by peroxysulfuric acid when the reaction was catalyzed by silver salt, and that iodide ion may be oxidized to iodate ion in acid solution, without intervention of a catalyst, although the reaction is quite slow. Walters<sup>5</sup> used the catalyzed reaction in an analytic method for the determination of chromium.

In this paper the results of an investigation of the catalysis of the chromium reaction by silver ion, and of the nature of the intermediate compound are presented. The ammonia reaction will form the subject of a further research on this interesting catalyst.

I am deeply indebted to Professor A. A. Noyes for his assistance and advice. Financial aid was received from a grant made to him by the Carnegie Institution of Washington.

<sup>1</sup> Du Pont Fellow in Chemistry.

<sup>2</sup> Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163-168 (1900). See also **24**, 88 (1902), where experiments on the catalytic decomposition of ammonium persulfate are described.

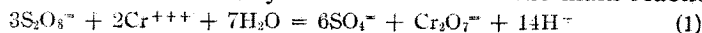
<sup>3</sup> The term "peroxy-" acid is here adopted, in accordance with a suggestion made by Professor W. C. Bray, for such acids as contain the peroxide grouping. This is done to distinguish them from ordinary compounds of higher valence, such as perchlorates, permanganates, perruthenates, etc., which do not contain the peroxide group. A more precise nomenclature would be to call  $\text{H}_2\text{S}_2\text{O}_8$  *peroxydisulfuric acid*, to distinguish it from  $\text{H}_2\text{SO}_5$  (Car's acid), which would then be called *peroxymonosulfuric acid*. The shorter name *peroxysulfuric acid* is, however, here used for the more stable acid.

<sup>4</sup> Dittrich and Bollenbach, *Ber.*, **38**, 747 (1905).

<sup>5</sup> Walters, *THIS JOURNAL*, **27**, 1550 (1905).

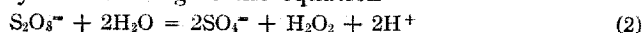
### General Discussion

The results of Marshall, as well as those of Walters, indicate that the reaction between peroxysulfuric acid and chromic ion goes to completion. It is also a known fact that dichromate does not convert sulfuric acid to peroxysulfuric acid. Hence it may be concluded that the main reaction



is not reversible under ordinary circumstances. Moreover, the peroxy acids are essentially complexes, their distinguishing feature being that they contain two, or some multiple of two, oxygen atoms in the form of peroxide oxygen; while the normal oxygen acids contain one or more oxygen atoms in the form of oxide oxygen. Thus peroxyvanadic acid,  $\text{HVO}_4$ , differs from vanadic acid,  $\text{HVO}_3$ , by having two peroxide oxygens in place of an oxide oxygen, not in that the vanadium atom itself has a higher valence. Now, it is fairly well established that peroxide oxygen is formed in ordinary chemical reactions by the reduction of  $\text{O}_3$  and not by the oxidation of oxide oxygen.<sup>6</sup> Hence, one may reasonably conclude that, if a reaction involving peroxy acids as oxidizing agents goes at all, it will go to completion in a thermodynamic sense.

It must be pointed out that, while peroxysulfuric acid is one of the strongest oxidizing agents known in aqueous solution, it may act as a reducing agent under some circumstances, oxygen being evolved during the reaction. This behavior may be explained by a consideration of the fact that its ion,  $\text{S}_2\text{O}_8^{2-}$ , hydrolyzes according to the equation<sup>7</sup>



The hydrogen peroxide then may act as a reducing agent. Reaction 2 takes place only in strongly acid solutions. Cain and Hostetter<sup>8</sup> reduced vanadic acid to vanadyl sulfate with peroxysulfuric acid in hot, strongly acid solutions as a step in an analytical procedure for the determination of vanadium. It seems probable that an oxidation-reduction reaction will be discovered wherein the net result will be the decomposition of peroxysulfuric acid, just as in the reaction between hydrogen peroxide and hydrogen bromide, the net result is the decomposition of hydrogen peroxide.<sup>9</sup>

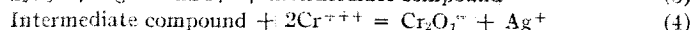
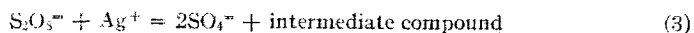
That silver ion catalyzes Reaction 1 through formation of an intermediate compound was suspected by Marshall when he observed that a black precipitate slowly formed when solutions of silver ion and persulfate ion were mixed. This important fact suggested that the reaction takes place in two stages.

<sup>6</sup> Traube, *Ber.*, **26**, 1471 (1893).

<sup>7</sup> There is an intermediate stage in this hydrolysis,  $\text{H}_2\text{SO}_5$  (Caro's acid) being formed, which finally comes to equilibrium with respect to  $\text{H}_2\text{O}_2$ ;  $\text{H}_2\text{SO}_5 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ .

<sup>8</sup> Cain and Hostetter, *THIS JOURNAL*, **34**, 274 (1912).

<sup>9</sup> Bray and Livingston, *ibid.*, **45**, 1251 (1923).



The net result of (3) and (4) is given by Reaction 1. The first step is a slow reaction, and the second and presumably final step is rapid or moderately rapid. That silver ion,  $\text{Ag}^+$ , is not permanently removed from the scene of the reaction in (3), but is regenerated in (4), is a conclusion drawn from the fact that no precipitate appears when chromic ion,  $\text{Cr}^{+++}$ , is present; a precipitate does appear, however, after the chromic ion is used up if peroxy sulfate ion is still present.

It was evident that much might be learned about the mechanism of the catalyzed Reaction 1 by measuring its rate and noting the effect of the concentrations of the substances upon it. Also, since the intermediate compound can be isolated, much may be learned by an investigation of its properties.

#### Analytical Method

To measure the rates, an accurate analytical method was necessary; and it was desirable that this method should be a volumetric one. The results of preliminary experiments showed that the catalyzed reaction could be effectively stopped by the addition of sufficient chloride ion to remove all the silver as chloride, and this made it unnecessary to place a time limit on the duration of the analysis. If a reducing agent could be found which would reduce either the peroxy sulfate or the dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) ion without affecting the other, and in addition would be one whose excess could be accurately determined, then the analytic problem would be solved; if no such reducing agent could be found, then one of the constituents might be removed by a suitable precipitant and the resulting precipitate analyzed. The results of many experiments showed that neither ferrous iron, potassium iodide nor oxalic acid could be used as the reducing agent, because the first two reacted too rapidly with both peroxy sulfate and dichromate ions to be of any value, and the last reacted too slowly with these ions. An analytic method based on the precipitation of barium or lead chromate and subsequent analysis of the precipitate, while accurate (though tedious) when chromate alone was present, was found to be quite inaccurate when peroxy sulfate ion was present, due to incomplete precipitation of barium chromate and lead chromate. It was finally found that under the proper conditions vanadyl sulfate,  $\text{VOSO}_4$ , would quantitatively reduce dichromate to chromic ( $\text{Cr}^{+++}$ ) ion without reducing the peroxy sulfate to sulfate ion. It was also found possible to titrate the excess of vanadyl salt with standard permanganate solution in the presence of peroxy sulfate and chromic ions.

The experiments on the vanadyl sulfate method indicated that three conditions must be maintained if it is to yield accurate results: (1) sufficient time must be allowed for the reaction to go to completion; (2) the

concentration of vanadyl sulfate must not be allowed to become too low; (3) the concentration of chromic ion must be low enough so that the green color does not obscure the end-point. Five minutes was found to be sufficient time if the concentration of vanadyl sulfate was not much less than 0.02 *N*. A correction, which depends on the concentration of chromic ion, must be made for the end-point; this correction, which is constant for a given concentration of chromic ion, varies from 0.00 to 0.10 cc. of 0.1 *N* potassium permanganate solution when the concentration of chromic ion varies from 0.0 *M* to 0.03 *M*. This method obviously restricts the concentration of chromium that may be used in the rate experiments.

The following procedure was found to be the most satisfactory.

A definite volume of the reaction mixture was pipetted into 10 or 25 cc. of standard vanadyl sulfate solution, which contained a few drops of 6 *N* hydrochloric acid. After five minutes the resulting mixture was diluted to 100 cc.; 5 cc. of 6 *N* sulfuric acid was added, and the excess of vanadyl sulfate was titrated with standard potassium permanganate solution. The vanadyl sulfate solution was about 0.1 *N*. The permanganate solution was also about 0.1 *N* and was standardized against sodium oxalate from the Bureau of Standards.

A series of ten experiments was made to determine the accuracy of this method, using a mixture consisting of 10 cc. of potassium dichromate solution, precipitated silver chloride, and arbitrary amounts of 0.1 *M* potassium peroxysulfate solution. The potassium chromate solution was standardized iodimetrically against thiosulfate solution by the method of Bray and Miller,<sup>10</sup> the thiosulfate having been previously standardized iodimetrically against the permanganate.

The method was found to give fairly accurate results; the maximum deviation from the mean (omitting one experiment) was 0.3%, and the average deviation of the separate values from the mean was only 0.2%.

#### Preparation of the Solutions

Stock solutions of the substances required were prepared and standardized as follows.

**Potassium Persulfate.**—The pure salt was dissolved in redistilled water. The solution was standardized by determining with permanganate how much ferrous iron was oxidized by a definite volume.

**Chromic Sulfate.**—Kahlbaum's potassium chrome alum was dissolved in redistilled water. A definite volume was treated with sodium peroxide, boiled and the resulting chromate determined iodimetrically.

**Silver Sulfate.**—The pure salt was dissolved in redistilled water. A definite volume of the solution was analyzed for silver by weighing the silver chloride precipitated from it with hydrochloric acid.

**Silver Perchlorate.**—Silver carbonate was first prepared by mixing solutions of silver nitrate and sodium carbonate. The precipitated silver carbonate was washed by decantation and then dissolved in a small excess of perchloric acid. The resulting solution after being filtered was diluted to the desired volume with redistilled water. The stock solution was standardized gravimetrically.

<sup>10</sup> Bray and Miller, *THIS JOURNAL*, 46, 2204 (1924).

**Acids.**—*N* sulfuric and perchloric acids were prepared by diluting the concentrated acids to the proper volume. These solutions were not accurately standardized.

### Description of the Reaction-Rate Experiments

Preliminary experiments established the fact that the rate of the reaction between peroxysulfate and chromic ion when catalyzed by silver ion is slow enough at ordinary temperatures to be measured with fair accuracy if the solutions of peroxysulfate and silver ions are sufficiently dilute. The initial concentrations of peroxysulfate ions used varied from approximately 0.06 *M* to 0.015 *M*; the silver ion concentrations varied from approximately 0.02 *M* to 0.006 *M*. In order to prevent the precipitation of the very slightly soluble silver chromate, enough perchloric or sulfuric acid was added to make the initial hydrogen-ion concentration 0.1 to 0.2 *N*. All measurements were made at 25°.

The reacting mixtures were prepared by mixing definite volumes of the stock solutions and water by means of pipets, the silver being added last, and the time counted from the moment of its addition. The reacting mixtures, in 500cc. Florence flasks, were placed in a thermostat, the temperature of which was maintained at 25°. The amount of peroxysulfate ion used up was calculated from the amount of dichromate ion formed during the reaction, the latter being determined by analysis. The amount used up was subtracted from the initial concentration to obtain the concentration at any given time.

### The Experimental Data

The results of the experiments are shown in Table I. In the first column is given the time elapsed in minutes, and in the second the corresponding concentration, in moles per liter of solution of the still undecomposed peroxysulfate ion. In the third column are given the values of a certain constant whose significance will be explained later. The initial concentrations are given at the head of each table. Expts. A and B were made at 35°.

TABLE I  
EXPERIMENTAL DATA OF THE REACTION-RATE EXPERIMENTS

EXPT. 1			EXPT. 2		
$\text{S}_2\text{O}_8^{2-} = 0.0642 \text{ M}; \text{Ag}_2\text{SO}_4 = 0.01007 \text{ N}$			$\text{S}_2\text{O}_8^{2-} = 0.0642 \text{ M}; \text{Ag}_2\text{SO}_4 = 0.01007 \text{ N}$		
$\text{Cr}^{+++} = 0.0218 \text{ M}; \text{H}_2\text{SO}_4 = 0.1968 \text{ N}$			$\text{Cr}^{+++} = 0.0109 \text{ M}; \text{H}_2\text{SO}_4 = 0.1968 \text{ N}$		
Time, min.	Concn.	Constant	Time, min.	Concn.	Constant
0	0.0642	...	0	0.0642	...
14	.0607	0.398	15	.0608	0.360
43	.0558	.324	30	.0579	.342
69	.0516	.314	50	.0546	.322
109	.0453	.313	66	.0519	.320
135	.0425	.303	87	.0486	.318
163	.0390	.304			
194	.0359	.297			
222	.0330	.298			

TABLE I (Continued)

EXPT. 3			EXPT. 4		
$\text{SeO}_3^{2-} = 0.0321 \text{ } M$ ; $\text{Ag}_2\text{SO}_4 = 0.01007 \text{ } N$			$\text{SeO}_3^{2-} = 0.0642 \text{ } M$ ; $\text{Ag}_2\text{SO}_4 = 0.00503 \text{ } N$		
$\text{Cr}^{+++} = 0.0218 \text{ } M$ ; $\text{H}_2\text{SO}_4 = 0.1968 \text{ } N$			$\text{Cr}^{+++} = 0.0218 \text{ } M$ ; $\text{H}_2\text{SO}_4 = 0.1968 \text{ } N$		
Time, min.	Concn.	Constant	Time, min.	Concn.	Constant
0	0.321	...	0	0.0642	...
22	.0296	0.366	25	.0616	0.328
44	.0276	.341	52	.0592	.310
67	.0252	.359	84	.0563	.311
97	.0230	.341	117	.0535	.310
127	.0210	.332	175	.0498	.289
157	.0192	.325	235	.0449	.302
191	.0175	.316			
217	.0165	.305			

EXPT. 5			EXPT. 6		
$\text{SeO}_3^{2-} = 0.0321 \text{ } M$ ; $\text{Ag}_2\text{SO}_4 = 0.02014 \text{ } N$			$\text{SeO}_3^{2-} = 0.0311 \text{ } M$ ; $\text{AgClO}_4 = 0.01178 \text{ } N$		
$\text{Cr}^{+++} = 0.0218 \text{ } M$ ; $\text{H}_2\text{SO}_4 = 0.1968 \text{ } N$			$\text{Cr}^{+++} = 0.01 \text{ } M$ ; $\text{HClO}_4 = 0.10 \text{ } N$		
Time, min.	Concn.	Constant	Time, min.	Concn.	Constant
0	0.0321	...	0	0.0311	...
18	.0278	0.391	15	.0293	0.337
37	.0248	.347	30	.0276	.338
67	.0204	.335	50.5	.0254	.340
99	.0170	.319	71	.0232	.351
132	.0139	.314	101	.0206	.346
169	.0112	.309	125	.0188	.342
209	.0084	.215			

EXPT. 7			EXPT. 8		
$\text{SeO}_3^{2-} = 0.01556 \text{ } M$ ; $\text{AgClO}_4 = 0.00589 \text{ } N$			$\text{SeO}_3^{2-} = 0.01556 \text{ } M$ ; $\text{AgClO}_4 = 0.01178 \text{ } N$		
$\text{Cr}^{+++} = 0.01 \text{ } M$ ; $\text{HClO}_4 = 0.10 \text{ } N$			$\text{Cr}^{+++} = 0.01 \text{ } M$ ; $\text{HClO}_4 = 0.10 \text{ } N$		
Time, min.	Concn.	Constant	Time, min.	Concn.	Constant
0	0.01556	...	0	0.01556	...
59	.0141	0.284	22	.0143	0.326
110	.0127	.314	44	.0131	.332
170	.0111	.337	75	.0114	.352
275	.0086	.366	106	.0101	.346
			144	.0087	.343
			193	.0071	.345
			273	.00512	.346

EXPT. 9			EXPT. 10		
$\text{SeO}_3^{2-} = 0.0311 \text{ } M$ ; $\text{AgClO}_4 = 0.01178 \text{ } N$			$\text{SeO}_3^{2-} = 0.0311 \text{ } M$ ; $\text{AgClO}_4 = 0.00589 \text{ } N$		
$\text{Cr}^{+++} = 0.02 \text{ } M$ ; $\text{HClO}_4 = 0.1 \text{ } N$			$\text{Cr}^{+++} = 0.01 \text{ } M$ ; $\text{HClO}_4 = 0.1 \text{ } N$		
Time, min.	Concn.	Constant	Time, min.	Concn.	Constant
0	0.0311	...	0	0.0311	...
14	.0294	0.341	13	.0305	0.254
29	.0277	.339	27	.0296	.311
50	.0254	.344	42.5	.0286	.335
70	.0234	.345	57.5	.0278	.331
100	.0208	.342	77.5	.0267	.334
124	.0190	.337	97	.0256	.341
168	.0166	.317	124	.0241	.349
			215	.0201	.345



TABLE I (Concluded)

EXPT. 11			EXPT. 12		
$\text{S}_2\text{O}_8^{2-} = 0.01556 \text{ M}; \text{AgClO}_4 = 0.01178 \text{ N}$			$\text{S}_2\text{O}_8^{2-} = 0.0311 \text{ M}; \text{Ag}^+ = 0.01178 \text{ N}$		
$\text{Cr}^{+++} = 0.01 \text{ M}; \text{HClO}_4 = 0.2 \text{ N}$			$\text{Cr}^{+++} = 0.01 \text{ M}; \text{H}_2\text{SO}_4 = 0.1 \text{ N}$		
Time, min.	Concn.	Constant	Time, min.	Concn.	Constant
0	0.01556	...	0	0.0311	...
22	.0146	0.246	23	.0287	0.296
44	.0133	.303	43	.0265	.316
75	.0118	.313	62	.0247	.315
106	.0105	.315	83	.0227	.322
144	.0092	.310	112	.0206	.312
193	.0076	.315			
279	.0058	.300			

EXPT. A (AT 35°)			EXPT. B (AT 35°)		
$\text{S}_2\text{O}_8^{2-} = 0.01115 \text{ M}; \text{AgClO}_4 = 0.00589 \text{ N}$			$\text{S}_2\text{O}_8^{2-} = 0.01115 \text{ M}; \text{AgClO}_4 = 0.01178 \text{ N}$		
$\text{Cr}^{+++} = 0.01 \text{ M}; \text{HClO}_4 = 0.10 \text{ N}$			$\text{Cr}^{+++} = 0.01 \text{ M}; \text{HClO}_4 = 0.1 \text{ N}$		
Time, min.	Concn.	Constant	Time, min.	Concn.	Constant
0	0.01115	...	0	0.01115	...
18	.0103	0.748	18	.0097	0.657
35	.0096	.726	35	.0082	.746
59	.0084	.815	59	.0064	.799
81	.0076	.804	81	.0052	.800
111	.0066	.802	110	.0040	.791
155	.0054	.794	156	.0028	.752
202	.0044	.782	203	.0019	.740
248	.0036	.774	248	.0014	.710

### Interpretation of the Mechanism of the Reaction

The effect of the concentration of chromic ion on the rate is easily settled. In Expts. 6 and 9 the initial concentrations of peroxy sulfate

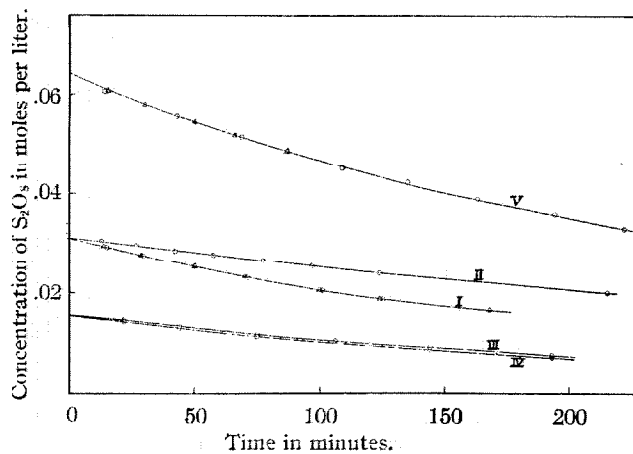


Fig. 1.

and silver ions were the same, while the concentration of chromic ion in Expt. 9 was double that in 6. However, when the results were plotted, the points for both experiments were found to lie on the same curve, as

may be seen by referring to Curve I, Fig. 1. Curve V represents the results for two other similar experiments, Nos. 1 and 2. From this it follows that the rate of the reaction (see Equation 1, above) when catalyzed by silver ion is independent of the concentration of chromic ion.

By varying only the initial concentration of peroxysulfate ion the manner in which it affects the reaction rate was determined. The initial concentration of peroxysulfate ion in Expt. 6 was double that in 8, while the time elapsed after a certain fraction had been used up was found to be nearly the same for both. Thus after one-third of the initial amount of peroxysulfate ion had been used up in both cases, the time elapsed was 100 minutes in Expt. 6 and 100 minutes in Expt. 8. Similar calculations established this relationship as general. It is, therefore, concluded that the reaction rate when catalyzed by silver ion is of the first order with respect to peroxysulfate ion.

Finally, by varying only the initial silver ion concentrations it was found that the reaction rate is directly proportional to the concentration of silver ion. In Curves I and II are plotted the results of Expts. 9 and 10. Initially, these experiments differed only in the concentrations of silver ion, which were in the ratio of 1:2. By drawing lines parallel to the time axis and comparing for any one line the times corresponding to the intersections with the curves, it may be readily established that the ratio of these times is very nearly 1:2. Similar calculations for other similar experiments established this relation as being general.

Expts. 8 and 11 differed only in the initial hydrogen-ion concentration, that in 11 being double that in 8. The effect of hydrogen ion was small, as may be seen by consulting Curves III and IV. The only effect seems to be that of changing the activity coefficients of the peroxysulfate and silver ions.

In view of the above facts, the differential equation representing the change in concentration of peroxysulfate ion with time when the reaction

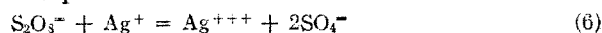


is catalyzed by silver ion and allowed to take place at 25°, may be written as

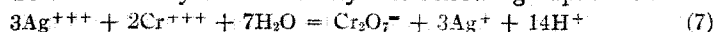
$$\frac{-d(S_2O_8^{2-})}{dt} = k (S_2O_8^{2-})(Ag^+) \quad (5)$$

The values calculated for  $k$  are given in Col. 3 of the tables. The average of the values obtained in 0.1 *N* perchloric acid solution was found to be  $k = 0.333$  at 25°. The average value at 35° was found to be  $k = 0.765$ . From these two values the temperature coefficient was found to be 2.30. The unit of time is the minute and the concentrations are expressed in moles per liter of solution.

This differential equation indicates that a possible mechanism of the reaction whose rate it represents is



This would be a slow reaction—the one whose rate is actually measured, and would be immediately succeeded by the following rapid reaction.



Evidently, the assumption is here made that the trivalent silver ion,  $\text{Ag}^{+++}$ , is the intermediate compound on whose formation the reaction depends. That the oxide of trivalent silver is formed by the electrolytic oxidation of solutions of silver salts has been fairly well established by Luther and Pokorny.<sup>11</sup> It has not been heretofore supposed, however, that trivalent silver was formed during the reaction between solutions of peroxysulfates and silver salts.<sup>12</sup> The further evidence that supports the conclusion that trivalent silver is formed during this reaction will now be presented.

#### The Chemical Properties of the Intermediate Compound Separated as a Black Precipitate

When solutions of peroxysulfuric acid and a silver salt are mixed, no reducing agent being present, there results, as is already known, a black precipitate. This is presumably closely related to the intermediate compound involved in the catalysis of the oxidation reactions. A number of qualitative experiments on the freshly prepared black precipitate established the following facts.

- a. During its precipitation the resulting solution increases in acidity.
- b. The precipitate is fairly soluble in 18 *N* sulfuric acid, 16 *N* nitric acid and 9 *N* perchloric acid, giving a deep brown color. The solubility increases rapidly with the concentration of acid; thus about 0.5 g. dissolves in 100 cc. of 6 *N* nitric acid and about 10 g. dissolves in 100 cc. of 16 *N* nitric acid, these quantities being rough estimates. Neither dil. nor concd. hydrofluoric or orthophosphoric acid has an appreciable solvent action on the substance. When a solution of it in concentrated nitric, sulfuric or perchloric acid is diluted with water, the substance is reprecipitated.
- c. The acid solutions of the substance give no test for hydrogen peroxide with titanium sulfate solution.
- d. The substance suspended in a dilute acid solution rapidly oxidizes iodide, chloride and bromide ions to iodine, chlorine and bromine, and iodide ion is further oxidized readily to iodate. It also rapidly oxidizes chromic to dichromate ion and ammonia to nitrogen. Manganous ion is oxidized to both manganese dioxide and permanganate ion. Ferrous iron is immediately oxidized to ferric iron in acid solution. In all these reactions the silver compound is reduced to silver ion, and no evolution of

<sup>11</sup> Luther and Pokorny, *Z. anorg. Chem.*, **57**, 290 (1908).

<sup>12</sup> In a recent paper by F. Jirsa, *Chem. Listy*, **19**, 3-9 (1925), the oxide  $\text{Ag}_2\text{O}_3$  is described as resulting from the energetic oxidation of metallic silver or of silver salts. Only the abstract, *C. A.*, **19**, 2480 (1925) is available, and it appeared since the present paper was written.

oxygen was noted in any case. It reacts rapidly with hydrogen peroxide with the evolution of oxygen.

*e.* The solid substance is decomposed into silver ion and oxygen when heated or allowed to stand in contact with acid solutions, the decomposition being apparently accelerated as the strength of the acid increases.

Experiments on the black precipitate after it had been dried for some time over calcium chloride in a desiccator yielded the following results.

*f.* Chromic, ferrous and chloride ions in acid solution are oxidized to dichromate and ferric ions and chlorine with the simultaneous evolution of oxygen. The reactions were not so rapid as with the freshly prepared material.

*g.* Experiments on solutions of silver sulfate showed that in acid solution silver ion does not give a precipitate with hydrogen peroxide, nor with  $\text{H}_2\text{SO}_5$  (prepared by hydrolysis of potassium peroxysulfuric acid with concd. sulfuric acid).

If the black precipitate is the final state of the intermediate compound when no reducing agent is present, then the experimental results just given show that it is a strong and rapid enough oxidizing agent to fulfil the conditions imposed upon it by Equation 4. The fact that no test for hydrogen peroxide is obtained, even after treatment with strong acids, shows conclusively that the substance is not a peroxide nor the salt of a peroxy acid. This conclusion combined with the fact that the substance is soluble in strong acids but not in weak acids indicates that it is an oxide or hydroxide of a weakly basic character. In its properties it resembles auric, thallic and cobaltic oxides.

#### Analysis of the Black Precipitate

A complete and accurate analysis of the black precipitate was made by Austin<sup>13</sup> who, making certain assumptions, concluded that it was a mixture of silver peroxysulfate and silver peroxide,  $\text{Ag}_2\text{O}_2$ . A study of Austin's results showed that they could be interpreted in other ways, and so it seemed desirable to repeat the analysis with some of the material which had been prepared in a different manner than that used by him. The method of preparation consisted in reprecipitating the freshly prepared black precipitate thrice from concd. nitric acid (see Expt. *b*) with thorough washing after each precipitation. The end product after being dried over calcium chloride in a desiccator showed on analysis 77.65% of silver, 11.5% of oxygen, 8.50% of sulfate and 2.9% of water. These analytical results correspond to the empirical formula  $\text{AgO}_{1.00}(\text{SO}_4)_{0.12}(\text{H}_2\text{O})_{0.22}$ . In spite of the striking equality of the numbers of silver and oxygen atoms, the formula does not show that the substance is essentially  $\text{Ag}_2\text{O}_2$ , since 0.12 or 0.24 atom of silver must be combined with the sulfate if the impurity is silver peroxysulfate or sulfate.

<sup>13</sup> Austin, *J. Chem. Soc. Trans.*, 99, 232 (1911).

Austin's attempts to determine the oxidizing power of the dried material by iodimetry did not lead to uniform results. The results of the experiment *e* described above furnish an explanation for this behavior, since it shows that oxygen is evolved during the oxidation of iodide ion to iodine. This difficulty is not encountered when the freshly prepared material is used in determining its oxidizing power, as shown by the following experiments.

A mixture of 10 cc. of 0.1 *M* potassium peroxysulfate solution and 10 cc. of silver sulfate solution (yielding 0.07579 g. of silver chloride) was allowed to stand for 20 to 35 minutes, the resulting mixture was filtered through asbestos in a perforated crucible, and the black precipitate was washed thoroughly and rapidly with water. The flask containing the filtrate was then replaced by an empty one, and 25 cc. of standard ferrous sulfate solution was poured through the filter followed by 50 cc. of water. This second filtrate was titrated with 0.1008 *N* potassium permanganate solution, and the first filtrate containing the excess of potassium peroxysulfate and silver sulfate was analyzed for silver. No silver was found on the filter after the treatment with ferrous sulfate; 25 cc. of the ferrous sulfate solution required 17.20 cc. of the potassium permanganate solution. Two experiments were made with the following results.

	Expt. 1	Expt. 2
KMnO <sub>4</sub> required for FeSO <sub>4</sub> in second filtrate, cc. ....	15.03	14.80
AgCl yielded by first filtrate, g. ....	0.0601	0.0572
Silver in black precipitate, milliequivalents. ....	.109	.130
FeSO <sub>4</sub> used up, milliequivalents. ....	.219	.242
Ratio of FeSO <sub>4</sub> oxidized to Ag in precipitate. ....	2.01	1.86

These results show that there are two oxidizing equivalents for each equivalent of silver in the black precipitate.

Experiments were also made on the number of oxidizing equivalents lost by the potassium peroxysulfate solutions for each equivalent of silver precipitated. Ten cc. of potassium peroxysulfate solution and 10 cc. of silver sulfate solution (yielding 0.7579 g. of silver chloride) were mixed and the mixture was allowed to stand for 20 to 35 minutes, then filtered through asbestos into a flask containing 25 cc. of standard ferrous sulfate solution, and the precipitate washed with 50 cc. of water, the washings also going into the ferrous sulfate solution; the filtrate was heated to 70° and titrated with 0.1008 *N* permanganate. The titrated mixture was analyzed for silver gravimetrically; 25 cc. of the ferrous sulfate solution

	Expt. 3	Expt. 4	Expt. 5
KMnO <sub>4</sub> used for filtrate, cc. ....	1.12	1.92	2.35
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> used, milliequivalents. ....	0.188	0.268	0.312
AgCl yielded by titrated mixture, g. ....	.0626	.05689	.0537
Silver precipitated, milliequivalents. ....	.0918	.132	.154
Ratio of S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> reduced to silver precipitated. ....	2.95	2.03	2.02

required 18.85 cc. of the potassium permanganate solution; 10 cc. of the potassium peroxysulfate solution required 19.60 cc. of potassium permanganate solution. Three experiments were made with the preceding results.

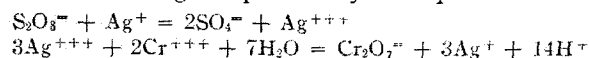
It is evident from these results that for every equivalent of silver that is precipitated as the black substance, two oxidation equivalents of potassium peroxysulfate are used up.

These two series of oxidation experiments clearly show that the substance is an oxide or basic sulfate of trivalent silver, that is,  $\text{Ag}_2\text{O}_3$  or  $\text{Ag}_2\text{O}_3 \cdot x\text{Ag}_2(\text{SO}_4)_3$ . The small proportion of sulfate found in the preparation purified by precipitation from nitric acid upon dilution indicates that the sulfate, though firmly retained, is not an essential constituent of the substance.

Finally, since the precipitated compound is an oxide of trivalent silver, and since the rate of the reaction between peroxysulfate and chromic ions when catalyzed by silver ion was found to be proportional to the first power of the concentration of the latter as well as to that of the peroxysulfate ion, we are justified in concluding that its mechanism is that previously suggested, which was expressed by Equations 6 and 7, above.

### Summary

The rate of the reaction between peroxysulfuric acid and chromic sulfate when catalyzed by silver salts has been measured at  $25^\circ$  and  $35^\circ$  and found to be proportional to the first power of the concentration of peroxysulfate ion and of silver ion, but to be independent of the concentration of chromic ion and not greatly affected by that of hydrogen ion. These facts indicate that silver ion acts as a carrier catalyst through the formation of a trivalent silver salt as the intermediate compound, and that the reaction takes place in the two stages expressed by the equations



The first of these must occur slowly and determine the rate of the reaction as a whole, while the second must take place very rapidly.

This conclusion was confirmed by an extended study of the black precipitate formed when potassium peroxysulfate and a silver salt are mixed; for this substance is presumably an hydrolysis product of the intermediate compound which in acid solution catalyzes the peroxysulfate reaction. Determinations of the ratio of its oxidizing power to the silver contained in it, and of the ratio of the equivalents of peroxysulfate destroyed per equivalent of silver precipitated as the black compound, showed that it was an oxide of trivalent silver ( $\text{Ag}_2\text{O}_3$ ) containing basic sulfate (presumably also of trivalent silver).

Of especial interest is the proof that trivalent silver is capable of existence in the form of this solid oxide and in the form of a salt in strongly

acid solutions. The properties of the mixtures resulting from suspending (or dissolving) the black precipitate in water, concentrated sulfuric, nitric or perchloric acid were studied in a qualitative way. The solution was found to be one of the most active and powerful oxidizing agents known. Thus it rapidly oxidizes chlorides with liberation of chlorine; chromic salt to chromate; manganous salt to permanganate and manganese dioxide, and ammonia to nitrogen. The substance is not a peroxide of the hydrogen peroxide type, since the solution gives no color with titanium salt; it resembles rather the oxides of trivalent cobalt, thallium and gold.

Representative values of the rate constants are 0.333 at 25° and 0.765 at 35°, the unit of time being the minute and concentrations being expressed in moles per liter of solution. From these values the temperature coefficient of the reaction is found to be 2.30.

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## THE CATALYTIC EFFECT OF SILVER AMMONIA ION IN THE OXIDATION OF AMMONIA BY PEROXYSULFATES

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### Introduction

In a former paper<sup>2</sup> there were presented the results of an investigation on the rate of the oxidation of chromic salts by peroxysulfuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ), under the influence of silver ion acting as catalyst. The results showed that the rate of the catalyzed reaction is directly proportional to the concentrations both of peroxysulfate ion and silver ion, but independent of the concentration of chromic and hydrogen ions. These facts clearly

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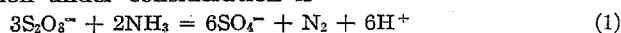
<sup>2</sup> Yost, *THIS JOURNAL*, **48**, 152 (1926).



indicated that the slow measurable reaction is that between peroxysulfate ion and silver ion, giving rise to an active intermediate compound. It was also shown that the intermediate compound is a salt of trivalent silver. It seems probable that essentially the same mechanism applies to all oxidation reactions involving peroxysulfates which require silver salts to catalyze them. Marshall<sup>3</sup> found that peroxysulfates oxidize ammonia to nitrogen in the presence of silver salts. He made only one rough quantitative experiment on the rate of the reaction, the results of which indicated that it was directly proportional to the concentration of peroxysulfate.

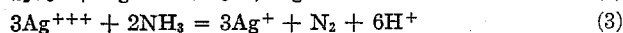
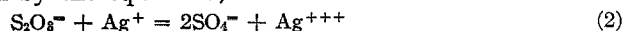
In the present paper the results of an investigation of the ammonia reaction are presented together with a comparison of them with those obtained with the chromium reaction.

The main reaction under consideration is



There is no tendency for the reverse reaction to take place, namely, for the nitrogen to react with sulfuric acid to give peroxysulfates and ammonia. The reaction as written no doubt takes place with a large decrease in free energy. Notwithstanding this, the reaction is a very slow one unless some catalyst is present. Such cases are by no means rare, the example of hydrogen and oxygen at ordinary temperatures having become classical for reactions involving the same conditions.

This oxidation in the presence of silver ion, like that of trivalent chromium, doubtless takes place in two stages, the univalent silver being first oxidized to trivalent silver by the peroxysulfate, and the trivalent silver being then reduced to univalent silver by the ammonia. This mechanism might be indicated by the equations,



The situation is, however, complicated by the fact that the silver ion exists almost wholly in the form of ammonia complexes. Thus it is well established<sup>4</sup> that the principal ion present in an ammoniacal solution of a silver salt is  $\text{Ag}(\text{NH}_3)_2^+$ , or a hydrated form of it. The fact that  $\text{Ag}(\text{NH}_3)_2\text{Cl}$  exists as a solid phase<sup>5</sup> indicates the probable presence also of  $\text{Ag}(\text{NH}_3)_2^+$ , at any rate in small amounts. Other ions of a still more complex nature may also be present, though probably in very small proportion. Now the nature of the groups attached to the silver may well have a marked effect on the rate with which the ion reacts with peroxysulfate ion. The results of the present work, compared with those obtained in the previous research, make possible a study of these unique effects.

I wish to acknowledge my appreciation of the advice and criticisms

<sup>3</sup> Marshall, *Proc. Roy. Soc. Edinburgh*, 23, 163 (1900).

<sup>4</sup> Bodländer and Fittig, *Z. physik. Chem.*, 39, 597 (1902).

<sup>5</sup> Isambert, *Compt. rend.*, 66, 1259 (1868).

given by Professor A. A. Noyes. Financial assistance was received from a grant made to him by the Carnegie Institution of Washington.

#### Method of Analysis

A simple and accurate volumetric method of analysis was adopted. The reaction mixture consisted of peroxy sulfate ion, ammonia, silver ammonia ion and potassium hydroxide. When this mixture is acidified, the silver ammonia complex is destroyed and the resulting silver ion may be precipitated by the addition of chloride ion, the reaction being effectively stopped by this procedure. The remaining peroxy sulfate may then be quantitatively reduced to sulfate by ferrous iron. These facts were made the basis of the analytical method adopted, which was as follows. A 25cc. sample of the reaction mixture was withdrawn with a pipet and run into 10 cc. of standard ferrous sulfate solution which contained a few drops of 6 *N* hydrochloric acid and was 1 *N* in sulfuric acid. The resulting mixture was heated to 60°, and after the addition of 50 cc. of water the excess of ferrous iron was titrated with standard permanganate solution. The permanganate was about 0.1 *N* and was standardized against sodium oxalate from the Bureau of Standards.

This method is known to give accurate and uniform results. It is evident that it makes possible the calculation of the concentration of peroxy sulfate in any solution.

#### Preparation of the Solutions

**Potassium Peroxy sulfate and Ammonium Peroxy sulfate.**—The c. p. salts were dissolved in redistilled water and made up to a strength of about 0.1 *M*. The solutions were standardized by means of ferrous iron and permanganate.

**Silver Perchlorate.**—Freshly precipitated silver carbonate was thoroughly washed with water and dissolved in a slight excess of 1 *N* perchloric acid. After filtration, the resulting solution was diluted with redistilled water. The solution was standardized gravimetrically.

**Ammonia.**—The concentrated solutions were diluted with redistilled water. The stock solutions were standardized by adding a definite volume to a known excess of standard hydrochloric acid and titrating the excess with sodium hydroxide, using methyl red as an indicator.

**Potassium Hydroxide.**—The c. p. sticks were dissolved in redistilled water, and the resulting solution was filtered and diluted to the desired strength.

#### Description of the Rate Measurements

A few preliminary experiments established the fact that the catalyzed ammonia reaction was more rapid than the chromium reaction. For this reason it was necessary to use lower concentrations of peroxy sulfate ion than for the latter reaction. With the concentrations used, the reaction was practically complete after a period of two hours.

All the measurements were made at 25°.

The stock solutions and water were mixed by means of pipets. The

silver perchlorate solution was added last, and the time was counted from the moment of its addition. The peroxysulfate, ammonia and potassium hydroxide solutions were first mixed in a 500cc. Florence flask, and this was then placed in the thermostat. After allowing sufficient time for the mixture to come to the temperature, the silver solution was added from the stock solution, which was kept in the thermostat.

### Results of the Reaction Rate Measurements

In Table I are given the detailed results of two experiments in which ammonium peroxysulfate was used. In the first column is given the time elapsed in minutes; in the second, the corresponding concentration of peroxysulfate, expressed in millimoles per liter of solution and in the third, the values of the reaction-rate constant calculated (with the concentrations expressed in molalities, not millimolalities) under the assumption that the rate is proportional to the concentrations of peroxysulfate and of total silver present, the significance of which will be discussed later.

TABLE I

#### RATE EXPERIMENTS WITH AMMONIUM PEROXYSULFATE

Initial millimolal concentrations					
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 13.8; NH <sub>3</sub> , 68.7; AgClO <sub>4</sub> , 5.9.			(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 13.8; NH <sub>3</sub> , 112.3; AgClO <sub>4</sub> , 5.9		
Time	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> concn.	Rate const.	Time	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> concn.	Rate const.
0	13.8	..	0	13.8	..
5.5	11.3	6.12	5	10.8	8.31
15.5	8.1	5.81	17	6.4	7.66
26	5.6	5.92	26	4.2	7.75
40	3.7	5.58	39.5	2.4	7.49
57	2.2	5.46	57.5	1.2	7.20
91	0.9	5.08	91	0.4	6.59
125	0.4	4.80	125	0.2	5.73

In Table II are given the detailed results of two typical experiments which were made using potassium peroxysulfate with potassium hydroxide added.

TABLE II

#### TYPICAL REACTION-RATE EXPERIMENTS WITH POTASSIUM PEROXYSULFATE

Initial millimolal concentrations					
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 9.0; NH <sub>3</sub> , 67.8; AgClO <sub>4</sub> , 5.0; KOH, 30.0			K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , 9.0; NH <sub>3</sub> , 33.9; AgClO <sub>4</sub> , 5.0; KOH, 30.0		
Time	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> concn.	Rate const.	Time	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> concn.	Rate const.
0	9.0	..	0	9.0	..
11	6.7	5.36	11	7.2	4.05
18	5.6	5.26	18	6.1	4.31
30	4.1	5.24	30	4.8	4.19
49	2.5	5.22	49	3.1	4.34
73	1.3	5.29	73	1.9	4.26
98	0.7	5.20	98	1.1	4.28
Mean 5.26			Mean 4.24		

In Table III are given the mean values of the rate constants for a number of experiments in which the initial concentrations of the separate substances were systematically varied.

TABLE III  
MEAN VALUES OF THE RATE CONSTANTS FOR EXPERIMENTS WITH VARIED INITIAL CONCENTRATIONS OF THE REACTING SUBSTANCES

K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Initial millimolal concentrations			Rate constant
	AgClO <sub>4</sub>	NH <sub>3</sub>	KOH	
9.0	5.0	32.6	30.0	4.18
9.0	5.0	33.9	30.0	4.24
9.0	5.0	58.6	30.0	4.86
9.0	5.0	65.2	30.0	5.01
9.0	5.0	67.8	30.0	5.26
9.0	5.0	117.4	30.0	6.34
9.0	5.0	130.4	30.0	6.45
9.0	5.0	234.8	30.0	8.89
8.6	5.0	38.3	90.4	3.41
8.1	5.0	76.6	90.4	4.30
8.1	5.0	153.1	90.4	5.84
9.0	5.0	58.6	30.0	4.86
9.0	10.0	58.6	30.0	4.47
8.6	5.0	38.3	17.0	5.0
8.6	5.0	38.3	34.0	4.45
8.6	5.0	38.3	51.9	4.01
8.6	5.0	38.3	90.4	3.41

#### The Primary Reaction Determining the Reaction Rate

In Table I are given the results of two experiments which differed only in the initial concentration of ammonia. It is evident from the results that the rate of the catalyzed reaction is not independent of the concentration of ammonia, but increases with it. Since its concentration during any one experiment will decrease not only by oxidation, but also by neutralization, owing to the acid formed by the reaction, this may well account for the steady decrease in the rate constants.

The effect of neutralization was obviated in the other experiments by adding to the solutions a moderate or large excess of potassium hydroxide. When this is done, the advantages of using potassium peroxysulfate instead of the ammonium salt are obvious. Therefore, of the experiments recorded in the tables only those in Table I were made with ammonium peroxysulfate.

By plotting the results of the experiments given in Table II and by taking tangents at corresponding points on the curves it was found that the rate of the second experiment was only about 20% greater than that of the first, although the initial concentration of ammonia was doubled. It is evident from this that the rate of the catalyzed reaction increased much less rapidly than proportional to the concentration of ammonia.

Since the effect of ammonia is not great, it was found possible to determine the effect of peroxysulfate ion and silver diammonia ion on the rate by the methods described in the former paper. The rate of the catalyzed reaction was thus found to be directly proportional to the concentration of peroxysulfate ion and to that of silver ammonia ion.

Potassium hydroxide was also found to have a definite effect on the rate. The rate was found to decrease as the hydroxide ion concentration increased, but not inversely proportional to it. Thus it was found that a two-fold increase in hydroxide ion decreased the rate about 15%. Since both hydroxide ion and ammonia are used up during the reaction, and since their effects are in opposite directions and approximately equal in magnitude, the following differential equation may be expected to express the rate in any one reaction mixture.

$$-d(S_2O_8^{2-})/dt = k(S_2O_8^{2-})(Ag(NH_3)_2^+) \quad (4)$$

The values of the rate-constants given in Table III were calculated from the integrated form of this equation, regarding the total peroxysulfate present as equivalent to  $(S_2O_8^{2-})$ , and the total silver present as equivalent to  $(Ag(NH_3)_2)^{++}$ . The constants show no marked trend, nor do they vary greatly from the average value.

#### The Effect of Ammonia on the Reaction Rate

The first two groups of experiments given in Table III were all made with the same initial concentration (0.030 or 0.090 *M*) of potassium hydroxide, but with different initial concentrations of ammonia. From the results it will be seen that an eight-fold increase in ammonia results in only a two-fold change in the value of the rate constant. By plotting the values of all the rate constants against the initial ammonia concentration minus twice the silver concentration, the two curves shown in Fig. 1 were obtained. The resulting graphs are seen to be straight lines.

Let us now take into consideration the effect that might result from the presence of the ion  $Ag(NH_3)_3^+$ . Considering that its rate of reaction with peroxysulfate ion may be different from that of silver diammonia ion, we may write the rate equation in the form

$$-d(S_2O_8^{2-})/dt = k_1(S_2O_8^{2-})(Ag(NH_3)_2^+) + k_2(S_2O_8^{2-})(Ag(NH_3)_3^+) \quad (5)$$

Since the reaction  $Ag(NH_3)_2^+ + NH_3 = Ag(NH_3)_3^+$  is doubtless practically an instantaneous one, we may assume that its equilibrium is established corresponding to the mass-action expression,

$$(Ag(NH_3)_3^+)/[(Ag(NH_3)_2^+)(NH_3)] = K \quad (6)$$

Combining (6) with (5) and simplifying, we have as the rate equation for reaction mixtures in which the initial concentration of hydroxide ion is the same,

$$-d(S_2O_8^{2-})/dt = (S_2O_8^{2-})(Ag(NH_3)_2^+) \{k_1 + k_2K(NH_3)\} \quad (7)$$

Since the concentration of ammonia in the experiments was high compared

with that of peroxy sulfate, the effect of the term  $k_2K(\text{NH}_3)$  must be practically constant for any one experiment, and the straight lines of Fig. 1 are in fact the graphs that would be obtained from the equation  $k = k_1 + k_2K(\text{NH}_3)$ , where  $k$  is the total rate constant which appears in Equation 4.

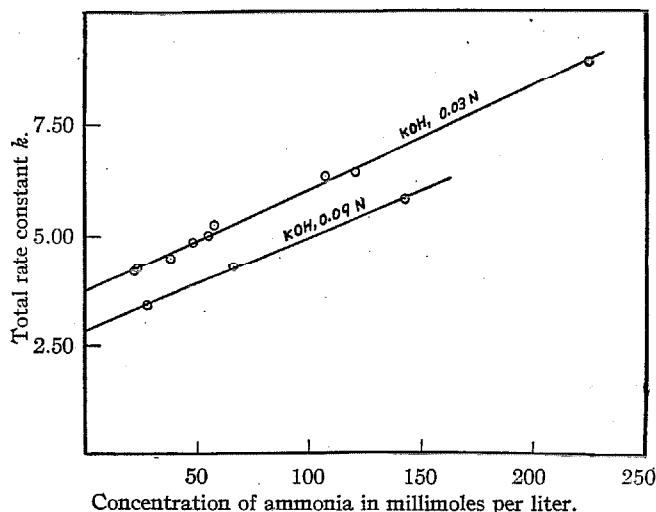


Fig. 1.

From a series of experiments, like those of Table III, there may be obtained a series of values of  $k$  and  $(\text{NH}_3)$ . The values of  $k_1$  and  $k_2K$  might then be found by solving the corresponding simultaneous equations; but it was considered simpler and more accurate to find the value of  $k_1$  by extrapolating the graph to zero ammonia concentration and then to calculate the value of  $k_2K$  from that of  $k$  for each experiment. The values of  $k_2K$  so found are given in Table IV for the first group of experiments (with the potassium hydroxide 0.03  $M$ ) recorded in Table III. The agreement of the  $k_2K$  values is satisfactory.

TABLE IV  
VALUES OF THE PARTIAL REACTION-RATE CONSTANTS

$k_1 = 3.70$			
Initial $\text{NH}_3$	$(2\text{NH}_3 - 2\text{Ag})$	$k$	$k_2K$
32.6	22.6	4.18	21.7
33.9	23.9	4.24	22.6
58.6	38.6	4.47	20.0
65.2	55.2	5.01	23.7
67.8	57.8	5.26	26.0
117.4	107.4	6.34	24.6
130.4	120.4	6.45	22.8
234.8	224.8	8.89	23.0
48.6	48.6	4.86	23.9

These results indicate that the first slow step in the catalyzed ammonia oxidation may consist in the two simultaneous reactions:  $S_2O_8^{2-} + Ag(NH_3)_2^+ = 2SO_4^{2-} + Ag^{+++} + 2NH_3$ ;  $S_2O_8^{2-} + Ag(NH_3)_3^+ = 2SO_4^{2-} + Ag^{+++} + 3NH_3$ ; and that these are followed by the rapid reaction  $3Ag^{+++} + 9NH_3 = 3Ag(NH_3)_2^+ + N_2 + 6H^+$ . Since  $K$  is small and  $k_2K$  large, it follows that the rate constant  $k_2$  of the second reaction is much larger than the rate constant  $k_1$  of the first reaction.

Others have previously considered that the total rate of oxidation may be the sum of two or more partial rates that refer to different compounds containing the oxidized or reduced element in different forms. Thus Mitchell<sup>6</sup> found that the results of his experiments on the rate of the reaction between phosphorous acid and iodine can be explained by assuming two isomeric forms of orthophosphorous acid, one of which reacts with  $I_2$  and the other with  $I_3^-$ , each reaction having a different rate; and it has been found by Spitalsky<sup>7</sup> that chromate ion and dichromate ion have different effects on the rate of decomposition of hydrogen peroxide, though the effect in mixtures is not very clear-cut. The simple example offered by the present research seems representative of this phenomenon.

At this point may be mentioned the reasons for rejecting certain other mechanisms that might at first sight seem possible. Such mechanisms might involve (1) a slow reaction between trivalent silver and ammonia, or (2) formation of a moderately stable complex of the type  $Ag(NH_3)_m^{+++}$ , which slowly decomposes with evolution of nitrogen and production of silver ion and hydrogen ion. These two possibilities are disposed of in turn by the following experimental facts. (1) Though trivalent silver oxide ( $Ag_2O_3$ ) is only very slightly soluble in neutral or alkaline solutions, yet no precipitate of it appears during the reaction. (2) When the freshly prepared oxide is mixed with solutions of ammonia, it decomposes with evolution of nitrogen, but seems to dissolve only to the extent to which it has decomposed. Evidently, if the reaction between  $Ag^{+++}$  and ammonia were slow,  $Ag^{+++}$  would accumulate and a precipitate of silver sesquioxide would form, since a complex  $Ag(NH_3)_m^{+++}$  does not form, as shown by the second of these facts.

#### The Effect of Hydroxide Ion on the Reaction Rate

The initial concentrations of ammonia were the same in the third group of experiments recorded in Table III, but that of potassium hydroxide was varied. The effect of the potassium hydroxide, while not great, is still much too great to be ascribed to the decreases in activity coefficients caused by it. When the rate constants are plotted against the initial concentration of potassium hydroxide, the resulting graph is not a straight

<sup>6</sup> Mitchell, *J. Chem. Soc.*, 123, 2241 (1923).

Spitalsky, *Z. anorg. Chem.*, 53, 184 (1907).

line, as may be seen from the curve in Fig. 2. The effect may be due to the fact that hydroxide ion unites with  $\text{Ag}(\text{NH}_3)_2^+$  to form the un-ionized base  $\text{Ag}(\text{NH}_3)_2\text{OH}$ , and that its rate of reaction with peroxysulfate ion is lower than that of  $\text{Ag}(\text{NH}_3)_2^+$  or  $\text{Ag}(\text{NH}_3)_3^+$ . This simple explanation cannot be regarded as complete, however, since rate Equation 5, when modified by the addition of a negative term  $-k_3K(\text{OH}^-)(\text{Ag}(\text{NH}_3)_3^+)(\text{S}_2\text{O}_8^{2-})$ , does not fit the experimental facts. It is possible, nevertheless, that this is because a decrease in the activity coefficient of peroxysulfate ion is superposed upon the effect of producing a less reactive substance. There is, however, no independent experimental evidence as to the degree of ionization of the silver ammonia hydroxide.

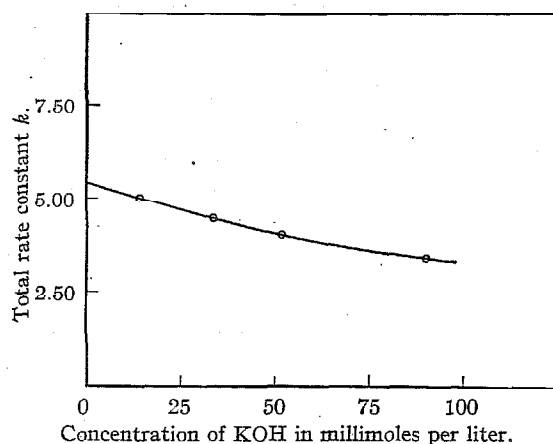


Fig. 2.

#### Comparison of the Rates of the Oxidation of Chromium and of Ammonia

It has been shown that the slow step in the silver salt catalysis of the chromium and ammonia oxidations consists in the oxidation of the univalent silver ion to trivalent silver. Since there seems to be no essential difference between a hydrated ion and an amminated one, it is natural to inquire whether the group present in the silver complex has an appreciable effect on the rate of oxidation of the silver which is the essential constituent of the ion from the oxidation viewpoint. The results described in this paper and the former one lead to the conclusion that the effect is a marked one. In the case of the simple hydrated silver ion, such as is present in the acid solution used for the chromium reaction, the rate constant was found to be 0.333, while in the case of the silver ammonia complex, the constant is more than ten times as large. Moreover, the increase in rate with the number of ammonias present in the complex, and its decrease on the addition of an hydroxide ion are further evidences that



the rate of reaction of complex ions containing a common oxidizable element depends considerably on the nature of the groups present.

#### Summary

The rate of the reaction between peroxysulfate ion and ammonia, when catalyzed by silver salts, has been measured and found to be directly proportional to the concentrations of peroxysulfate ion and silver ammonia ion. The rate was also found to increase with the concentration of ammonia, and decrease with that of hydroxide ion, but not to be directly proportional to the former, nor inversely proportional to the latter. To explain the effect of ammonia it was concluded that, inasmuch as silver triammonia chloride  $\text{Ag}(\text{NH}_3)_3\text{Cl}$  exists as a solid phase, the ion  $\text{Ag}(\text{NH}_3)_3^+$  probably exists in solution (though in small amounts) and that peroxysulfate ion  $\text{S}_2\text{O}_8$  reacts with it at a rate different from that with  $\text{Ag}(\text{NH}_3)_2^+$ . The experimental results were found to be in accord with this conclusion. It was also shown that the effect of ammonia could not be explained as due to a slow reaction between the trivalent silver ion and ammonia, since freshly prepared silver sesquioxide reacts rapidly with ammonia. It is suggested that the effect of hydroxide ion may be due in part to the formation of the un-ionized compound  $\text{Ag}(\text{NH}_3)_2\text{OH}$ , and that this reacts more slowly with peroxysulfate ion than does  $\text{Ag}(\text{NH}_3)_2^+$ , and in part to the decrease in the activation of peroxysulfate ion caused by it. According to these explanations the slow steps of the catalyzed reaction consist of three simultaneous reactions involving the oxidation by peroxysulfate ion of  $\text{Ag}(\text{NH}_3)_2^+$ , of  $\text{Ag}(\text{NH}_3)_3^+$ , and of  $\text{Ag}(\text{NH}_3)_2\text{OH}$ , to trivalent silver ion,  $\text{Ag}^{+++}$ ; and the rapid and final step is the reaction between trivalent silver and ammonia to produce nitrogen, silver ion and acid.

A comparison of the rates of the catalyzed chromium and ammonia reactions showed that silver when present in the form of silver ammonia reacts more than ten times as fast with peroxysulfate ion as it does when present as hydrated silver ion. This fact shows that the rates of reactions involving various compounds of a reacting element may depend to a large extent on the nature of the groups attached to the element.

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## THE KINETICS OF THE OXIDATION OF TRIVALENT TITANIUM BY IODINE

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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,<sup>1</sup> 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,  $\text{HBrO}_3 + \text{HI} = \text{HIO} + \text{HBrO}_2$ , followed by  $\text{HIO} + \text{HI} = \text{I}_2 + \text{H}_2\text{O}$ .

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,<sup>2</sup> it consists in the formation of an addition product whose charge is the algebraic sum of the two reacting ions); the reaction  $\text{Fe}^{+++} + \text{I}^- = \text{Fe}^{++} + \frac{1}{2}\text{I}_2$  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,  $\text{I}_2 + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} = 2\text{HI} + \text{H}_3\text{AsO}_4$ , has been shown by Roebuck<sup>3</sup> to depend on the concentration of hypo-iodous acid which arises from the hydrolysis of iodine.<sup>4</sup> On the other hand, the reaction between phosphorous acid and iodine does not admit of

<sup>1</sup> Bray, *Z. physik. Chem.*, **54**, 463 (1906).

<sup>2</sup> Brönsted, *ibid.*, **102**, 169 (1922).

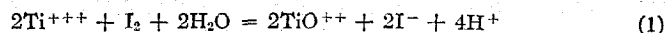
<sup>3</sup> Roebuck, *J. Phys. Chem.*, **6**, 365 (1902).

<sup>4</sup> Noyes, *Z. physik. Chem.*, **47**, 121 (1904).

a hypo-iodite mechanism but has been shown by Mitchell<sup>5</sup> 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,  $2\text{Fe}^{++} + \text{I}_2 = 2\text{Fe}^{+++} + 2\text{I}^-$  is the best example of this class, but it was not studied<sup>6</sup> 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



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

<sup>5</sup> Mitchell, *J. Chem. Soc.*, 117, 1322 (1920); 123, 2241 (1923).

<sup>6</sup> 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

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

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.<sup>7</sup> 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:

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

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

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

<sup>7</sup> 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

Expt.	(Ti <sup>+++</sup> )	Molal concentrations (H <sup>+</sup> )'	(H <sup>+</sup> )"	10 <sup>3</sup> <i>k</i> <sub>1</sub> '	10 <sup>3</sup> <i>k</i> <sub>1</sub> "
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

Expt.	Σ(I <sub>2</sub> )	Molal concentrations Σ(I <sup>-</sup> )	(Ti <sup>+++</sup> )	(H <sup>+</sup> )'	10 <sup>3</sup> <i>k</i> <sub>1</sub> '	10 <sup>3</sup> <i>k</i> <sub>2</sub>
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 <sup>a</sup>	.0112	.0617	.0101	.275	16.8	1.06
18 <sup>b</sup>	.0112	.263	.0101	.275	14.4	3.8

<sup>a</sup> KCl = 0.600 *N*.

<sup>b</sup> 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*<sub>1</sub>' and *k*<sub>1</sub>" 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*<sub>1</sub>' 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*<sub>1</sub>' and *k*<sub>2</sub>, so that one cannot decide whether the value of *q* is one or two. The values of *k*<sub>1</sub>' increase with a decrease in the concentration of I<sup>-</sup>, while the effect on *k*<sub>2</sub> is in the opposite direction. The results indicate that, in accordance with the theory proposed by Brönsted,<sup>2</sup> 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

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

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

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

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

$$-\frac{d(I_3^-)}{dt} = \frac{k_1' K_H}{K} (TiOH^{++})(I_2) \quad (8)$$

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,  $Ti(OH)^{++} = I_2 = Ti(OH)^{++} \cdot I_2$ . This would then be followed by the rapid reaction,  $TiOH^{++} \cdot I_2 + Ti(OH)^{++} = 2TiO^{++} + 2H^+ + 2I^-$ .

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

$Ti^{+++} + HIO = TiO^{++} + \frac{1}{2}I_2 + H^+$ , the rate equation would be  $-\frac{d(I_3^-)}{dt} = k(Ti^{+++})(HIO)$ . If now the mass-action expressions for the hydrolysis of iodine and the formation of  $I_3^-$  from  $I_2$  and  $I^-$  are substituted in this equation, it becomes  $-\frac{d(I_3^-)}{dt} = k_2 \frac{(Ti^{+++})(I_3^-)}{(H^+)(I^-)^2}$ . This equation differs

from equation (6), which actually expresses the rate, only in the exponent of  $(I^-)$ ; 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<sup>8</sup> found that the rate of the reaction,  $8Ti^{+++} + ClO_4^- + 4H_2O = 8TiO^{++} + Cl^- + 8H^+$ , 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

<sup>8</sup> Bredig and Michel, *Z. physik. Chem.*, **100**, 124 (1922).

$\text{TiClO}_4^{++}$  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  $\text{TiOH}^{++}$ . 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  $\text{Ti(OH)}^{++}$  and iodine of an addition product which in turn reacts rapidly with more  $\text{Ti(OH)}^{++}$  to give the final products of the reaction. A mechanism is also suggested which involves the existence of quinquivalent titanium.

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## Examination of Some Methods for the De- termination of Sul- fites and of Ferrous Iron<sup>1</sup>

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**D**URING the progress of some work in this laboratory it became necessary to determine accurately sulfurous acid in the presence of ferric and ferrous iron. This problem has proved a stubborn one, and has not yet reached a solution. However, it led to a careful consideration of the various volumetric methods available for determining sulfites and iron, with the discovery that, although the analysis of sulfites has received considerable attention, there is nowhere available a critical comparison of the various methods. Moreover, it was not possible, from the published data, to make such a comparison. The writers have therefore made the following examination of volumetric sulfite determinations, and have added to it a short discussion of two unusual reagents for ferrous iron.

### Sulfite Determinations

Since solutions of sulfites or of sulfurous acid are unstable, the procedure of Ferguson<sup>2</sup> was adopted, which consists in adding weighed quantities of a finely pulverized sample of the sulfite to the solutions containing the oxidizing agent.

In all cases a weighed sample of sodium sulfite was added to a known excess of oxidizing agent in an Erlenmeyer or glass-stoppered flask. After the reaction was complete, solid potassium iodide was dissolved therein and the whole allowed to stand for about 10 minutes. The liberated iodine was then titrated with 0.1 *N* thiosulfate. The strength of the known volume of oxidizing agent was determined in the same manner, being recorded in cubic centimeters of thiosulfate.

In making these comparisons the iodine method is assumed to give accurate results, and the merit of any other method is

<sup>1</sup> Received July 6, 1925.

<sup>2</sup> *J. Am. Chem. Soc.*, **39**, 372 (1917).

judged by its agreement with the iodine method. Bureau of Standards burets were used throughout.

#### Comparison of Oxidizing Agents

**STANDARD IODINE SOLUTION**—Twenty-five cubic centimeters of potassium triiodide solution were pipetted into a 250-cc. Erlenmeyer flask, and followed by 2 cc. of 6 *N* sulfuric acid and 50 cc. of water. To the resulting solution 0.1260 gram of sodium sulfite was added, this amount being used in all subsequent experiments. The contents of the flask were shaken until the salt was completely dissolved, and after 2 to 5 minutes the excess iodine was titrated with approximately 0.1 *N* thiosulfate. The average of seven titrations gave 18.80 cc.  $\pm$  0.05 as the thiosulfate corresponding to 0.1260 gram of sodium sulfite. The effect of acid on the titrations is very marked. Omitting the 2.0 cc. of 6 *N* sulfuric acid lowers the thiosulfate value from 18.80 to 18.65 cc.

In order to be certain that the assumption of accuracy for the iodine method is justifiable, the foregoing results were compared with a set of gravimetric determinations. 0.1260 gram of the same sodium sulfite was oxidized with the same potassium triiodide solution, and weighed as barium sulfate. The average of five determinations, after correcting for sulfate already present in the sulfite, was  $0.2135 \pm 0.0003$  gram barium sulfate, corresponding to 0.0586 gram sulfur dioxide in 0.1260 gram sodium sulfite. The weight of sulfur dioxide in the same weight of sodium sulfite was, by the above volumetric determination, 0.0587 gram. The thiosulfate solution was standardized by liberating iodine from a neutral solution of potassium iodide and iodate and by means of standard acid.

During these gravimetric determinations it was noticed that the barium sulfate settled very quickly in the solutions containing iodine, and was ready for filtering in less than half the time needed for those solutions containing no iodine. It has since been the practice of this laboratory to add a small amount of iodine solution to barium sulfate precipitates, with quite uniform success in facilitating the settling and filtering.

**POTASSIUM PERMANGANATE**—It is well known that the reaction between potassium permanganate and sulfurous acid gives rise to dithionic acid in varying amounts, depending upon experimental conditions. As a consequence a volumetric sulfite determination using permanganate always gives a low result. The average of a number of concordant titrations gave 17.23 cc. of thiosulfate corresponding to 0.1260 gram of sulfite. Since permanganate oxidizes sulfite to both sulfate and dithionate, it seemed possible that increasing the permanganate concentration might decrease the experimental error. It was found, however, that a sevenfold increase in permanganate concentration did not alter the experimental result.

POTASSIUM DICHROMATE—Since the completion of this work, the paper by Hendrixson<sup>3</sup> has appeared, making it unnecessary to repeat the results here. The average of a large number of titrations gave 18.31 cc. as the thiosulfate corresponding to 0.1260 gram sulfite.

HYPOCHLOROUS ACID—Hypochlorous acid solutions are not stable in the presence of excess acid, so that reactions involving it must be carried out in faintly acid, neutral, or alkaline solutions. The experimental conditions were varied considerably, and many experiments were performed but accurate and consistent results could not be obtained. In some cases pure hypochlorous acid solutions were used, in others an alkaline solution was used, and in still others the reaction was carried out in a buffer solution,<sup>4</sup> of an equimolal mixture of disodium and monosodium phosphates. The results, however, were all low and erratic. The results given here were obtained in alkaline solution—i. e., an approximately 0.1 *N* solution of sodium hypochlorite.

0.1260 gram of sodium sulfite was dissolved in 25 cc. of sodium hypochlorite solution in an Erlenmeyer flask. The solution was then diluted to 150 cc. and solid potassium iodide dissolved therein, followed by 5 cc. 6 *N* sulfuric acid. The liberated iodine was titrated with thiosulfate. The average of a large number of titrations gave  $18.45 \pm 0.05$  cc. of thiosulfate, corresponding to 0.1260 gram of sodium sulfite. It will be noted that loss of chlorine would tend to give high results rather than low.

SODIUM BROMATE—Here again the results are low, the average being  $18.24 \pm 0.10$  cc. of thiosulfate corresponding to 0.1260 gram sodium sulfite.

POTASSIUM IODATE—The recent work of Hendrixson<sup>3</sup> makes it unnecessary to give the results in detail. It should be pointed out, however, that the iodate solution must be initially acid. It would be advantageous to allow the oxidation to occur in neutral solution, and acidify only for the determination of the excess iodate. Unfortunately, when this is done the titer is always low. When the iodate solution was initially about 1 *N* with acid, an average of 18.83 cc. of thiosulfate, corresponding to 0.1260 gram sulfite was obtained. When the oxidation took place in neutral iodate solution the thiosulfate value was only 18.18 cc.

STANDARD BROMINE SOLUTION—It is necessary to give only a few results for the bromine method, in view of the work of Manchot and Oberhauser.<sup>5</sup> They, however, used an indicator to determine the end point, while the writers carried their work out along the lines already described. With no acid initially present in the bromine solution,  $18.76 \pm 0.03$  cc. of thiosulfate corresponding to 0.1260 gram sulfite was obtained. When the bromine solution was initially 1 *N*

<sup>3</sup> *J. Am. Chem. Soc.*, **47**, 1319 (1925).

<sup>4</sup> Abbot and Bray, *J. Am. Chem. Soc.*, **31**, 729 (1909)

<sup>5</sup> *Ber.*, **57B**, 29 (1924).

with sulfuric acid, the result was the same. These results compare favorably with those obtained by the iodine method, although they are unmistakably lower.

### Summary of Results for Sulfites

The averages of the results obtained by the various methods (Table I) give a bird's-eye view of their accuracy. The writers are well aware, however, that the averages in some cases have no meaning in themselves, but serve for comparison only.

Table I

Method	Cc. thio corresponding to 0.1260 gram $\text{Na}_2\text{SO}_3$
$\text{KI}_2$	18.80
$\text{KBr}_3$	18.76
$\text{KIO}_3$	18.83
$\text{HClO}$	18.45
$\text{K}_2\text{Cr}_2\text{O}_7$	18.81
$\text{NaBrO}_3$	18.25
$\text{KMnO}_4$	17.23

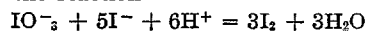
### Analytic Oxidation of Iron

Of the oxidizing agents tried for the analysis of sulfites, three are known to oxidize  $\text{Fe}^{++}$  quantitatively to  $\text{Fe}^{+++}$ —namely, potassium permanganate, potassium dichromate, and sodium bromate. Hypochlorous acid and potassium tribromide are the only other ones which probably are rapid enough or powerful enough to be of any use. Since both of these oxidizing agents are most easily determined iodometrically, the main reaction had to be carried out in the presence of a buffer solution which would keep the  $\text{Fe}^{+++}$  concentration so low that the reaction



could not take place to any appreciable extent, and which would also keep the  $\text{H}^+$  concentration low when hypochlorous acid was used as an oxidizing agent.

If  $\text{Fe}^{++}$  is added to a solution of disodium phosphate containing hypochlorous acid, it is immediately oxidized to ferric iron, which precipitates as the phosphate. When potassium iodide is added to the resulting mixture, iodine is liberated by the excess hypochlorous acid. Iodate may also be formed. On addition of acid to this mixture the precipitated ferric phosphate is dissolved with the formation of  $\text{Fe}(\text{PO}_4)_2^{--}$ .<sup>6</sup> Owing to the formation of this complex, the  $\text{Fe}^{+++}$  concentration is diminished to such a low value that Reaction 1 does not proceed to a measurable extent during 10 minutes.<sup>7</sup> Any iodate which may have been formed is reduced to  $\text{I}_2$ , according to the reaction:



The procedure used was based on this set of reactions. Ten cubic centimeters of  $\text{Fe}^{++}$  solution gave the following

<sup>6</sup> Wineland and Engraber, *Z. anorg. Chem.*, **84**, 340 (1913).

<sup>7</sup> Barneby, *J. Am. Chem. Soc.*, **37**, 1496 (1915).

equivalents in cubic centimeters of thiosulfate solution: highest, 7.90; lowest, 7.71; average of eighteen determinations, 7.80; calculated from potassium permanganate titration, 7.79.

The same general procedure was used with standard bromine solution as the oxidizing agent. Here, 25 cc. of  $\text{Fe}^{++}$  solution gave the following thiosulfate equivalents:

Sample	No. detns.	Highest	Lowest	Av.	Calcd. from $\text{KMnO}_4$ titration
1	6	8.25	8.10	8.17	8.90
2	6	8.31	7.94	8.13	8.97
3	4	19.80	19.63	19.74	20.58

#### Summary

The most satisfactory volumetric reagents for the determination of sulfurous acid or of sulfites are iodine solution, bromine solution, and iodate solution. The iodine was checked with a gravimetric method, and the results were comparable.

Iodate solution is preferred to iodine and to bromine, as it is more stable:

Potassium permanganate is quite unsuitable to use as a volumetric reagent for sulfites.

Hypochlorite, dichromate, and bromate solutions give better results than does permanganate. They are not sufficiently accurate for use in quantitative estimations, and this inaccuracy increases in the order named.

Hypochlorous acid is a satisfactory oxidizing reagent for  $\text{Fe}^{++}$ , and a method is given for its use in volumetric analysis. The tribromide method for  $\text{Fe}^{++}$  does not give accurate results.