[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 80]

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

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RECEIVED OCTOBER 5, 1925 PUBLISHED JANUARY 8, 1926

In the course of his researches Marshall[2] found that aqueous solutions of peroxysulfuric acid[3] ($H_2S_2O_8$) 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 peroxysulfate ion, $S_2O_8^{=}$. Dittrich and Bollenbach[4] 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[5] 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.

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[1] Du Pont Fellow in Chemistry.

[2] 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.

[3] 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 $H_2S_2O_8$ *peroxydisulfuric acid*, to distinguish it from H_2SO_5 (Caro's acid), which would then be called *peroxymonosulfuric acid*. The shorter name *peroxysulfuric acid* is, however, here used for the more stable acid.

[4] Dittrich and Bollenbach, *Ber.*, **38**, 747 (1905).

[5] 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

$$3S_2O_8^{=} + 2Cr^{+++} + 7H_2O = 6SO_4^{=} + Cr_2O_7^{=} + 14H^+ \qquad (1)$$

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, HVO_4, differs from vanadic acid, 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 O_2 and not by the oxidation of oxide oxygen.[6] 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, $S_2O_8^{=}$, hydrolyzes according to the equation[7]

$$S_2O_8^{=} + 2H_2O = 2SO_4^{=} + H_2O_2 + 2H^+ \qquad (2)$$

The hydrogen peroxide then may act as a reducing agent. Reaction 2 takes place only in strongly acid solutions. Cain and Hostetter[8] 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.[9]

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.

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[6] Traube, *Ber.*, **26**, 1471 (1893).

[7] There is an intermediate stage in this hydrolysis, H_2SO_5 (Caro's acid) being formed, which finally comes to equilibrium with respect to H_2O_2; $H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$.

[8] Cain and Hostetter, THIS JOURNAL, **34**, 274 (1912).

[9] Bray and Livingston, *ibid.*, **45**, 1251 (1923).

$$S_2O_8^{=} + Ag^{+} = 2SO_4^{=} + \text{intermediate compound} \qquad (3)$$

$$\text{Intermediate compound} + 2Cr^{+++} = Cr_2O_7^{=} + Ag^{+} \qquad (4)$$

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, 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, Cr^{+++}, is present; a precipitate does appear, however, after the chromic ion is used up if peroxysulfate 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 peroxysulfate or the dichromate ($Cr_2O_7^{=}$) 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 peroxysulfate 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 peroxysulfate ion was present, due to incomplete precipitation of barium chromate and lead chromate. It was finally found that under the proper conditions vanadyl sulfate, $VOSO_4$, would quantitatively reduce dichromate to chromic (Cr^{+++}) ion without reducing the peroxysulfate to sulfate ion. It was also found possible to titrate the excess of vanadyl salt with standard permanganate solution in the presence of peroxysulfate 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,[10] 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.

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[10] 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

$S_2O_8^-$ = 0.0642 *M;* Ag_2SO_4 = 0.01007 *N*
Cr^{+++} = 0.0218 *M;* H_2SO_4 = 0.1968 *N*

Time, min.	Concn.	Constant
0	0.0642	...
14	.0607	0.398
43	.0558	.324
69	.0516	.314
109	.0453	.313
135	.0425	.303
163	.0390	.304
194	.0359	.297
222	.0330	.298

EXPT. 2

$S_2O_8^{=}$ = 0.0642 *M;* Ag_2SO_4 = 0.01007 *N*
Cr^{+++} = 0.0109 *M;* H_2SO_4 = 0.1968 *N*

Time, min.	Concn.	Constant
0	0.0642	...
15	.0608	0.360
30	.0579	.342
50	.0546	.322
66	.0519	.320
87	.0486	.318

TABLE I (*Continued*)

EXPT. 3

$S_2O_8^{=} = 0.0321\ M$; $Ag_2SO_4 = 0.01007\ N$
$Cr^{+++} = 0.0218\ M$; $H_2SO_4 = 0.1968\ N$

Time, min.	Concn.	Constant
0	0.321	...
22	.0296	0.366
44	.0276	.341
67	.0252	.359
97	.0230	.341
127	.0210	.332
157	.0192	.325
191	.0175	.316
217	.0165	.305

EXPT. 4

$S_2O_8^{=} = 0.0642\ M$; $Ag_2SO_4 = 0.00503\ N$
$Cr^{+++} = 0.0218\ M$; $H_2SO_4 = 0.1968\ N$

Time, min.	Concn.	Constant
0	0.0642	...
25	.0616	0.328
52	.0592	.310
84	.0563	.311
117	.0535	.310
175	.0498	.289
235	.0449	.302

EXPT. 5

$S_2O_8^{=} = 0.0321\ M$; $Ag_2SO_4 = 0.02014\ N$
$Cr^{+++} = 0.0218\ M$; $H_2SO_4 = 0.1968\ N$

0	0.0321	...
18	.0278	0.391
37	.0248	.347
67	.0204	.335
99	.0170	.319
132	.0139	.314
169	.0112	.309
209	.0084	.215

EXPT. 6

$S_2O_8^{=} = 0.0311\ M$; $AgClO_4 = 0.01178\ N$
$Cr^{+++} = 0.01\ M$; $HClO_4 = 0.10\ N$

0	0.0311	...
15	.0293	0.337
30	.0276	.338
50.5	.0254	.340
71	.0232	.351
101	.0206	.346
125	.0188	.342

EXPT. 7

$S_2O_8^{=} = 0.01556\ M$; $AgClO_4 = 0.00589\ N$
$Cr^{+++} = 0.01\ M$; $HClO_4 = 0.10\ N$

0	0.01556	...
59	.0141	0.284
110	.0127	.314
170	.0111	.337
275	.0086	.366

EXPT. 8

$S_2O_8^{=} = 0.01556\ M$; $AgClO_4 = 0.01178\ N$
$Cr^{+++} = 0.01\ M$; $HClO_4 = 0.10\ N$

0	0.01556	...
22	.0143	0.326
44	.0131	.332
75	.0114	.352
106	.0101	.346
144	.0087	.343
193	.0071	.345
273	.00512	.346

EXPT. 9

$S_2O_8^{=} = 0.0311\ M$; $AgClO_4 = 0.01178\ N$
$Cr^{+++} = 0.02\ M$; $HClO_4 = 0.1\ N$

0	0.0311	...
14	.0294	0.341
29	.0277	.339
50	.0254	.344
70	.0234	.345
100	.0208	.342
124	.0190	.337
168	.0166	.317

EXPT. 10

$S_2O_8^{=} = 0.0311\ M$; $AgClO_4 = 0.00589\ N$
$Cr^{+++} = 0.01\ M$; $HClO_4 = 0.1\ N$

0	0.0311	...
13	.0305	0.254
27	.0296	.311
42.5	.0286	.335
57.5	.0278	.331
77.5	.0267	.334
97	.0256	.341
124	.0241	.349
215	.0201	.345

TABLE I *(Concluded)*

EXPT. 11

$S_2O_8^{=}$ = 0.01556 *M*; $AgClO_4$ = 0.01178 *N*
Cr^{+++} = 0.01 *M*; $HClO_4$ = 0.2 *N*

Time, min.	Concn.	Constant
0	0.01556	...
22	.0146	0.246
44	.0133	.303
75	.0118	.313
106	.0105	.315
144	.0092	.310
193	.0076	.315
279	.0058	.300

EXPT. 12

$S_2O_8^{=}$ = 0.0311 *M*; Ag^+ = 0.01178 *N*
Cr^{+++} = 0.01 *M*; H_2SO_4 = 0.1 *N*

Time, min.	Concn.	Constant
0	0.0311	...
23	.0287	0.296
43	.0265	.316
62	.0247	.315
83	.0227	.322
112	.0206	.312

EXPT. A (AT 35°)

$S_2O_8^{=}$ = 0.01115 *M*; $AgClO_4$ = 0.00589 *N*
Cr^{+++} = 0.01 *M*; $HClO_4$ = 0.10 *N*

0	0.01115	...
18	.0103	0.748
35	.0096	.726
59	.0084	.815
81	.0076	.804
111	.0066	.802
155	.0054	.794
202	.0044	.782
248	.0036	.774

EXPT. B (AT 35°)

$S_2O_8^{=}$ = 0.01115 *M*; $AgClO_4$ = 0.01178 *N*
Cr^{+++} = 0.01 *M*; $HClO_4$ = 0.1 *N*

0	0.01115	...
18	.0097	0.657
35	.0082	.746
59	.0064	.799
81	.0052	.800
110	.0040	.791
156	.0028	.752
203	.0019	.740
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 peroxysulfate 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

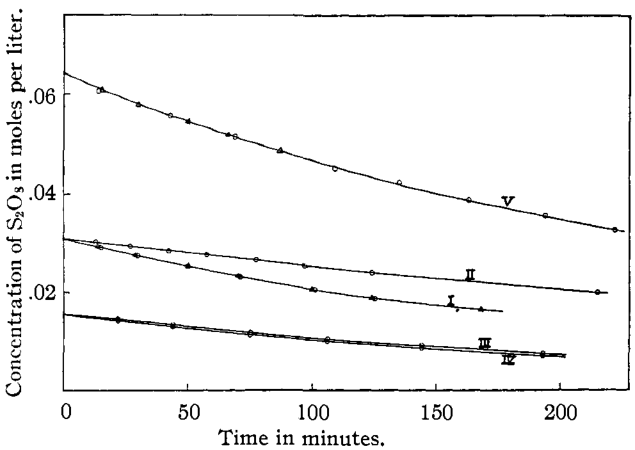

Fig. 1.

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

$$3S_2O_8^{=} + 2Cr^{+++} + 7H_2O = 6SO_4^{=} + Cr_2O_7^{=} + 14H^{+} \qquad (1)$$

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

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

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

$$S_2O_8^{=} + Ag^{+} = Ag^{+++} + 2SO_4^{=} \qquad (6)$$

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

$$3Ag^{+++} + 2Cr^{+++} + 7H_2O = Cr_2O_7^{=} + 3Ag^{+} + 14H^{+} \qquad (7)$$

Evidently, the assumption is here made that the trivalent silver ion, 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.[11] It has not been heretofore supposed, however, that trivalent silver was formed during the reaction between solutions of peroxysulfates and silver salts.[12] 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

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[11] Luther and Pokorny, *Z. anorg. Chem.*, **57**, 290 (1908).

[12] In a recent paper by F. Jirsa, *Chem. Listy*, **19**, 3–9 (1925), the oxide Ag_2O_3 is described as resulting from the energetic oxidation of metallic silver or of silver salts. Only the abstract, *C. A.*, **19**, 2460 (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 H_2SO_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[13] who, making certain assumptions, concluded that it was a mixture of silver peroxysulfate and silver peroxide, Ag_2O_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 $AgO_{1.00}(SO_4)_{0.12}(H_2O)_{0.22}$. In spite of the striking equality of the numbers of silver and oxygen atoms, the formula does not show that the substance is essentially Ag_2O_2, since 0.12 or 0.24 atom of silver must be combined with the sulfate if the impurity is silver peroxysulfate or sulfate.

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[13] Austin, *J. Chem. Soc. Trans.*, 99, 242 (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
$KMnO_4$ required for $FeSO_4$ 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
$FeSO_4$ used up, milliequivalents	.219	.242
Ratio of $FeSO_4$ 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
$KMnO_4$ used for filtrate, cc.	1.12	1.92	2.35
$K_2S_2O_8$ 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 $S_2O_8^=$ 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, Ag_2O_3 or $Ag_2O_3.xAg_2(SO_4)_3$. 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° and 35° 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

$$S_2O_8^{=} + Ag^{+} = 2SO_4^{=} + Ag^{+++}$$
$$3Ag^{+++} + 2Cr^{+++} + 7H_2O = Cr_2O_7^{=} + 3Ag^{+} + 14H^{+}$$

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 (Ag_2O_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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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 82]

CONFIRMATION OF THE PRESENCE OF A NON-TETRAHEDRAL CARBON ATOM IN CRYSTALS OF PENTA-ERYTHRITOL

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RECEIVED OCTOBER 13, 1925 PUBLISHED JANUARY 8, 1926

The crystal structure of penta-erythritol, $C(CH_2OH)_4$, has recently been investigated by Mark and Weissenberg,[2] using the rotating crystal method. Their conclusions may be summarized as follows. The structure possesses ditetragonal pyramidal symmetry, the space group being C_{4v}^9. The lattice is body centered. The unit cell, containing two molecules, has the dimensions $a_0 = 6.16$ Å. and $c_0 = 8.76$ Å. The symmetry of the position occupied by the central carbon atom of each molecule is that of the point group C_{4v}; the four surrounding carbon atoms must therefore be structurally equivalent and all in the same plane, at the corners of a square, although not necessarily in the same plane as the central atom. Similarly, all four oxygen atoms of each molecule are equivalent and coplanar.

It seemed to us that these results, indicating that the carbon atom in aliphatic organic compounds is not always tetrahedral in shape, are of such importance as to deserve verification, especially in view of the fact that similar methods had yielded[3] a structure of tin tetra-iodide which have been shown by Laue photographic data obtained in this Laboratory[4] to be incorrect. We have therefore investigated the structure of penta-

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[2] Mark and Weissenberg, *Z. Physik*, **17**, 301 (1923).

[3] Mark and Weissenberg, *ibid.*, **16**, 1 (1923).

[4] Dickinson, THIS JOURNAL, **45**, 958 (1923).