[Contribution from the Department of Chemistry of Columbia University,
No. 577]

SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. IV. OXIDATION OF OXALATE ION[1]

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Received April 20, 1928 Published August 4, 1928

Introduction

It was found by R. Kempf[2] that oxalic acid is only slowly, if at all, oxidized by persulfates, at room temperature, in the absence of any catalyst, while in the presence of a small amount of a silver salt the oxidation proceeds quite rapidly, and presumably quantitatively, according to the following reaction

$$H_2C_2O_4 + K_2S_2O_8 \longrightarrow 2KHSO_4 + 2CO_2 \qquad (1)$$

This oxidation is given as a quantitative method for estimating persulfates by Treadwell and Hall.[3] A neutral oxalate seems to be oxidized just as completely and rapidly as an acid solution (perhaps more rapidly); silver salts have a much greater catalytic effect than in some of the other persulfate oxidations.[4] The purpose of this investigation was to study the velocity of the reaction quantitatively with a view to the elucidation of its mechanism and its differences from the other reactions mentioned.

Theoretical

This reaction was expected, in accordance with the others, to proceed in two steps, as follows

$$S_2O_8^{--} + Ag^+ \longrightarrow 2SO_4^{--} + Ag^{+++} \text{ (slow)} \qquad (2)$$
$$C_2O_4^{--} + Ag^{+++} \longrightarrow 2CO_2 + Ag^+ \text{ (faster)} \qquad (3)$$

If reaction (3) were extremely fast, then the net rate should be "pseudo-unimolecular," and independent of the oxalate ion concentration, so long as the oxalate, and not the persulfate, is in excess in the solution; if the persulfate is in excess a modified unimolecular curve will result. On the other hand, if reaction (3) is comparatively slow, trivalent silver ion will increase in concentration as the reaction proceeds and autocatalytic curves may be obtained as in the case of the ammonium ion oxidation.[5] From the complete ionic equation

$$S_2O_8^{--} + C_2O_4^{--} \xrightarrow{Ag^+} 2SO_4^{--} + 2CO_2 \qquad (4)$$

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[1] Sections I, II and III of this series will be found in This Journal, **49**, 2689 (1927) and **50**, 2080 (1928).

[2] Kempf, *Ber.*, **38**, 3965 (1905).

[3] Treadwell-Hall, "Analytical Chemistry," Vol. II, 6th ed., John Wiley and Sons, Inc., New York, **1924**, p. 535.

[4] See Section II of this series.

[5] Section III of this series.

it is seen that there is no change in ionic strength in the solution during the course of the reaction (or very little; a small amount of ionized carbonic acid will be formed) and consequently there will be little salt effect during the course of the reaction. Of course, with different initial concentrations or in the presence of a foreign salt the velocity will be changed.

However, the oxidation proceeds, it will be seen, much faster than does reaction (2)—judging from the velocity of the reactions studied before. Consequently, the preceding mechanism is perhaps entirely ruled out as an explanation for this reaction. No complete explanation for the results obtained in this investigation can be offered, but some of the factors involved will be discussed and tentative explanations proposed.

Experimental

Potassium persulfate, sodium oxalate, silver sulfate and nitrate were all prepared by recrystallization and thorough drying of the crystals; the salts were either weighed directly for each experiment or to make standard solutions.

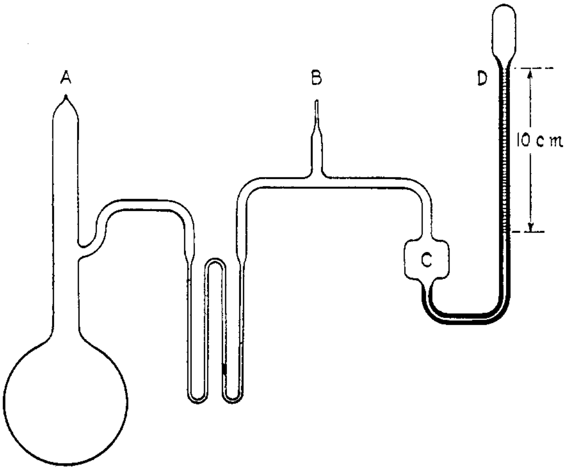

Fig. 1.—The modified apparatus for measuring the rate of gas evolution.

Since carbon dioxide is evolved, the easiest way to follow the reaction is to follow the evolution of this gas. This was done in a modification of the apparatus designed by Brönsted.[6] The modified apparatus is shown in Fig. 1. All stopcocks and ground stoppers were eliminated. The solution, containing (usually) the oxalate and the silver salt, was introduced into the flask and the solid persulfate was suspended in a small glass capsule, from a platinum loop sealed in the side of the neck of the flask. D was a closed manometer, well evacuated and "boiled out," with a 5cc. bulb at the top, to prevent error from any traces of gases remaining above the mercury. The bulb C was made large enough to accommodate this extra mercury. When all was ready for an experiment, A was sealed off, the system evacuated through a capillary at B and this

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[6] (a) Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1926); (b) Brönsted and King, This Journal, **47**, 2523 (1925).

then sealed off. At the close of an experiment only the tip of B was broken off at first, so that the air entered the apparatus slowly; otherwise the mercury, rising rapidly in the manometer, might break the bulb D.

This form of the apparatus is somewhat more difficult to manipulate than the older style but if it is made of Pyrex glass the seals are not difficult and it has the advantages that accidental leaks are almost completely eliminated and, besides, it can be used for reactions in which gases are evolved that attack the usual vacuum-tight stopcock lubricants.

Some of the experiments were carried out at 20 ± 0.02°, others at 25 ± 0.02°, as indicated in the tables. During each experiment the room temperature was kept slightly higher than that of the bath to prevent distillation of water from the reaction flask to other parts of the apparatus.

The Measurements

Some preliminary Experiments and Experiments 44, 45, 46 and 47 were made to find whether the reaction between $S_2O_8^{--}$ and $C_2O_4^{--}$ had an appreciable velocity with no silver ion present as catalyst. The velocity is small; the results are not in very good quantitative agreement and it is possible that the reaction is due to traces of "accidental" catalysts. The velocity is negligible compared to that in most of the experiments with silver ion as the catalyst. The results are given in Table I.

TABLE I

THE REACTION BETWEEN $S_2O_8^{--}$ AND $C_2O_4^{--}$ WITH NO CATALYST AT 25°

Concentrations: 0.01 M $Na_2C_2O_4$, 0.005 M $K_2S_2O_8$

Time, min.	Frac. persulfate decomposed Expt. 44	Frac. persulfate decomposed Expt. 45	Time min.	Frac. persulfate decomposed Expt. 46	Frac. persulfate decomposed Expt. 47
120	0.001	0.000	120	0.007	0.007
240	.007	.007	210	.010	.015
440	.015	.010	360	.019	.030
620	.025	.018	420	.025	.034
1380	.104	.061	1110	.142	.136

In Experiments 34 and 35, which have the same concentrations as the above, with the addition of 0.00002 M silver nitrate, the velocity was nearly unimolecular. Table II gives a part of the experimental figures to illustrate this, and the entire curves are shown graphically in Fig. 2.

TABLE II

VELOCITY "CONSTANTS" WITH A SILVER SALT PRESENT AT 25°

Concentrations: 0.01 M $Na_2C_2O_4$, 0.005 M $K_2S_2O_8$, 0.00002 M $AgNO_3$

$$\text{"}k\text{"} = \frac{2.3}{t \times C_{Ag^+}} \ln \frac{a}{a-x}$$

Expt. 34	Time, min.	50	70	120	240
	"k"	213.2	217.9	208.4	190.7
Expt. 35	Time, min.	50	70	120	240
	"k"	263.6	260.5	251.5	237.5

However, the experiments recorded in Table II, although carefully made up duplicates in concentration, do not agree with each other within reasonable experimental error, and this is by no means the worst case of disagreement in the velocity in solutions that duplicated each other in concentration. Further, the velocity was not always as nearly unimolecular as in the above cases. In several instances typical autocatalytic curves were obtained, while in others there was a very short autocatalytic period at the beginning of the reaction, as in the ammonium ion oxidation; sometimes this autocatalytic period was not evident but the velocity curve was flattened at the beginning, no doubt due to the same cause. Table III gives the details of concentration and temperature, and Figs. 3–5 show the data graphically for several experiments carried out with an excess of oxalate present.

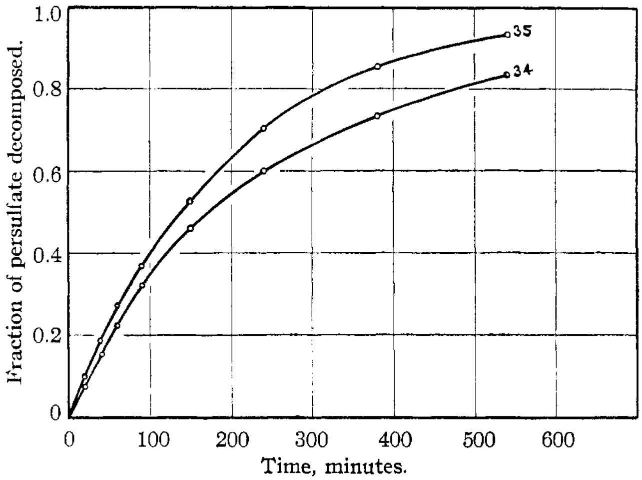

Fig. 2.

TABLE III

CONCENTRATION AND TEMPERATURE FOR EXPERIMENTS PLOTTED IN FIGS. 3–5

Expt. no.	$Na_2C_2O_4$, *M*	$K_2S_2O_8$	$AgNO_3$	Ag_2SO_4, *N*	Temp., °C.
4, 6, 7, 8, 9, 17	0.01	0.005	....	0.00002	20
36, 37	.005	.0025	0.00003	....	25
38, 39	.005	.0025	.00004	....	25
40, 41, 54, 55	.005	.0025	.00002	....	25
42, 43	.005	.0025	.00001	....	25

All of the experiments in Fig. 3 were duplicates and should agree; but their velocity is far different. As a rule, when experiments were run with different concentrations, the velocity was changed in the direction expected, but there was no quantitative agreement. For instance, 43, with 10^{-5} *M* Ag^+ is slower than 38, with 4×10^{-5} *M* Ag^+, but much more than one-fourth as fast. Many other similar discrepancies can be noted. Nevertheless, the order of magnitude of the velocity was always the same. The experiments at 25°, for instance, were run about a year later than those at 20°, with entirely new salts and new reaction flasks, and still are of the same order of magnitude.

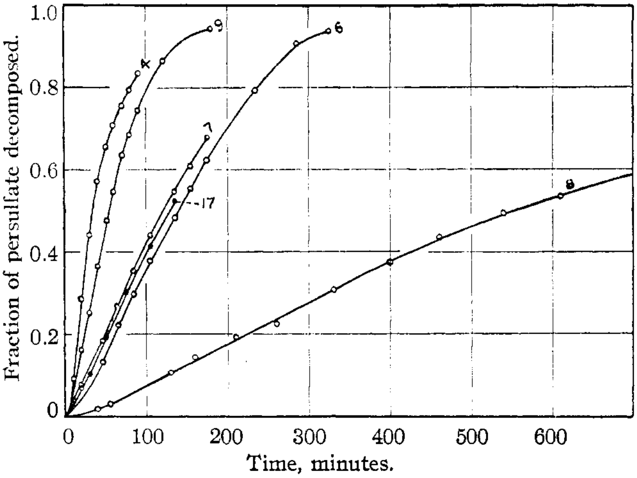

Fig. 3.

When persulfate is present in excess instead of oxalate, conditions are somewhat different. While the velocity may be somewhat dependent on the concentration of oxalate, it is more dependent on the persulfate concentration, as is shown by the nearly unimolecular nature of some of the above curves. The autocatalytic character of some of these curves

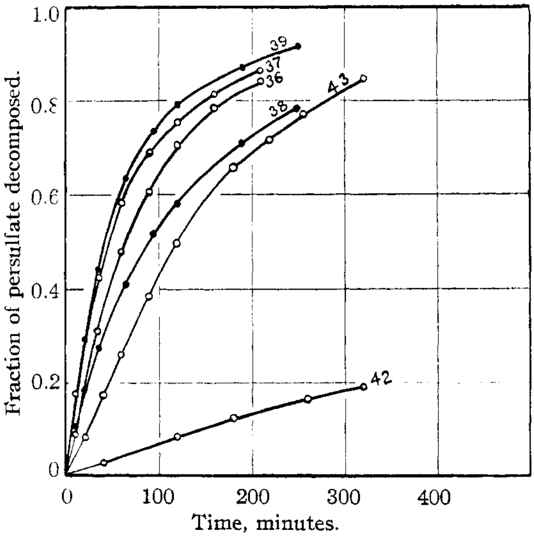

Fig. 4.

indicates, however, that an intermediate, unstable compound is formed, presumably by the interaction of the persulfate and silver ions, and if persulfate is present in sufficient excess, the silver ion concentration is high enough and the reaction involving the decomposition of the intermediate compound is slow enough, there is no reason why this intermediate should not keep on increasing in concentration throughout the entire reaction and consequently the rate of oxalate oxidation increase continuously. Several experimental curves were found to have this character; in Table IV are given the details of concentration and temperature and in Figs. 6–8 are shown graphically several examples, some with twice as much persulfate as oxalate, some with a larger excess. Again, however, it must be noted that experiments could not at all be duplicated, in spite of care in making up the solutions and in cleaning the vessels used, and attempts to trace the cause of these discrepancies were not very successful.

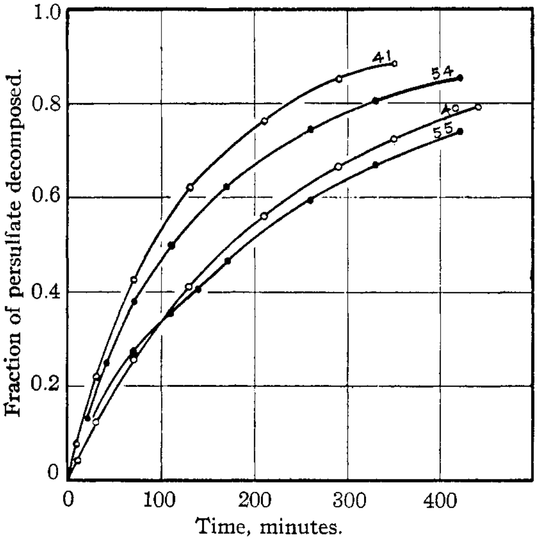

Fig. 5.

TABLE IV

CONCENTRATIONS AND TEMPERATURE FOR EXPERIMENTS PLOTTED IN FIGS. 6–8

Expt. no.	$Na_2C_2O_4$, *M*	$H_2C_2O_4$, *M*	$K_2S_2O_8$, *M*	$AgNO_3$	Ag_2SO_4, *N*	Temp., °C.
3, 14, 15, 19	0.005	..	0.01	....	0.00002	20
11, 13, 21, 22	...	0.005	.01	....	.00002	20
23, 24	.005	..	.05	0.00001	....	25
25, 26	.005	..	.05	.00002	....	25
27, 28	.0025	..	.05	.00002	....	25
29	.0025	..	.05	.00001	....	25
48, 49, 50	.0025	..	.01	.00003	....	25
51, 52, 53	.0025	..	.01	.00002	....	25

It was suspected that the reaction might be catalyzed by the diffuse daylight or electric light that reached the flasks, but a 200-watt tungsten lamp placed just outside the thermostat quite near one of the reaction

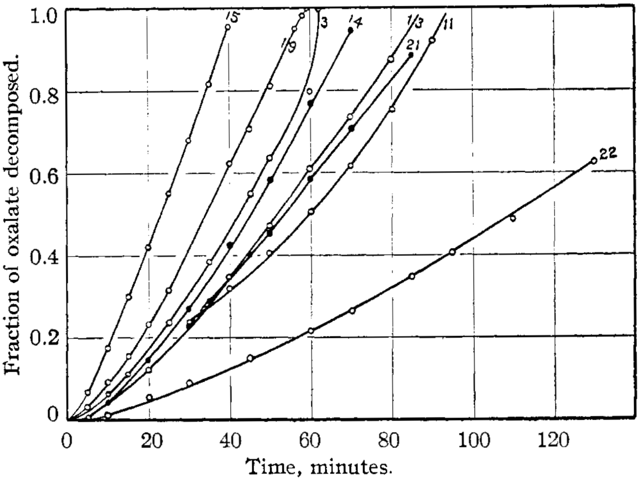

Fig. 6.

flasks had no appreciable effect on one rather slow experiment. Also, the divergences could scarcely be ascribed to a difference in illumination of the two flasks used, or of one flask at different times. It was suspected

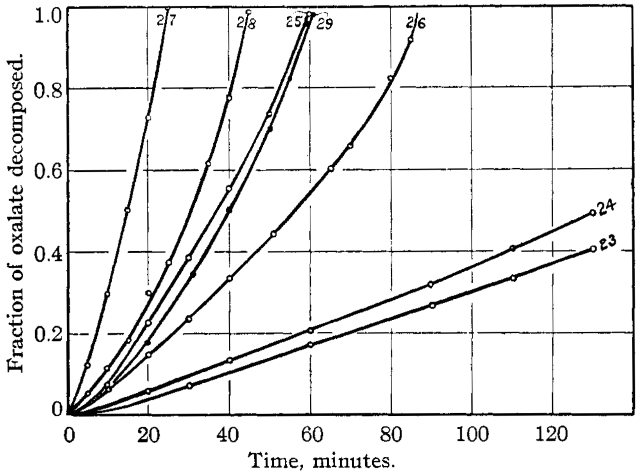

Fig. 7.

that the exact manner of mixing the last reagent in the solution caused the velocity to vary. Usually the persulfate was dropped in last, and sometimes it dissolved rapidly (30–40 sec.), sometimes more slowly (2–4 min.)

depending on the exact manner in which the glass capsule fell into the solution. So in Experiments 38 and 40 the solid persulfate was allowed to dissolve slowly (6 min.) with very little shaking of the flask, while in 39 and 41, run side by side with 38 and 40, the persulfate was dropped in and dissolved in a few seconds. The difference is no greater than in many other experiments in which the rate of solution of the persulfate was approximately the same. In other experiments the silver nitrate was dropped in last, and in general these experiments seemed to have a slightly higher velocity than the others with the same concentrations, but the effect was not pronounced.

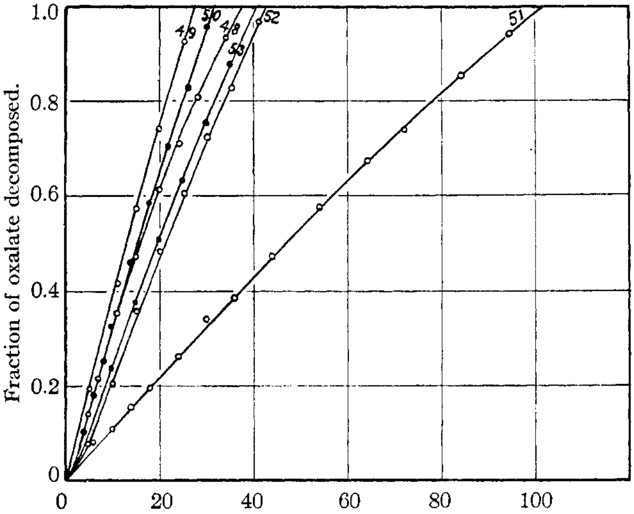

Fig. 8.

If the autocatalytic effect is due to an accumulation of intermediate compound formed by reaction of the persulfate and silver ions, then if these two are mixed and allowed to react until the maximum amount of the intermediate is present, the autocatalytic character should disappear and the curve be either a "zero order" curve—if this maximum concentration of the intermediate is maintained—or a concave curve, if the concentration of the intermediate diminishes after the oxalate is added. For Experiment 15, the persulfate and silver sulfate were mixed, and one hour later the oxalate was added and the experiment started. The autocatalytic character almost disappeared, and the reaction was somewhat faster than the others of the same concentrations. Possibly the reaction between the persulfate and silver ions was not complete in one hour.

Only one consistent discrepancy was noticed in any series of experiments;

for a time, when duplicates were run side by side in the two pieces of apparatus, those in apparatus No. 1 were consistently slower than those in apparatus No. 2. This is shown by Experiments 34, 36, 38, 40, 42 and 48, which were run in apparatus No. 1, and were, respectively, duplicates of and were run beside Experiments 35, 37, 39, 41, 43 and 49 in apparatus No. 2. This suggested catalysis by the flask walls and to see if an increase in the glass surface would change the velocity considerable broken glass was introduced into flask No. 1 while Experiments 42 and 43 were run. If there was any catalytic effect it was negative. Next the wall of flask No. 1 was thoroughly etched with hydrofluoric acid, and Experiments 52 and 54 were run side by side with 53 and 55. Fifty-three in No. 2, was slightly faster than 52, in No. 1; while 54, in No. 1, was faster than 55 in No. 2. Any effect was slight, however, compared to the differences between duplicate solutions run in the same apparatus on different days.

It is possible that there was some catalysis by "dust" in the solutions,[7] though there was probably no large effect from this source. Small amounts of precipitated silver oxalate could scarcely be responsible; in all the solutions reported here, care was taken that the concentrations should be below those at which silver oxalate would precipitate and no precipitation was discernible. Several experiments were run with concentrations high enough to cause a slight visible precipitation, without any pronounced effect that would indicate such a catalysis.

Discussion

The experiments mentioned before make it seem quite likely that there is some wall catalysis. No simple procedure is sufficient to prevent this or make it possible to duplicate its effects except accidentally. The fact that broken glass in the flask, or etching the flask, had no pronounced effect, makes it seem impossible that this wall catalysis could be responsible for the enormous difference in velocity between these experiments and the oxidation of other reducing agents. It is just possible that "dust" or some unknown impurities could be responsible, for many reactions are extremely sensitive to traces of catalysts. For example, the effect of Cu^{++} and Fe^{++} and mixtures of these two on the persulfate oxidation of iodide ion may be cited,[8] also the effect of traces of impurities on some isomeric changes.[9]

If most of the catalysis were heterogeneous, one would expect a zero order or a unimolecular reaction in all cases. This is nearly true in some of the solutions. Expts. 48, 49, 50, 51, 52 and 53 are almost of zero order, and further showed irregularities that might very well attend wall catalysis when the shaking of the flask is not quite uniform, but the auto-

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[7] See F. O. Rice, THIS JOURNAL, **48**, 2099 (1926).

[8] Price, *Z. physik. Chem.*, **27**, 474 (1898).

[9] Rice, "Homogeneous Organic Reactions," The Chemical Catalog Co., New York, **1928**, Chapter V.

catalytic effect, especially in solutions containing excess persulfate, indicates rather that the phenomenon is at least largely some peculiarity of the reactions between the various ions and intermediate products, and that this makes the reaction so much faster than the others, while the wall catalysis probably accounts for the comparatively small differences between the individual experiments.

It should be noted that the irregularities cannot be accounted for by supersaturation of the solution with carbon dioxide and consequent failure of the manometer readings to represent the rate of reaction. This may cause small errors in such velocity measurements (say 1–3%) but not the wide variations found here, especially since precautions were taken to shake the reaction flasks in approximately the best manner.[10]

Various explanations can be advanced for the high velocity of this reaction. As was mentioned before, the oxalate is, apparently, oxidized faster than trivalent silver ion is formed. Dr. R. Livingston[11] has suggested one explanation for this. Assume that the persulfate and silver ions form first a complex ion that is relatively inactive, that is, can oxidize only good reducing agents, as the oxalate ion, but not ammonium or chromic ion. From this is formed a more active silver ion, AgO^+ or Ag^{+++}, which can oxidize the poorer as well as the better reducing agents. To fit all the existing data a series of simultaneous and consecutive reactions can be formulated which will account for the various rates, for the autocatalytic character of some of the curves and for any dependency on the concentration of the reducing agent.

We can scarcely expect the initial reaction to be represented merely by Equation (2)

$$Ag^+ + S_2O_8^{--} \longrightarrow Ag^{+++} + 2SO_4^{--}$$

except perhaps as an approximation under certain conditions. In the thermal decomposition of persulfates in water solution there are at least three reversible steps, before the final product of SO_4^{--} ion is formed from the $S_2O_8^{--}$ ion.[12] In the photochemical decomposition in water solution, sulfate ion is the only detectable product obtained,[13] but it is nevertheless quite likely that there are undetectable intermediate stages. The constitution of the persulfates is not well understood but it is unlikely that sulfate ion can be formed directly by splitting of persulfate ion, that is,

$$S_2O_8^{--} + 2\ominus \longrightarrow 2SO_4^{--}$$

(the silver ion supplying the electrons). So some mechanism similar to that of Livingston's is quite probable.

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[10] See Pedersen, This Journal, **49**, 2681 (1927).

[11] Private communication.

[12] See Price, "Per-acids and their Salts," Longmans, Green and Company, **1912**, p. 31; Palme, *Z. anorg. chem.*, **112**, 97 (1920).

[13] Morgan and Crist, This Journal, **49**, 16 (1927).

One might also formulate a mechanism in which the silver ion is oxidized in two steps, first to bivalent and then to trivalent silver. The slower oxidations would be sensitive only to the trivalent silver while the oxalate ion would be oxidized by the bivalent silver. Intermediate reducing agents could be oxidized rapidly by the trivalent, slowly by the bivalent form.

It is unfortunate that the irreproducibility of these experiments makes it quite impossible to tell whether the velocity is proportional to the first or the second power of the silver-ion concentration or to test properly any suggested mechanism for the reaction. Consequently, the chemistry of the persulfate oxidations cannot be much further elucidated.

Summary

The rate of oxidation of oxalate ion by persulfate ion in dilute water solution has been measured, using silver salts as the catalyst, and the following conclusions have been reached.

With no added catalyst the reaction proceeds very slowly, and it is not known whether or not this slow action is due to "accidental" catalysts or the vessel walls.

With silver salts added as a catalyst, the reaction is very much faster than the similar oxidation of ammonia, ammonium ion and chromic ion.

There is undoubtedly some catalytic effect, either positive or negative, by the glass reaction vessel walls and possibly some catalysis by accidental impurities.

However, the major portion of the difference between the velocity in this and the other oxidations is most likely due to some peculiarity in the reaction itself.

The autocatalytic character of some of the curves indicates that some intermediate compound decomposes at a speed comparable with that of its formation and that in certain cases it accumulates in the solution. This cannot be the trivalent silver ion that was postulated as the intermediate substance in the other oxidations.

Possible mechanisms for the main part of the reaction (not the wall catalysis) are discussed.

The extreme irregularity of the velocity even in carefully prepared duplicate solutions makes it impossible to elucidate the mechanism further or to study other aspects of the problem such as "salt effect" on the velocity.

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