[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,
No. 576]

SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. III. THE OXIDATION OF AMMONIUM ION[1]

BY CECIL V. KING

RECEIVED APRIL 20, 1928 PUBLISHED AUGUST 4, 1928

Introduction

It was found by Marshall[2] that ammonium persulfate in solution, in the presence of silver salts, decomposes at a measurable velocity, according to the following equation

$$NH_4^+ + 4S_2O_8^{--} + 3H_2O \xrightarrow{Ag^+} 10H^+ + 8SO_4^{--} + NO_3^- \qquad (1)$$

Presumably, according to the recent work of Yost, the first step in this oxidation will be[3]

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

It is difficult to postulate a mechanism for the succeeding reaction; the following occurs, but whether in one step or more, one cannot say

$$4Ag^{+++} + NH_4^+ + 3H_2O \longrightarrow 4Ag^+ + NO_3^- + 10H^+ \qquad (3)$$

In any case, from the preceding work on persulfate oxidations catalyzed by silver ion, it was expected that reaction (2) would be the velocity determining reaction; that is, (3) or its equivalent would be comparatively immeasurably rapid. Then, since the Ag^+ ion is regenerated and its concentration would remain constant, one should obtain a "pseudo-unimolecular" reaction with the velocity independent of the concentration of ammonium ion, *provided the salt concentration is held constant throughout the course of the reaction.* The above two conditions were practically fulfilled in the experiments of Marshall and Inglis, with 0.5 N and 1.0 N salt solutions.

These investigators found that with 0.25 molar ammonium persulfate and 0.0005 molar silver nitrate the reaction proceeded practically according to a unimolecular curve; that the acid formed did not interfere much with the reaction—though it appears that there was a little oxidation of water and that this was greater if the solution contained 0.25 molar nitric or sulfuric acid at the start; and that the salt effect was negative. All of this agrees with the above postulated mechanism. However, if one starts with quite dilute solutions, the change in salt concentration during the reaction is comparatively enormous—for instance, if one starts with 0.0005 molar ammonium persulfate and 0.0005 molar silver nitrate, the total equivalent concentration at the beginning will be 0.0015, and at the

---

[1] Sections I and II of this series will be found in THIS JOURNAL, **49**, 2689 (1927).

[2] (a) Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163 (1900); (b) Marshall and Inglis, *ibid.*, **24**, 88 (1902).

[3] (a) Yost, THIS JOURNAL, **48**, 152 (1926); (b) *ibid.*, **48**, 374 (1926).

end 0.0026. With such concentrations, the salt effect will be quite pronounced, and in this case we should not expect the velocity to follow the unimolecular scheme, but to fall off from this considerably as the reaction progresses. Then we should expect the velocity to follow the Brönsted scheme

$$\frac{\mathrm{d}C_{S_2O_8^{--}}}{\mathrm{d}t} = kC_{S_2O_8^{--}}C_{Ag^+}f_2 \qquad (4)$$

where f_2 is the activity coefficient of the $S_2O_8^{--}$ and is continually decreasing as the reaction proceeds; and C_{Ag^+} is a constant. Now in sufficiently dilute solutions f_2 can be expressed as a function of the concentration, according to the formula

$$-\log f_2 = 0.5 \times 2^2 \sqrt{\mu} \text{ at } 25° \qquad (5)$$

where μ is the ionic strength; whence

$$f_2 = 10^{-2\sqrt{\mu}} \qquad (6)$$

and (4) becomes

$$\frac{\mathrm{d}C_{S_2O_8^{--}}}{\mathrm{d}t} = kC_{S_2O_8^{--}}C_{Ag^+}10^{-2\sqrt{\mu}} \qquad (7)$$

μ can be expressed as a function of $C_{S_2O_8^{--}}$; if we let the initial $C_{S_2O_8^{--}} = a$, at time t, $C_{S_2O_8^{--}} = (a - x)\ F$ and $C_{Ag^+} = b$, then $\mu = 3a + 3.25x + b$, and (7) becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kb(a - x)\ 10^{-\sqrt{3a \times 3.25x + b}} \qquad (8)$$

It was hoped that this equation might be applied but as will be shown later the correct expression for the velocity of this reaction is probably much more complicated than (8); in fact, (8) could scarcely be used even as a first approximation.

The fact that the ion concentration changes by such a large amount during the reaction makes it possible to find the rate of reaction by following the conductivity of the solution, provided the mechanism above is correct. The conductivity does change enormously, especially since hydrogen ion is formed. The conductivity of a solution containing 0.0005 M ammonium persulfate and 0.0005 M silver nitrate was 2.2×10^{-4} reciprocal ohms at the start and 6.2×10^{-4} reciprocal ohms at the end of the reaction. In other solutions the change was smaller or greater according to the concentrations.

Materials and Measurements

Ammonium persulfate and silver nitrate were prepared by recrystallizing from distilled water. No measurements were made on solutions having a conductivity less than 100 times that of the water and consequently ordinary distilled water was used.

Conductances were measured in cells with constants ranging from 0.3455 to 0.3819, as measured with 0.005 N KCl. The electrodes were unplatinized. The source of current for the measurements was a radio tube oscillator adjusted to near 1000 cycles per second.[4] The bridge was a Leeds and Northrup ratio coil bridge and resistance box which had been checked with 1000 cycle current against a standard A. C. bridge. A two-stage radio amplifier was used to make the reading of the null point easy. Air and mica condensers were used across the resistance arm of the bridge to balance capacity effects of the cells. The cells were immersed in a small thermostat electrically controlled to ±0.02°. All errors due to temperature and to conductance measurements were undoubtedly well within the other errors of reaction velocity measurements.

Solutions of ammonium persulfate and silver nitrate were made up of twice the concentration desired for the experiments; 10 cc. of one was placed in the conductivity cell in the thermostat and 10 cc. of the other withdrawn from a bottle standing in the thermostat and allowed to run into the cell, which was then shaken to mix the solutions thoroughly. The first conductivity reading could be taken one minute, or two minutes at the most, after the solutions were mixed. This turned out to be quite important, as it gave valuable information about the first stages of the reaction, showing that it has an autocatalytic character, a fact which is not evident if one discards the measurements of the first hour. This factor is not apparent in the before-mentioned measurements of Marshall and Inglis, since measurements were not made during the first few minutes of the reaction; however, perhaps an effect of it is seen in the fact that their "unimolecular" constants seem to increase steadily by 3–6% throughout the course of the reaction.

TABLE I

THE CONDUCTIVITY CHANGE IN AMMONIUM PERSULFATE–SILVER NITRATE SOLUTIONS AT 25°

Experiment 3				Experiment 6			
0.0005 M $(NH_4)_2S_2O_8$; 0.0005 M $AgNO_3$				0.001 M $(NH_4)_2S_2O_8$; 0.0005 M $AgNO_3$			
Time, min.	$\kappa \times 10^4$	Time, min.	$\kappa \times 10^4$	Time, min.	$\kappa \times 10^4$	Time, min.	$\kappa \times 10^4$
0	2.203	87	2.442	0	3.620 (extrap.)	165	4.407
1	2.203	248	2.859	1	3.633	253	4.788
2	2.203	452	3.314	2	3.647	389	5.336
6	2.206	626	3.655	3	3.656	486	5.700
8	2.209	721	3.824	4	3.663	746	6.586
10	2.213	1199	4.521	6	3.670	1282	7.938
14	2.222	1559	4.910	10	3.681	1512	8.388
18	2.231	1974	5.250	15	3.702	1861	8.950
22	2.243	3151	5.792	20	3.728	2185	9.369
32	2.274	∞	6.181	25	3.754	2980	10.10
42	2.305			58	3.954	3545	10.44
						∞	11.24

---

[4] The author wishes to thank Mr. W. W. Macalpine of the Columbia University Department of Physics for assistance in building and adjusting this oscillator.

Results of the Measurements

Table I gives the details of two typical experiments, and several experiments are shown graphically in Figs. 1 and 3. Figs. 2 and 4 show the first stages of these same experiments on a much enlarged scale. These figures show that experiments could not be duplicated with certainty.

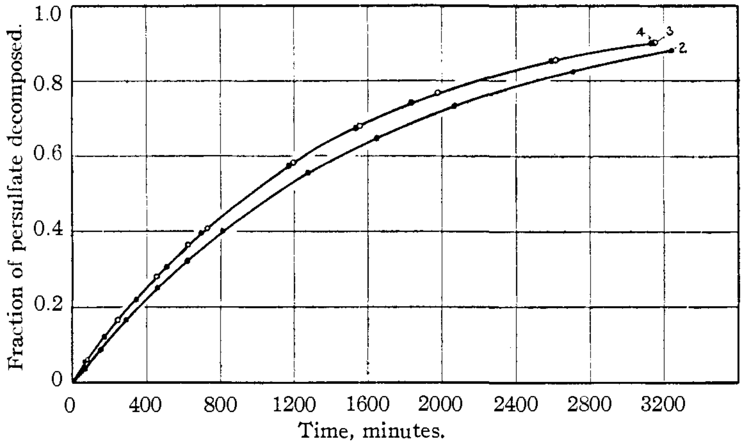

Fig. 1.—Rate of decomposition of 0.0005 *M* ammonium persulfate with 0.0005 *M* silver nitrate as catalyst.

In general, the reaction seemed to be autocatalytic, as shown in Experiments 2, 3, 4, 7 and others not recorded here, but sometimes such effects as shown in Experiments 5 and 6 were present. At any rate, the divergence of the results for duplicate experiments seemed to be due to divergence at the start: this was probably dependent on the exact manner of mixing the solutions, though several experiments failed to show this conclusively. Catalytic effects by the walls of the cell, by the platinum electrodes or by "dust" particles are not ruled out, though rather unlikely.

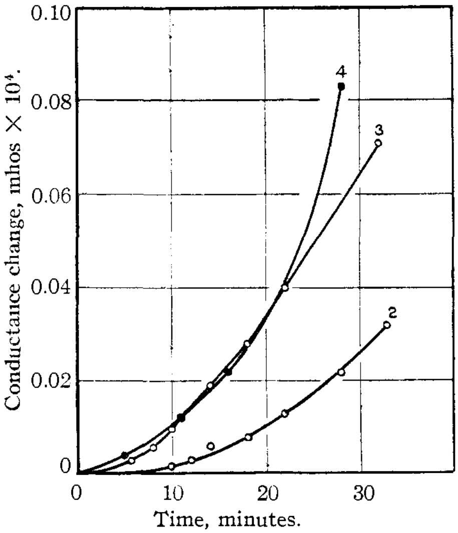

Fig. 2.—The initial part of the curves of Fig. 1.

It has been assumed above that the measured conductivity change is proportional to the amount of persulfate decomposed, an assumption which must be proved. The autocatalytic character of the curves indicates that reaction (3) is not immeasurably rapid, and this means that some small concentration of Ag^{+++} ion is built up in the solution.

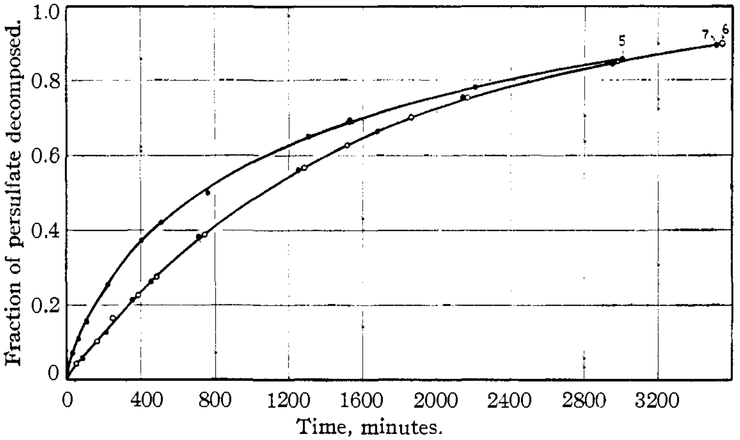

Fig. 3.—The rate of decomposition of 0.001 *M* ammonium persulfate with 0.0005 *M* silver nitrate as catalyst.

The conductance of 0.001 *M* $AgNO_3$ at 25° was 1.360×10^{-4} mhos; that of 0.001 *M* $(NH_4)_2S_2O_8$ was 3.042×10^{-4} mhos. The mean of these is 2.201×10^{-4} mhos. When 10 cc. of each of these solutions were mixed, the conductance was 2.203×10^{-4} mhos. This indicates that in this dilute solution the conductances were additive and there was little, if any, immediate compound formation or reaction of any kind. In the experiments recorded in Table II, various proportions of the freshly mixed solution and the same solution after complete decomposition were mixed and the conductance of these mixtures was compared with the points on the conductance curve to which they would be expected to correspond. To make this clear: in Experiment 3, the freshly made solution had the conductance 2.203×10^{-4} mhos. The conductivity after the persulfate was

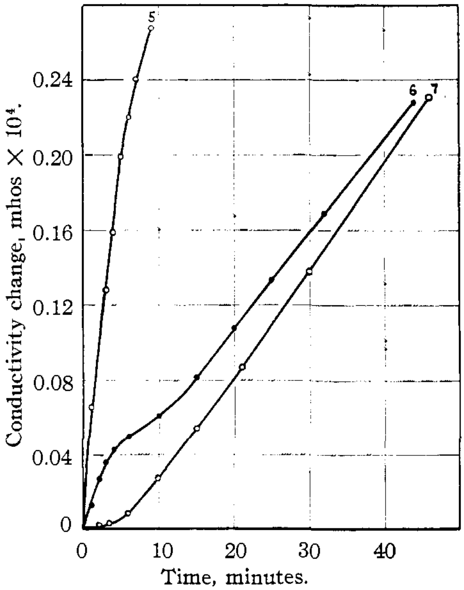

Fig. 4.—The initial part of the curves of Fig. 3.

entirely decomposed was 6.181 × 10^{-4} mhos. The mean of these is 4.192 × 10^{-4} mhos. A mixture of 10 cc. each of the fresh solution and the decomposed solution gave 4.198 × 10^{-4} mhos. Further values are given in Table II.

Table II

Comparison of Conductivities of Mixtures of Initial and Final Solutions with Corresponding Points on the Velocity Curve

Solutions of Experiment 3	$\kappa \times 10^4$	Corresponding κ from curve	Solutions of Experiment 6	$\kappa \times 10^4$	Corresponding κ from curve
40 cc. init., 10 cc. final	3.05	3.00	40 cc. init., 10 cc. final	5.20	5.14
20 cc. init., 10 cc. final	3.59	3.53	20 cc. init., 10 cc. final	6.25	6.16
10 cc. init., 10 cc. final	4.20	4.19	10 cc. init., 10 cc. final	7.55	7.43
20 cc. init., 30 cc. final	4.57	4.59	10 cc. init., 20 cc. final	8.88	8.70
10 cc. init., 20 cc. final	4.86	4.85			
10 cc. init., 30 cc. final	5.23	5.19			

This shows that there are no intermediate compounds formed in the solution in concentration high enough to affect the conductance by more than, say, 1% and that the conductance change really corresponds closely to the persulfate changes.

Discussion of Results

The autocatalytic character of the curves indicates that both reaction (2) and reaction (3) are comparatively slow. As (1) proceeds, a higher and higher concentration of the intermediate compound is built up and reaction (3), being dependent on the concentration of this, proceeds faster and faster, though there is never enough of the intermediate to greatly affect the conductance. There must soon be reached an equilibrium concentration of this intermediate compound; otherwise the "induction" period would be longer; or if persulfate were present in excess of the amount required for all the ammonium ion, the velocity would perhaps keep on increasing indefinitely, until all the ammonium ion was used up. Also, if any appreciable concentration of the intermediate compound were built up in the solution, we should expect it to precipitate. No such precipitation occurred in any of the solutions recorded, but if more concentrated solutions are used, this does occur. If equal volumes of 0.05 *M* solutions of ammonium persulfate and silver nitrate are mixed, the solution becomes discolored at once and there is a slow precipitation of the black compound of trivalent silver. This reaches a maximum amount and if the solution is shaken, all disappears in the course of two hours. This also indicates that the oxidation of the ammonium ion by the trivalent silver is not "instantaneous."

If we were sure that Equation (3) is correct, we could set up an equation for the resultant velocity of the two reactions. However, there are several reasons why this is impracticable. First, we do not know that (3) is the correct expression of the second slow reaction. Second, the equation would be too complicated to test experimentally. Third, the non-reproducibility of the experiments shows the presence of some factor that is as yet unknown. It seems probable that the velocity of the second reaction is of the following form

$$\frac{\mathrm{d}C_{\mathrm{NH_4^+}}}{\mathrm{d}t} = k_2C^n_{\mathrm{Ag^{+++}}}C_{\mathrm{NH_4^+}}F \qquad (9)$$

where F is the kinetic activity factor and depends on the value of n, the number of Ag^{+++} ions taking part in the velocity determining reaction. A combination of (4) and (9) would then give the velocity of oxidation of the ammonium ion in terms that could be tested experimentally, were the expression not so complicated. The mathematics of some types of consecutive reactions has been thoroughly worked out and tested by Wegscheider, Skrabal and others,[5] but no case similar to this, where there is both a continually regenerated catalyst and an activity factor in one or both velocity expressions, has been worked out.

If one neglects the short induction period, and calculates "k" in equation (4), considering $f_2 = 1$, it might be expected that "k" will be much higher than the unimolecular constants obtained by Marshall and Inglis for 1 N and 0.5 N solutions; and that "k" will decrease throughout the reaction as the salt concentration increases. That this is true is shown in Table III. The corresponding k for the 1 N solution is 0.218. In these solutions of equivalent salt concentration 0.0015 to 0.0025, the velocity is, at the start of the reaction (after the induction period), about eight times as rapid.

TABLE III

"k" FROM THE UNIMOLECULAR EQUATION FOR EXPERIMENT 3

Time, min.	67	135	228	432	606	1179	1539	1954
"k"	1.86	1.70	1.59	1.51	1.50	1.48	1.49	1.49

It is seen too, in Table III, that the value of "k" does not decrease as much during the course of the reaction as would be expected from the salt concentration change. This is, no doubt, due to the effect of the second reaction.

Discussion of Other Reactions

In the oxidation of ammonia by persulfate, in alkaline solution, catalyzed by silver ion, studied by Yost and by the present author, there was no noticeable autocatalytic effect. The reaction is much faster, however, in the same salt concentration than the present reaction; and the facts

---

[5] Wegscheider and others, *Monatsh.*, **36**, 471 (1915); *ibid.*, **37**, 137 (1916); *ibid.*, **39**, 741 (1918), and other papers.

that none of the black compound of trivalent silver is precipitated even from comparatively concentrated solutions, and that this black compound, prepared by mixing potassium persulfate and silver nitrate, dissolves very rapidly in ammonia, with evolution of nitrogen, indicate that in this case the second reaction is very much faster. This undoubtedly makes the autocatalytic character of the curve disappear.

Equation (9) makes the velocity dependent on the concentration of reducing agent. The effect of ammonium ion concentration was not thoroughly studied in this investigation; but while experiments 3 and 4 should be faster than 6 and 7, due to the lower salt concentration, they show about the same velocity. This is probably due to the fact that the ammonium ion concentration was lower in experiments 3 and 4. Some experiments with 0.0001 M ammonium persulfate and 0.0005 M silver nitrate showed a somewhat higher velocity, though again not as much higher as would be expected with the lower salt concentration. This was probably also due to the fact that the ammonium ion concentration was lower, as well as the total salt concentration. Yost[3] found a linear relation between ammonia concentration and reaction velocity; this he explained by assuming that in more concentrated ammonia solutions more of a higher complex with Ag^+ ion than $Ag(NH_3)^+_2$ is formed. The present work makes it seem quite possible that even though the second step of the oxidation is fast compared to the first, it is not so fast that the concentration of the reducing agent does not have some influence on the resultant velocity.[6]

One might suspect that other "catalytic" reactions would show this autocatalytic type of velocity curve. The unimolecularity of the inversion of sugar, catalyzed by acid, has been questioned; it seems that the first part of the curve may be irregular.[7] The measured velocity constants increase as the reaction proceeds, even if correction is made for the "mutarotation lag" of the inversion products. This would be in accord with a slight autocatalytic effect, in a reaction where there is no salt effect due to change in ion concentration during the course of the reaction. It is probable that a hydrated sugar molecule is inverted by hydrogen ion in

---

[6] It should be noted that the oxidation of ammonia and ammonium ion has not been investigated in solutions containing both these ions over a wide range of relative concentrations. Marshall's work indicated that the oxidation to nitrate is quantitative in solutions originally containing only neutral ammonium persulfate and silver salt. An experiment by the present writer showed that no appreciable amount of nitrogen was evolved during twenty-four hours from such a solution. Some of the solutions recorded in section I of this series contained ammonium ion, increasing in concentration as the reaction progressed, but also an excess of free ammonia, and no diminution in the amount of nitrogen evolved was observed. It would be valuable to investigate the nature of the reaction in solutions of intermediate P_H.

[7] Fales and Morrell, THIS JOURNAL, **44**, 2071 (1922); Pennycuick, *ibid.*, **48**, 6 (1926); see, however, Scatchard, *ibid.*, **48**, 2259 (1926).

two steps, which we may represent as follows, neglecting hydration of the hydrogen ion and the corresponding complications

$$C_{12}H_{22}O_{11}\cdot nH_2O + H^+ \longrightarrow C_{12}H_{22}O_{11}\cdot nH_2O\cdot H^+ \qquad (10)$$

$$C_{12}H_{22}O_{11}\cdot nH_2O\cdot H^+ \longrightarrow \text{invert sugar} + H^+ \qquad (11)$$

Only if reaction (11) is "instantaneous" would we expect a unimolecular sugar inversion; if (11) is slow enough that the intermediate compound increases in concentration for a time, the curve will have at least some indication of an autocatalytic character.

The hydrogen ion catalysis of ester hydrolysis does not present the irregularities that the sugar inversion does. If the mechanism is similar to that of the sugar inversion, this would mean that the reaction corresponding to (11) is very rapid compared to that corresponding to (10).

The ester–acid–water system has been investigated to find if there are any ternary compounds formed immediately on mixing the solution and no conclusive evidence of any appreciable concentration of such compounds was found,[8] although previous work made it seem quite certain that the hydrolysis proceeds through the formation of intermediate compounds.[9] However, the investigation mentioned was not extended to looking for a slow accumulation of such ternary compounds as the reaction proceeds; but as mentioned before, the unimolecularity, or rather "pseudo-unimolecularity" of the hydrolysis makes it unlikely that there is any such accumulation. On the other hand, in the case of the sugar inversion, it is possible that there is a slight accumulation of such an intermediate, and this might be detected experimentally.

Summary

The velocity of oxidation of ammonium ion by persulfate ion, catalyzed by silver ion, has been measured in much more dilute solutions than before.

It is shown that the conductance method used gives a nearly correct measure of the velocity.

The velocity curves are mostly autocatalytic, though not strictly reproducible, showing that the reaction proceeds through at least two steps of comparable velocity. In previous work on persulfate oxidations catalyzed by silver ions it has been assumed that the second step is immeasurably fast.

It is suggested that the irregularities in sugar inversion catalyzed by hydrogen ion may be due to a slight autocatalytic effect similar to the one measured here.

New York, N. Y.

---

[8] Kendall and King, *J. Chem. Soc.*, **127**, 1778 (1925).

[9] Kendall and Booge, This Journal, **38**, 1712 (1916); *J. Chem. Soc.*, **127**, 1768 (1925).