REDUCTION OF PEROXYSULFATE BY VANADYL ION WITH SILVER ION AS CATALYST

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Introduction

Investigation[1] of the catalytic effect of silver ion on the reduction of peroxysulfates by chromic salts has shown that the mechanism consists simply in the slow oxidation of the silver to the trivalent state and in subsequent rapid reaction between the oxidized silver and chromic salt to form chromate ion and univalent silver.   When ammonia[2] is the reducing agent, however, the reaction proceeds much more rapidly than would be the case if only the free silver ion were the reactive substance.   It was assumed in this case that the silver–ammonia ion was also reactive, and that, moreover, it reacted much more rapidly with the peroxysulfate ion than did the free silver ion.   To explain the effect of the concentration of the ammonia on the reaction, it was also assumed that a silver ammonia complex containing three ammonia molecules was present in the solution, that this was in equilibrium with the diammine complex and reacted more rapidly than the latter with peroxysulfate ion.

In a very interesting series of papers King[3] has described further investigations upon the ammonia reaction, as well as upon reactions in which ammonium ion and oxalate ion are the reducing agents.   He found that the influence of potassium hydroxide on the ammonia reaction is an ion-concentration effect, as established in other cases by Brönsted, and not a specific effect as was at first supposed.   He also found that, when oxalate ion acts as the reducing agent, the reaction is not so simple as in the case of chromic ion, inasmuch as it showed certain specific effects of the reducing reagent.   In this case the rate is many times greater than that of the ammonia reaction.

These results seem to indicate that the reducing agent in each case has a specific influence, and that it does not serve merely to reduce rapidly the trivalent silver that forms as a result of the slow reaction between the univalent silver and peroxysulfate ions.   To determine whether or not this is the case, it is necessary to have another reaction which proceeds at the same rate as the chromium reaction where the possibility of complex ion formation is not involved.   That specific effects, in some cases, do exist is, of course, not questioned.

[1] D. M. Yost, THIS JOURNAL, **48**, 152 (1926).

[2] D. M. Yost, ibid., **48**, 374 (1926).

[3] C. V. King, ibid., **49**, 2689 (1927); **50**, 2080 (1928); **50**, 2089 (1928); **52**, 1493 (1930).

The experiments described in this paper were made with vanadyl ion VO^{++} as the reducing agent. This reaction, which has not been previously studied, was investigated with the view to determine whether or not the vanadyl ion exhibits any specific effects on the catalyzed reaction, and to determine also the effect of changes in the ionic strength of the solutions on the rate.

That vanadyl ion does not react appreciably with peroxysulfate ion at room temperatures was found by one of us some time ago, and was confirmed before the present work was begun. Preliminary experiments showed that in the presence of silver ion vanadyl ion is oxidized to vanadic acid at a measurable rate at 25° in accord with the over-all reaction

$$S_2O_8^- + 2VO^{++} + 4H_2O = 2SO_4^- + 2HVO_3 + 6H^+ \qquad (1)$$
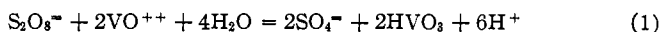
Preparation of the Stock Solutions

Potassium Peroxysulfate.—The pure salt was dissolved in distilled water. Its concentration was determined by adding an excess of standard, acidified ferrous sulfate solution and subsequently determining the excess with standard permanganate.

Vanadyl Perchlorate.—A weighed amount of vanadium pentoxide, prepared by carefully heating ammonium vanadate in the presence of oxygen, was suspended in a solution which contained slightly less than the calculated amount of perchloric acid necessary to form vanadyl perchlorate. The mixture was then treated with hydrogen sulfide until all the vanadium had been reduced to the tetravalent state. Additional acid was added to redissolve any precipitate of vanadium formed, the amount required being small and only slightly greater than that necessary to form vanadyl perchlorate. The sulfur formed was filtered off and the filtrate heated to boiling to remove the excess hydrogen sulfide. The resulting blue solution was again treated with hydrogen sulfide, the small precipitate of sulfur filtered off and the filtrate heated to expel the hydrogen sulfide. The final solution was deep blue in color and contained no sulfate, sulfide or ammonium salts.

Silver Perchlorate.—Precipitated silver carbonate was treated with just enough perchloric acid to dissolve it. The filtered solution was very nearly neutral.

Magnesium Nitrate.—The oxide was treated with nitric acid until the resulting solution was neutral.

Experimental Procedure

The stock solutions of potassium peroxysulfate, vanadyl perchlorate, silver perchlorate and perchloric acid were kept in the thermostat at 25°. In each experiment portions of these solutions were pipetted into a flask, the silver being added last and the time counted from its addition. At suitable intervals portions of the reacting mixture were withdrawn with a pipet and run into a flask which contained enough hydrochloric acid to cause the precipitation of all the silver present. The unoxidized vanadium was titrated with permanganate.

Results of the Measurements upon the Rate Mechanism

In Table I are given the detailed results of representative experiments in which the ionic strengths are comparable with those used in the former

experiments with chromic salt as the reducing agent. The values of the specific reaction rate k given in the last column were calculated on the assumption that the rate is directly proportional to the concentrations of peroxysulfate and silver ions, but is independent of the concentration of vanadyl ion (*cf.* Eq. 6, below). All experiments were made at 25°. The concentrations are all expressed in moles per liter of solution and the time in minutes.
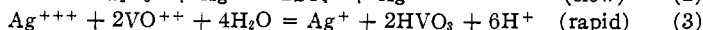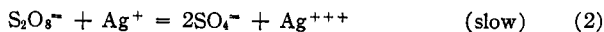
<div align="center">TABLE I</div>

<div align="center">RESULTS OF RATE EXPERIMENTS MADE TO DETERMINE THE MECHANISM</div>

Experiment 1			Experiment 2		
$K_2S_2O_8 = 0.0508$; $AgClO_4 = 0.0202$; $VO(ClO_4)_2 = 0.1047$; $HClO_4 = 0.1000$			$K_2S_2O_8 = 0.0508$; $AgClO_4 = 0.0202$; $VO(ClO_4)_2 = 0.0524$; $HClO_4 = 0.1000$		
Minutes	$S_2O_8^-$	k	Minutes	$S_2O_8^-$	k
0	0.0508	..	0	0.0508	..
17.6	.0439	0.413	19.3	.0423	0.466
37.1	.0388	.360	38.2	.0375	.392
50.3	.0361	.336	58.2	.0329	.368
66.3	.0327	.329	70.1	.0304	.362
85.8	.0293	.318	87.1	.0267	.366
105.1	.0266	.305			
151.8	.0202	.300			
195.9	.0151	.306			

Experiment 3			Experiment 4		
$K_2S_2O_8 = 0.0508$; $AgClO_4 = 0.0101$; $VO(ClO_4)_2 = 0.1047$; $HClO_4 = 0.1000$			$K_2S_2O_8 = 0.0254$; $AgClO_4 = 0.0202$; $VO(ClO_4)_2 = 0.1047$; $HClO_4 = 0.1000$		
Minutes	$S_2O_8^-$	k	Minutes	$S_2O_8^-$	k
0	0.0508	..	0	0.0254	..
29.0	.0440	0.491	35.8	.0185	0.438
53.1	.0414	.383	60.0	.0157	.396
70.8	.0383	.394	84.4	.0134	.375
88.9	.0367	.362	103.4	.0112	.392
110.5	.0349	.336	136.2	.0101	.336
224.3	.0244	.324	170.8	.0080	.335
337.5	.0171	.318	221.8	.0061	.313

The results of Expts. 1 and 2, which differ only in the concentration of vanadyl ion, show that the specific rate k is independent of the concentration of vanadyl ion, as was assumed. A comparison of Expts. 1 and 3 shows that the rate is directly proportional to the concentration of silver ion, whose concentration was varied two-fold in the two runs. The effects of all the reactants were also determined by the well-known graphical methods, and the results of such determinations are in complete accord with the comparisons of the specific reaction rates just made.

The average value of all specific rates for the reaction where chromic chromium was the reducing agent was given as $k = 0.333$,[1] and this value is in good agreement with those given in Table I. The mechanism and rate of the present reaction are therefore without much doubt the same

as that found for the reaction with chromium salts. It follows from this that neither the chromic ion nor the vanadyl ion has any specific effect on the reaction, and that they serve merely to reduce rapidly the trivalent silver formed in the slow reaction.

The reactions indicating the mechanism are, accordingly

$$S_2O_8^- + Ag^+ = 2SO_4^- + Ag^{+++} \qquad \text{(slow)} \qquad (2)$$
$$Ag^{+++} + 2VO^{++} + 4H_2O = Ag^+ + 2HVO_3 + 6H^+ \quad \text{(rapid)} \qquad (3)$$

It seems safe to conclude that in those cases where the rate is greater than that found for the chromium and vanadium reactions, the increase very probably results from the greater reactivity of a complex ion formed between the silver ion and the reducing agent. The same explanation can also be applied to cases where the rate is slower. These statements refer only to the rate of disappearance of the peroxysulfate ion.

The statement that the rate is independent of the concentration of vanadyl ion must, to be sure, be modified somewhat, since a decrease in its concentration decreases the ionic strength of the solution. And Brönsted has shown in the case of many reactions where the slow reaction is between a negatively and positively charged ion, that this results in an increase in the rate. This effect is noticeable when the specific rates for Expts. 1 and 2 are examined more closely. Moreover, these specific rates decrease in value with time, which is in accord with the fact that the ionic strength of a given reaction mixture increases as the reaction proceeds.

Bjerrum's modification of the theory proposed by Brönsted[4] to explain the effect of the ionic strength on the rates of ionic reactions, rests upon the assumption that the reacting ions are in equilibrium with a complex ion formed by the union of the reacting ions, and that the rate of decomposition of the complex is dependent only upon its concentration. The equilibrium concentration of the complex is, of course, dependent upon its activity coefficient and upon the concentrations and activity coefficients of the reacting ions. In the present case the formula of the complex would be $AgS_2O_8^-$, and its concentration would be given by the mass action expression

$$(AgS_2O_8^-) = K(Ag^+)(S_2O_8^-)f_1f_2/f_3 \qquad (4)$$

where K is the equilibrium constant and f_1, f_2 and f_3 are the activity coefficients of the silver, peroxysulfate and complex ions, respectively. If now, as a first approximation, it be assumed that the activity coefficients f_1 and f_3 of the two univalent ions are equal, then the rate equation takes the form

$$- \frac{d(S_2O_8^-)}{dt} = k_0K(Ag^+)(S_2O_8^-)f_2 \qquad (5)$$

[4] J. N. Brönsted, "The Theory of Velocity of Ionic Reactions" (cf. "Contemporary Developments in Chemistry"), Columbia University Press, New York, 1927. See also Z. physik. Chem., 102, 169 (1922); Bjerrum, ibid., 108, 82 (1924).

The activity coefficient f_2 of the doubly charged peroxysulfate ion decreases rapidly as the ionic strength μ of the solution increases and hence the measured specific reaction rate $k = k_0 K f_3$ also decreases with increasing ionic strength. For very dilute solutions, according to the interionic attraction theory,[5] $\log f_2 = -\beta Z^2 \sqrt{\mu}$, where β is a constant, Z the ionic charge, and $\mu = \frac{1}{2} \Sigma Z_i^2 C_i$ the ionic strength. This formula shows quantitatively how f_2 changes with the ionic strength and shows also that at infinite dilution the specific reaction rate is equal to $k_0 K$.

To bring out more clearly the effect of the ionic strength on the rate of the vanadyl reaction, experiments were made with more dilute solutions and with solutions containing varying amounts of magnesium nitrate.[6] In Table II are given the detailed results of four representative experiments made as before at 25°. The values of k were calculated as before from the integrated rate equation.

$$k = 2.3 \log \frac{C_0}{C} /(\text{Ag}^+)t \tag{6}$$

where C_0 is the initial concentration of peroxysulfate ion and C its concen-

TABLE II

EXPERIMENTS ON THE EFFECT OF IONIC STRENGTH ON THE RATE

Experiment 5

$K_2S_2O_8 = 0.01205$; $AgClO_4 = 0.01049$; $VO(ClO_4)_2 = 0.02065$; $Mg(NO_3)_2 = 0.607$; $\mu = 1.930$

Minutes	$S_2O_8^-$	k
0	0.01205	..
50.9	.01039	0.218
94.7	.00988	.200
139.1	.008915	.200
199.7	.00782	.202
264.5	.00683	.202

Experiment 6

$K_2S_2O_8 = 0.0195$; $AgClO_4 = 0.01707$; $VO(ClO_4)_2 = 0.0336$; $Mg(NO_3)_2 = 0.493$; $\mu = 1.651$

Minutes	$S_2O_8^-$	k
0	0.01959	..
60.3	.01554	·0.224
99.5	.01352	.219
143.5	.01144	.219
203.6	.00931	.215
267.3	.00725	.218

Experiment 7

$K_2S_2O_8 = 0.01205$; $AgClO_4 = 0.01049$; $VO(ClO_4)_2 = 0.02065$; $\mu = 0.1089$

Minutes	$S_2O_8^-$	k
0	0.01205	..
46.2	.00905	0.588
80.5	.00761	.545
135.3	.00578	.518
170.2	.00487	.507
208.8	.00402	.502
240.7	.00356	.481

Experiment 8

$K_2S_2O_8 = 0.00603$; $AgClO_4 = 0.01049$; $VO(ClO_4)_2 = 0.01033$; $\mu = 0.0595$

Minutes	$S_2O_8^-$	k
0	0.00603	..
52.6	.00430	0.609
85.0	.00355	.563
141.9	.00259	.523
173.0	.00221	.581
211.2	.00170	.615

[5] A. A. Noyes, THIS JOURNAL, **46**, 1080 (1924).

[6] That nitrate or nitric acid, at the concentrations used in the experiments, does not oxidize the quadrivalent vanadium at a measurable rate at 25° was established by independent experiments. It was not possible to use magnesium perchlorate, since its resulting high concentration would cause the precipitation of potassium perchlorate, which in turn might carry down with it some of the reactants.

tration at the time t. The time is expressed in minutes and the concentrations in moles per liter of solution.

The experiments made at high and therefore nearly constant ionic strengths yield rate constants which show no definite trends,[7] as may be seen in the table. Moreover, the constants are much smaller than those resulting from experiments made at lower ionic strengths, as a comparison of Expts. 5 and 6 with Expts. 7 and 8 shows. This behavior is that which would be predicted from Brönsted's theory. It was not possible to carry out experiments at still lower ionic strengths, and therefore the limiting value of the specific rate k and the limiting slope of the log $k/\sqrt{\mu}$ curve could not be determined. The qualitative agreement with the theory is satisfactory.

Summary

The catalytic effect of silver ion on the reaction between peroxysulfate and vanadyl ions has been studied. It was found that the rate is directly proportional to the concentrations of peroxysulfate and silver ion, but independent of the concentration of vanadyl ion. The specific reaction rate was found to be the same as that when chromic chromium is the reducing agent, showing that no specific effect of the reducing agent is involved in either case. The facts indicate that the two reactions have the same mechanism, and that this consists in a slow oxidation of the univalent silver to the trivalent state, followed by rapid reduction of the trivalent silver by the vanadyl ion to yield vanadic acid and univalent silver. It was suggested that the specific effects of other reducing agents may be ascribed to the different reactivity of a complex compound formed from the silver ion and the reducing agents.

It was also found that the effect of an increase in ionic strength upon the rate is qualitatively that which is predicted when Brönsted's theory is assumed.

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[7] For a treatment of the problem for cases where the ionic strength varies with time, cf. Scatchard, THIS JOURNAL, **52**, 52 (1930).