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Reduction of Peroxysulfate by Manganous Ion and by Hydrazine with Silver Ion as Catalyst

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Investigation of the catalytic effect of silver ion on the reduction of peroxysulfates by chromic ion[1] and by vanadyl ion[2] has shown that the mechanism consists simply in the slow oxidation of univalent silver to the trivalent state followed by a rapid reaction between the oxidized silver and the reducing agent to form univalent silver and chromate or vanadate ions. Furthermore, the specific reaction rates for these two reducing agents were found to be approximately equal, showing that in these cases the reducing agent has little or no specific effect upon the reaction, but serves only to reduce rapidly the oxidized silver.

When ammonia[3] is the reducing agent, however, the rate is much more rapid than would be the case if free silver ion were the only reactive substance. It was assumed in that case that the silver–ammonia complexes were also reactive and that they reacted more rapidly with peroxysulfate ion than did free silver ion. Further investigations by King[4] using ammonia, ammonium ion, and oxalate ion as reducing agents showed that in these reactions specific effects due to the reducing agent are present. Bekier and Kijowski have studied the reactions in which manganous ion[5] and acetone[6] are the reducing agents. Their experiments with manganous ion were not, however, made at ionic strengths comparable with those of previous experiments, and do not prove the presence or absence of a specific influence. Their study of the acetone reaction made at comparable ionic strengths shows that acetone exerts a specific effect. Work in progress at this Laboratory indicates that formic acid also exhibits a specific effect.

The experiments described in this paper were made with manganous ion and hydrazine, respectively, as reducing agents. The reactions were investigated to determine whether or not these ions exhibit any specific influence on the silver catalyzed reduction of peroxysulfate.

That neither manganous ion nor hydrazine reacts appreciably with peroxysulfate ion in the absence of silver was determined by preliminary experiments. When the catalyst is present the reactions proceed at a measurable rate at 25° under the conditions of the experiments in accord with the over-all equations

$$S_2O_8^{=} + Mn^{++} + 2H_2O = 2SO_4^{=} + MnO_2 + 4H^+ \quad (1)$$

$$2S_2O_8^{=} + N_2H_5^+ = 4SO_4^{=} + N_2 + 5H^+ \quad (2)$$

Hydrazine does not reduce silver ion to metallic silver in 0.1 formal perchloric acid.

Preparation of Solutions

Potassium Peroxysulfate.—The pure salt was dissolved in distilled water and the solution standardized by determining with permanganate or dichromate how much ferrous ion was oxidized by a definite volume.

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

Silver Nitrate.—The pure salt was dissolved in distilled water and its concentration corrected in each experiment for the small amount of chloride present in the manganous nitrate.

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

Manganous Nitrate.—The pure salt was dissolved in distilled water and the solution standardized by the bismuthate method.

Hydrazine Perchlorate.—Hydrazine hydrate (E. K. Co.) was diluted with distilled water, and perchloric acid was added until the resulting solution was neutral. It was standardized by adding a portion to an excess of standard bromine in potassium bromide solution, adding a large excess of potassium iodide, and titrating the liberated iodine with sodium thiosulfate.[7]

Experimental Procedure.—In each experiment a portion of the potassium peroxysulfate solution was pipetted into a flask; portions of the other stock solutions were pipetted into a separate flask; the two flasks were placed in the thermostat for two hours and mixed at an observed time. At suitable intervals portions of the reacting mixture were withdrawn, and in the case of the manganous reaction run into a dry flask, and shaken with enough solid sodium chloride to precipitate all the silver present. The solution was filtered through asbestos to remove the manganese dioxide and silver chloride and a definite volume withdrawn for analysis. The concentration of

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(1) Don M. Yost, THIS JOURNAL, **48**, 152 (1926).

(2) Don M. Yost and W. H. Claussen, *ibid.*, **53**, 3349 (1931).

(3) Don M. Yost, *ibid.*, **48**, 374 (1926).

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

(5) Bekier and Kijowski, *Roczniki Chem.*, **14**, 1004 (1934).

(6) Bekier and Kijowski, *ibid.*, **15**, 136 (1935).

(7) W. C. Bray and E. J. Cuy, THIS JOURNAL, **46**, 858 (1924).

peroxysulfate was determined by adding an excess of standard ferrous sulfate and subsequently titrating the excess with permanganate.

In the hydrazine reaction the presence of nitrogen bubbles in the pipetted sample introduced a slight uncertainty in the volume. The method of analysis chosen consisted in oxidizing the hydrazine present with chlorine, removing the excess chlorine with a stream of air and finally determining the peroxysulfate with ferrous iron. To this end an excess of hydrochloric acid was added to the sample to remove the silver ion and the sample then subjected to the following treatment. An excess of chlorine water was added and the solution let stand for fifteen minutes. It was then placed in a water-bath at 40° for fifteen minutes in order to remove the last trace of hydrazine, which interferes with the indicator reaction in the subsequent titration. A moderate stream of air was bubbled through the solution for a quarter hour to remove the unreacted chlorine. An excess of standard ferrous sulfate solution was then added and the excess titrated with dichromate using diphenylamine as indicator.

Results of the Rate Measurements

In Tables I and II are given the detailed results of representative experiments on the rates of the manganous ion and hydrazine reactions, respectively. In each case the values given are the averages of the results of two exactly duplicate experiments which agreed closely with each other. All experiments were made at 25.00°. The concentrations are all expressed in moles per liter of solution and the time is expressed in minutes. μ is the initial ionic strength. 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

TABLE I

RESULTS OF RATE EXPERIMENTS WITH MANGANOUS ION AS THE REDUCING AGENT

Experiment 1			Experiment 2		
$K_2S_2O_8 = 0.0488$; $AgNO_3 = 0.01956$; $Mn(NO_3)_2 = 0.1012$; $HNO_3 = 0.1000$; $\mu = 0.570$			$K_2S_2O_8 = 0.0488$; $AgNO_3 = 0.01982$; $Mn(NO_3)_2 = 0.0506$; $HNO_3 = 0.1000$; $\mu = 0.418$		
t, min.	$(S_2O_8^{=})$	k	t, min.	$(S_2O_8^{=})$	k
0	0.0488	...	0	0.0488	...
33.0	.0409	0.274	30.5	.0405	0.308
59.7	.0354	.275	60.3	.0342	.298
93.7	.0300	.266	90.9	.0288	.293
121.5	.0259	.267	119.8	.0246	.289
153.4	.0222	.263	150.3	.0208	.286
179.7	.0198	.257	180.8	.0179	.280
208.9	.0171	.257	209.9	.0158	.271

Experiment 3			Experiment 4		
$K_2S_2O_8 = 0.0488$; $AgNO_3 = 0.00956$; $Mn(NO_3)_2 = 0.1012$; $HNO_3 = 0.1000$; $\mu = 0.560$			$K_2S_2O_8 = 0.0239$; $AgNO_3 = 0.01956$; $Mn(NO_3)_2 = 0.1012$; $HNO_3 = 0.1000$; $\mu = 0.495$		
0	0.0488	...	0	0.0239	...
31.3	.0445	0.311	31.0	.0199	0.298
59.9	.0413	.291	59.8	.0169	.292
91.4	.0381	.283	90.7	.0143	.286
120.0	.0358	.270	120.1	.0123	.279
150.7	.0330	.272	150.5	.0103	.282
180.6	.0306	.270	181.7	.0089	.274
211.0	.0285	.267	210.6	.0076	.275

The effect of ionic strength μ on the rate

Experiment 5			Experiment 6		
$K_2S_2O_8 = 0.00950$; $AgNO_3 = 0.00989$; $Mn(NO_3)_2 = 0.0202$; $\mu = 0.0990$			$K_2S_2O_8 = 0.00941$; $AgNO_3 = 0.00989$; $Mn(NO_3)_2 = 0.0202$; $Mg(NO_3)_2 = 0.600$; $\mu = 1.899$		
0	0.00950	...	0	0.00941	...
32.6	.00805	0.514	32.8	.00875	0.224
60.8	.00700	.507	61.2	.00820	.227
91.1	.00603	.505	94.1	.00770	.215
119.5	.00533	.489	121.9	.00736	.204
151.5	.00460	.484	151.8	.00688	.209
183.8	.00405	.469	195.8	.00613	.221
210.5	.00355	.473			

TABLE II

RESULTS OF RATE EXPERIMENTS WITH HYDRAZINE AS THE REDUCING AGENT

Experiment 1			Experiment 2		
$K_2S_2O_8 = 0.0398$; $AgClO_4 = 0.01925$; $N_2H_5ClO_4 = 0.0280$; $HClO_4 = 0.0926$; $\mu = 0.259$			$K_2S_2O_8 = 0.0398$; $AgClO_4 = 0.01925$; $N_2H_5ClO_4 = 0.0140$; $HClO_4 = 0.0926$; $\mu = 0.245$		
t, min.	$(S_2O_8^{=})$	k	t, min.	$(S_2O_8^{=})$	k
0.0	0.0398	...	0.0	0.0398	...
30.2	.0294	0.521	10.8	.0358	0.509
60.6	.0220	.508	20.9	.0326	.496
90.4	.0171	.485	32.0	.0293	.497
120.8	.0133	.471	45.8	.0261	.478
150.7	.0103	.466	60.8	.0230	.468
180.4	.0080	.462			
210.9	.0065	.446			

Experiment 3			Experiment 4		
$K_2S_2O_8 = 0.0398$; $AgClO_4 = 0.00963$; $N_2H_5ClO_4 = 0.0280$; $HClO_4 = 0.0926$; $\mu = 0.250$			$K_2S_2O_8 = 0.0199$; $AgClO_4 = 0.01926$; $N_2H_5ClO_4 = 0.0280$; $HClO_4 = 0.0926$; $\mu = 0.200$		
0.0	0.0398	...	0.0	0.0199	...
30.8	.0338	0.551	30.6	.0141	0.598
61.0	.0292	.527	60.4	.0104	.558
91.2	.0254	.511	90.4	.00764	.550
120.3	.0221	.507	121.1	.00562	.542
150.5	.0194	.496	150.0	.00406	.550
180.6	.0170	.489	180.2	.00294	.551
210.6	.0152	.472	210.8	.00226	.536

The effect of ionic strength μ on the rate

Experiment 5			Experiment 6		
$K_2S_2O_8 = 0.0382$; $AgClO_4 = 0.0228$; $N_2H_5ClO_4 = 0.0201$; $HClO_4 = 0.0926$; $Mg(NO_3)_2 = 0.1099$; $\mu = 0.580$			$K_2S_2O_8 = 0.0377$; $AgClO_4 = 0.0228$; $N_2H_5ClO_4 = 0.0201$; $HClO_4 = 0.0926$; $Mg(NO_3)_2 = 0.2317$; $\mu = 0.945$		
0.0	0.0382	...	0.0	0.0377	...
30.8	.0298	0.353	60.5	.0228	0.363
60.0	.0236	.351	90.0	.0175	.373
90.2	.0192	.335	120.5	.0153	.327
120.0	.0158	.322	152.5	.0116	.338
150.5	.0137	.299	181.0	.00984	.325
181.0	.0104	.315	210.0	.00830	.316
210.0	.00878	.306			

peroxysulfate and silver ions, but is independent of the concentration of the reducing agent. That is

$$k = 2.3 \log \frac{C_0}{C} \Big/ (\mathrm{Ag}^+)t$$

where C_0 is the initial concentration of peroxysulfate ion and C its concentration at the time t.

In each table the results of Experiments 1 and 2, which differ only in the concentration of the respective reducing agent, show that the specific rate k is independent of the concentration of reducing agent. A comparison of Experiments 1 and 3 for each series shows that the rate is directly proportional to the concentration of silver ion. Experiments 1 and 4 show that the rate is also directly proportional to the peroxysulfate concentration. The well-known graphical methods lead to the same conclusions.

Experiments 5 and 6 were made to bring out clearly the effect of ionic strength on the rate of each reaction. Magnesium nitrate[8] was used to increase the ionic strength of the solutions. The change in rate is in qualitative agreement with the predictions of the Brönsted[9] theory of the effect of ionic strength on the rates of reactions for the case involving oppositely charged ions. Moreover, the specific rates decrease in value with time, in accord with the fact that the ionic strength of each reaction mixture is at the end of the reaction from 2 to 8% greater than at the beginning.

In Table III are given the initial ionic strengths and corresponding mean specific reaction rates for the first three to three and one-half hours for the chromic ion and vanadyl ion reactions, which apparently involve no specific effects, and for the manganous ion and hydrazine reactions.

While the agreement is short of quantitative it is close enough to suggest that specific effects due to the four reducing agents result from changes in the activities of the reacting ions rather than from side reactions or reactions other than those to be postulated for the mechanism.

TABLE III

Reducing agent	Initial ionic strength, μ	Mean specific reaction rate, k
Chromic ion[1]	0.234	0.341
	.485	.319
Vanadyl ion[2]	.0595	.578
	.109	.524
	.587	.334
	1.651	.219
	1.930	.204
Manganous ion	0.0990	.491
	.418	.289
	.570	.266
	1.899	.217
	2.317[5]	.188
Hydrazine	0.200	.555
	.259	.480
	.580	.326
	.945	.340

The experiments indicate that the two reactions described here proceed for the most part according to the usual simple mechanism consisting in the initial slow step

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

followed by the rapid reactions

$$\mathrm{2Ag^{+++} + N_2H_5^{+} = 2Ag^{+} + N_2 + 5H^{+}}\ \text{(rapid)} \qquad (4)$$

or

$$\mathrm{Ag^{+++} + Mn^{++} + 2H_2O = Ag^{+} + MnO_2 + 4H^{+}}\ \text{(rapid)} \qquad (5)$$

as the case may be.

Summary

The catalytic effect of silver ion on the reduction of peroxysulfate ion by manganous ion and by hydrazine has been studied. It was found that the rate was directly proportional to the concentrations of peroxysulfate and silver ion, but independent of the concentration of the reducing agent. The specific reaction rates where manganous ion and hydrazine are reducing agents were found to differ only slightly from those found previously for chromic chromium and vanadyl ion, showing that little or no specific effect of the reducing agent is involved in each case. The reaction mechanism appears to be essentially the same in all four cases and is assumed to consist in the slow oxidation by peroxysulfate of silver from the univalent to the trivalent state, followed by the rapid reaction between the reducing agent and trivalent silver to form univalent silver.

The effect of the ionic strength on the rate of each reaction was found to be in qualitative agreement with the predictions from Brönsted's theory.

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(8) It was determined independently that neither nitrate or nitric acid at the concentrations used in the experiments oxidizes hydrazine at an appreciable rate at 25°.

(9) J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); *Chem. Rev.*, **5**, 231 (1928).