[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF IDAHO]

The Reduction of Peroxydisulfate by Cerous Ion, Catalyzed by Silver Nitrate

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The rate of reduction of peroxydisulfate by chromic ion,[1] by vanadyl ion[2] and by manganous ion and hydrazine[3] has been shown to be independent of the concentration of the reducing agent. The reaction rate could be represented by the equation, $2.3/t(\mathrm{Ag}^+) \log C_0/C$, where C_0 is the initial concentration of peroxydisulfate and C is the concentration of peroxydisulfate at time t. The experiments described in this paper were performed to see if the reduction of peroxydisulfate by cerous sulfate followed the same equation, and to study the effect of temperature on the reaction rate.

Experimental

Cerous Sulfate.—The cerous sulfate was freed of chloride by adding a small amount of silver nitrate to a nearly saturated solution which was acid with sulfuric acid. This solution was filtered and crystals of cerous sulfate obtained by evaporation. The crystals were washed with dilute sulfuric acid to remove traces of silver ion and then dissolved in approximately molar sulfuric acid.

Potassium Peroxydisulfate.—Reagent grade peroxydisulfate was used without purification but was assayed by adding weighed samples to an excess of ferrous sulfate and back titrating the ferrous sulfate with a standard solution of ceric nitrate.

Silver Nitrate.—A solution of silver nitrate was prepared and analyzed by the Mohr method.

Experimental Procedure.—Analysis of the reaction mixture was made colorimetrically by means of an American Instrument Company type V photometer. A solution of ceric sulfate of known strength was diluted with the prepared solution of cerous sulfate to form a series of dilute ceric ion solutions. These solutions were successively placed in a cell of 10.015 mm. thickness and readings of the photometer taken for each dilution. A calibration curve of photometer readings *vs.* ceric ion concentration was then plotted, which served to convert photometer readings into concentration of ceric ion.

The experiments were carried out by pipeting 50 or 100 ml. of the cerous sulfate solution into a 200-ml. flask, which was placed in a thermostat regulated to ±0.05°. After thirty minutes, a weighed portion of the peroxydisulfate was added and allowed to dissolve. The photometer cell was filled with this solution and the instrument adjusted to zero reading. The silver nitrate was added and the time recorded. At frequent intervals, the cell was filled and readings on the photometer were taken. From the photometer reading-time curves, and the calibration curve, the concentration of ceric ion was determined.

Table I summarizes the reaction rates which were calculated at times of equal concentration of ceric ion.

TABLE I

RATE CONSTANTS CALCULATED AT TIME WHEN 0.000305 MOLE OF PEROXYDISULFATE HAD BEEN REDUCED

Expt.	Initial molarity cerous ion $\times 10^2$	Initial molarity $K_2S_2O_8$ $\times 10^2$	Molarity $AgNO_3$ $\times 10^3$	μ	Temp., °C.	Time, min.	k
1	1.806	0.3663	0.9818	3.019	25	380	0.234
2	1.754	1.423	3.813	2.936	25	22.5	.247
3	1.788	0.7262	1.944	2.925	25	88	.248
4	1.754	.7113	3.813	2.915	25	41	.281
5	0.903	.3663	0.9818	2.952	25	327	.272
6	.903	.3663	.9818	1.516	25	304	.292
7	.903	.3663	.9818	1.516	35	199	.447
8	1.754	1.423	3.813	2.936	35	12.5	.444
9	1.806	0.3663	0.9818	3.019	35	192	.463

Values for the energy of activation calculated from the simple Arrhenius equation are: from Expts. 6 and 7, 7,778 cal.; from Expts. 2 and 8, 10,720 cal.; and from Expts. 1 and 9, 12,480 cal.

Values of k are tabulated in Table II to show the variation of the reaction rate with time.

TABLE II

VALUES OF k AT VARIOUS TIME INTERVALS

Expt.	60 min.	120 min.	180 min.	240 min.
1	0.270	0.270	0.256	0.251
2	.247	.255	.236	.308
3	.269	.233	.208	.191
4	.272	.265	.274	.275
5	.297	.297	.295	.283
6	.352	.307	.330	.307
7	.547	.584	.511	.513
8[a]	.450	.449	.460	.444
9	.559	.489	.456	.440

[a] The time intervals for no. 8 are 20, 30, 60, and 90 min.

Discussion

These results indicate that the rate is independent of the concentration of the cerous ion. There is a general tendency for the values of k to decrease with increase in time. This decrease may be due to an increase in ionic strength. Because cerous sulfate hydrolyzes so readily, it is impossible to work at low enough ionic strengths to test adequately this effect.

Summary

The rate of reduction of peroxydisulfate ion by cerous ion was found to be directly proportional to the concentrations of the peroxydisulfate ion and the silver ion, but independent of the concentration of the cerous ion.

The specific reaction rate was approximately the same as the values for the chromic ion, vanadyl ion, manganous ion, and hydrazine.

The energy of activation was calculated.

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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) Dekker, Lévy and Yost, *ibid.*, **59**, 2129 (1937).