KINETICS OF THE REDUCTION OF PEROXODISULFATE ION BY BENZOIC ACID

R. A. HERMENS and W. H. CONE
Millikin University, Decatur, Illinois
and
University of Idaho, Moscow.

ABSTRACT.—The kinetics of the reduction of peroxodisulfate ion by benzoic acid with silver ion as a catalyst has been studied by iodometric determination of the peroxodisulfate ion. Hydrogen peroxide formed during the reaction was destroyed by the use of catalase. Two concurrent reactions, one first order and one second order with respect to peroxodisulfate, are involved.

Peroxodisulfate ion in the presence of silver ion, as a catalyst is capable of oxidizing many benzene ring compounds (Baron, 1960) with the formation of a resinous material. Since benzoic acid presented fewer analytical difficulties than most of the other benzene derivatives, it was chosen for this study.

Preliminary studies showed that the rate of the reaction was zero order with respect to benzoic acid and first order with respect to silver ion. This was in agreement with earlier investigations which showed that the reduction rate is independent of the concentration and character of the reducing agent (Cone, 1945; Gupta, 1959).

The reaction was nearly first order with respect to peroxodisulfate ion but careful examination of the data indicated that two simultaneous reactions were taking place. The first order reaction may be represented by the following mechanism:

$$(1)\quad S_2O_8^{2-} + Ag^{+} \longrightarrow \left[\begin{matrix}\text{activated}\\ \text{complex}\end{matrix}\right] \longrightarrow SO_4^{\cdot-} + Ag^{2+} + SO_4^{2-}$$

$$(2)\quad Ag^{2+} + H_2O \longrightarrow H^{+} + Ag^{+} + HO\cdot$$

$$(3)\quad SO_4^{\cdot-} + H_2O \longrightarrow SO_4^{2-} + H^{+} + HO\cdot$$

Equation (1) is the slow reaction and is rate determining.

The second reaction was second order and can be represented by the following equation:

$$(4)\quad 2S_2O_8^{2-} + 3H_2O \longrightarrow H_2O_2 + [O] \longrightarrow 4HSO_4^{-}$$

The differential equation for the two simultaneous reactions is shown below.

$$(5)\quad \frac{d[S_2O_8^{2-}]}{dt} = -k_1[S_2O_8^{2-}] - k_2[S_2O_8^{2-}]^2$$

which on integration yields:

$$(6)\quad \log\left[\frac{[S_2O_8^{2-}]_0}{[S_2O_8^{2-}]_t}\right]\left[\frac{k + k_2[S_2O_8^{2-}]_t}{k - k_2[S_2O_8]_0}\right] = \frac{k_1 t}{2.303}$$

In order to calculate k_2, the first order rate constant, k_1 had to be known. The first order rate constant was taken from another work (Cone, 1945) in which the rate constant of the first order reaction was found by determining the concentration of the product oxidized by peroxodisulfate ion. Cone's work would have not detected any side reactions involving peroxidisulfate ion.

The value of the first order rate constant is 0.447 min^{-1} at 35° (Cone, 1945) and a calculated value, using the Arrhenius equation, of 0.650 min^{-1} at 44.55°. With the use of these rate constants calculations were made to determine the concentration of the peroxodisulfate ion if only the first order reaction had occurred. From these values are substracted the concentrations of peroxodisulfate ion determined experimentally. The difference between these two values is the concentration of peroxodisulfate ion which was reduced by means of the second order reaction.

If the left side of equation 6 is plotted against time, by use of experimental data (at 34.91°C) from Table 1, a linear plot is observed as

TABLE 1.—Data and Calculated Values for the Determination of the Second Order Rate Constant at 34.91°C and 44.55°C.

Data at 34.91°C

Time (min.)	A	B	C	D
0	9.750	9.750	0.000	....
30	9.092	9.621	0.529	0.147
60	8.577	9.499	0.922	0.153
90	8.126	9.365	1.239	0.150
120	7.669	9.241	1.572	0.152
150	7.242	9.118	1.876	0.153
180	6.858	8.996	2.137	0.152
210	6.527	8.878	2.316	0.149
240	6.154	8.758	2.604	0.150
270	5.816	8.642	2.826	0.150

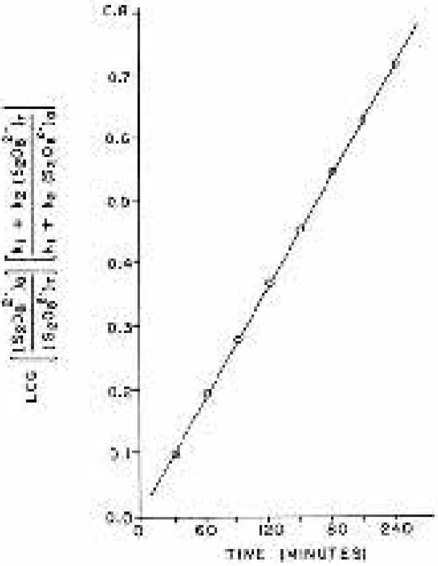
Data at 44.55°C

Time (min.)	A	B	C	D
0	9.875	9.875	0.000	....
30	8.471	9.684	1.213	0.437
60	7.344	9.498	2.154	0.455
90	6.449	9.314	2.865	0.448
120	5.639	9.134	3.495	0.453
150	4.963	8.958	3.995	0.451
180	4.348	8.786	4.437	0.453
210	3.852	8.615	4.763	0.444
240	3.362	8.449	5.087	0.442

Code to Table: A—Experimental molarity of the peroxodisulfate ion $\times 10^3$; B—Molarity of peroxodisulfate ion calculated from Cone's first order rate constant; C—Molarity of peroxodisulfate ion consumed by the second order reaction; and D—Reaction rate constant, k_2, for the second order reaction in liter per mole per minute.

The concentration of silver ion in both cases is 1.00 millimolar.

FIGURE 1.—A time dependent plot from data taken from Table 1 at 34.01°C showing remarkable linearity.



is shown in Figure 1. A similar plot is obtained if one uses the data at 44.55°.

The progress of the reaction was followed by determining the oxidizing power of the solution by an iodometric titration of aliquot samples. Aliquots were withdrawn at intervals of 30 minutes. Before each aliquot was analyzed one milliliter of a 0.5% solution of catalase was added. Catalase is known to be specific for the decomposition of hydrogen peroxide (Beers, 1954). The aliquot sample was then flushed with nitrogen for 60 seconds to eliminate oxygen from the solution.

Preliminary experiments showed that the enzyme did not interfere with the analysis of the peroxodisulfate ion. This method is a quantitative method for determination of peroxodisulfate ion in the presence of hydrogen peroxide.

Debye-Huckel calculations involving ionic strength did not correct the experimental data so that it would follow a simple first order rate law. Deviations from first order data are much too great to involve only ionic strength corrections.

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