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# Kinetics of the Reaction of Silver(II) with Dithionate[1a]

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The reaction $2Ag(II) + S_2O_6^{2-} + 2H_2O = 2Ag^+ + 2HSO_4^- + 2H^+$ proceeds by a mechanism in which the oxidizing agent, silver(II), participates in the rate-determining step. This is unlike previously known reactions of dithionate with certain strong oxidizing agents, for which disproportionation or hydrolysis of dithionate has been rate determining. The dominant term in the rate law is $-d[Ag(II)]/dt = k[H^+][Ag(II)][S_2O_6^{2-}]$, with $k = 5.5 \times 10^{-2}\ M^{-2}\ sec^{-1}$ at $I = 3.5\ M$ and 25.0°.

## Introduction

Certain redox reactions of silver(II) have been found by previous workers to take place by a mechanism in which silver(III) participates in the rate-determining step.[2-7] The silver(III) arises from the rapid disproportionation of silver(II), although the position of equilibrium is well on the side of silver(II).[8-10] Exceptions to such a mechanism have also been found, however.[11,12] Since relatively few systems have been examined kinetically so far, it seems worthwhile to examine selected reactions of silver(II) with respect to the question of the possible participation of silver(III) in the rate-determining step. Dithionate ion ($S_2O_6^{2-}$) is of interest as a reducing agent in view of its relative inertness toward oxidation.[13] With a number of oxidizing agents, the rate-determining step in the redox reaction is actually the slow disproportionation to $SO_2$ and $HSO_4^-$.[14]

## Experimental Section

**Chemicals.**—The principal chemicals used were as follows: Baker Analyzed perchloric acid (60–62%), G. F. Smith $AgClO_4 \cdot H_2O$, G. F. Smith $NaClO_4$, Alpha Inorganics $Na_2S_2O_6 \cdot 2H_2O$, and Fisher No. S-290 $Na_2S_2O_6 \cdot 2H_2O$. Runs 62–71 used recrystallized $Na_2S_2O_6 \cdot 2H_2O$. For the kinetic runs water was purified by ion exchange or distillation from alkaline permanganate. Each solution of silver perchlorate in perchloric acid was filtered to remove any silver chloride just prior to use. Silver(II) was then generated in the solution electrolytically, using platinum electrodes. The spiral anode was isolated in a glass cylinder with a sintered-glass frit and was rotated by an electric motor. Electrolysis of 150–250 ml of 0.3 $M$ $AgClO_4$ in 3 $M$ $HClO_4$ with a current of 40–100 ma represents a fairly typical set of conditions for preparation of the silver(II) solutions.

**Kinetic Runs.**—Silver(II) concentration was followed spectrophotometrically using a Beckman DB spectrophotometer with recorder. Kirwin, *et al.*,[4] found that Ag(II) in $HClO_4$ has an absorption maximum at 474 mμ (extinction coefficient 140 ± 7 l mole$^{-1}$ cm$^{-1}$) which appears to be independent of the acid concentration in the neighborhood of 3 $M$ $HClO_4$. On the Beckman DB, the maximum was observed at about 470 mμ, and the initial concentrations of Ag(II) used were in the range $(1–8) \times 10^{-3}\ M$.

The cell compartment of the spectrophotometer was thermostated by circulating water from a constant-temperature bath, using an Eastern self-priming pump. The water passed through the pump only after going through the spectrophotometer, so as to minimize heating. Temperature was maintained at 25.0 ± 0.1°, measured at the constant-temperature bath. Reactant solutions were generally mixed in a ratio of 10 parts of silver(II) solution to 1 part of dithionate solution. The resulting solution was swirled rapidly and a fraction was poured into a 1-cm rectangular cell. In runs 1–21, silver(I) and acid concentrations are based on analysis of stock solutions. In most of the subsequent experiments, the silver(I) and acid concentrations were determined by titration for each kinetic run after completion of the reaction. Dithionate concentrations were calculated on the basis of weight of $Na_2S_2O_6 \cdot 2H_2O$ used in preparing stock solutions. In a number of runs, ionic strength was adjusted with $NaClO_4$, added as such or formed from NaOH. Amperometric titrations carried out in determination of stoichiometry were done using a Fisher Electropode polarograph with recorder.

**Stoichiometry.**—The stoichiometry of the reaction between Ag(II) and $S_2O_6^{2-}$ was investigated by measuring the amount of sulfate formed from a known initial amount of silver(II), with dithionate added in excess. Initial concentrations were approximately 0.3 $M$ $Ag^+$, 3 $M$ $H^+$, 0.02 $M$ $S_2O_6^{2-}$, and $(6–8) \times 10^{-3}\ M$ Ag(II). Difficulty was experienced in the sulfate analysis, owing to the large amounts of other ions present in comparison with the amount of sulfate, and our early attempts at this analysis were not successful. Two independent analytical procedures were eventually worked out which gave results which were in adequate agreement with known sulfate mixtures and with each other. The reaction mixtures analyzed were prepared by slow (1–2 min) addition of 0.1 $M$ $S_2O_6^{2-}$ solution in excess, with stirring, to give a solution of the composition indicated previously. After completion of reaction, the reaction mixture (50 ml) was diluted to 100 ml, and four 25-ml aliquots were taken for analysis by gravimetric and amperometric procedures, using $Ba(NO_3)_2$ and $Pb(NO_3)_2$, respectively. The samples were adjusted to pH 2, and sulfate was precipitated using 0.01 $M$ $Ba(NO_3)_2$ or 0.01 $M$ $Pb(NO_3)_2$, respectively, and allowed to stand for several hours. After the addition of $Pb(NO_3)_2$ (but not $Ba(NO_3)_2$), enough ethanol was added to make the supernatant liquid 20% ethanol. The $BaSO_4$ was filtered, dried, and weighed. The $PbSO_4$ was filtered; then 0.01 $M$ $Na_2CO_3$ was cycled repeatedly over the precipitate to convert $PbSO_4$ to $PbCO_3$ and put $SO_4^{2-}$ back into solution. The solution was acidified to pH 2, boiled gently, adjusted to pH 3.5–4, and made about 20% in ethanol. A little $PbSO_4$ and

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TABLE I

RATE CONSTANTS

| Runs | Concentration ranges, *M* $[H^+]$ | $10[Ag^+]$ | $10^2[S_2O_6^{2-}]$ | $I$, *M* | $10^2k$, $M^{-2}$ sec$^{-1}$ |
|---|---|---|---|---|---|
| 22–31, 35–40 | 1.36–1.57 | 1.38–3.14 | 1.26–5.09 | 1.9 ± 0.1 | 5.8 ± 0.7 |
| 1–18 | 2.03–2.04 | 2.10–3.65 | 2.50–10.0 | 2.6 ± 0.1 | 6.6 ± 0.4 |
| 41–54, 56–71 | 1.42–3.04 | 1.62–3.96 | 1.93–5.04 | 3.5 ± 0.1 | 6.3 ± 0.7 |
| 62–71 | 1.99–3.03 | 1.62–3.25 | 2.52–5.04 | 3.46 ± 0.03 | 5.5 ± 0.1 |

Triton X-100 were added, and an amperometric titration[15] was carried out at $-1.2$ v *vs.* sce, using 0.01 *M* $Pb(NO_3)_2$ as titrant; the end point came at about 7 ml of titrant.

## Results[16]

**Stoichiometry.**—Two reaction mixtures prepared by adding dithionate slowly with stirring were analyzed for sulfate using the final versions of the two analytical methods in independent determinations in each case. Each reaction mixture was divided into four parts, two of which were analyzed by the gravimetric $BaSO_4$ procedure, and two by the amperometric titration procedure, for a total of eight samples. The average number of moles of sulfate found per mole of silver(II) present initially was 0.98 ± 0.03 and 1.04 ± 0.02 for the gravimetric and amperometric procedures, respectively. Known solutions of composition similar to the reaction mixtures with sulfate added but without silver(II) were similarly analyzed for the sulfate as a check on the analytical methods. Four samples were used, two for each method. Per mole of sulfate added, the average number of moles of sulfate found was 1.07 ± 0.02 and 1.04 ± 0.04 for the gravimetric and amperometric methods, respectively. Thus the analytical results are consistent with the following stoichiometry for the Ag(II)–$S_2O_6^{2-}$ reaction

$$2Ag(II) + S_2O_6^{2-} + 2H_2O = 2Ag^+ + 2HSO_4^- + 2H^+$$

**Kinetics.**—Plots of log $A$ *vs.* $t$ or $(1/T)(\Delta T/\Delta t)$ *vs.* $A$ (where $A$ and $T$ designate absorbance and transmittance, respectively) indicate that the dominant term in the rate law is first order in Ag(II). The most accurate data should be those from runs 62–71 using recrystallized sodium dithionate, with $[H^+] = 2.0$–$3.0$ *M*, $[Ag^+] = 0.16$–$0.32$ *M*, $[S_2O_6^{2-}] = 0.025$–$0.050$ *M*, and $I = 3.4$–$3.5$ *M*. For this set of runs, in plots of $(1/T)(\Delta T/\Delta t)$ *vs.* $A$, deviations of $(1/T)(\Delta T/\Delta t)$ from a straight line were 5% or less over at least the range $A = 0.04$–$0.27$. In some runs of this set, the rate deviations had a small tendency to be in the downward direction near the beginning of the run. In some previous runs using sodium dithionate which had not been recrystallized, the rate deviations were larger and tended to be in the upward direction in the early portion of the run. Table I presents the first-order rate constant $k_1$ for each run. The rate of oxidation of water by $Ag^{2+}$, though not corrected for, is small in comparison with the rate of oxidation of $S_2O_6^{2-}$ by Ag(II).[4] The order with respect to $S_2O_6^{2-}$ was determined as the slope of log $k_1$ *vs.* log $[S_2O_6^{2-}]$, comparing runs at similar $[H^+]$, $[Ag^+]$, and ionic strength. Least-squares analyses were carried out for six sets of runs[16] (1–11; 28–31, 35–38, 40; 41–46; 47–52; 53–58; 62–67), with $[S_2O_6^{2-}]$ in the range 0.019–0.100 *M*. The weighted average of the slope together with its average deviation is 0.96 ± 0.10. Thus in this concentration range the major term in the rate law is first order with respect to $S_2O_6^{2-}$. Similar analyses based on runs 41–52 and 66–69, using $k_2 = k_1/[S_2O_6^{2-}]$, give $-0.16$ and $-0.02$ for the order with respect to $Ag^+$, indicating that the dominant term in the rate law is zero order in $Ag^+$. Least-squares analysis of runs 41–61 gives 0.84 as the slope of log $k_2$ *vs.* log $[H^+]$. In runs 62–71, using recrystallized sodium dithionate, this slope is 1.02. Thus the dominant term in the rate law is

$$\frac{-d[Ag(II)]}{dt} = k[H^+][Ag(II)][S_2O_6^{2-}]$$

Average values of $k$ were calculated for three ionic strengths at 25.0 ± 0.1°. The results are given in Table I. Runs 62–71 use recrystallized sodium dithionate.

## Discussion

Dithionate ion is known to be quite resistant to oxidation.[13] Oxidation of sulfite frequently yields dithionate as one of the products, along with sulfate.[13] In fact, dithionate is such a sluggish reducing agent that its oxidation commonly proceeds by a mechanism[13,14] in which the rate-determining step is disproportionation or hydrolysis, forming $H_2SO_3 + HSO_4^-$.

The distinctive feature of the silver(II)–dithionate reaction is that the oxidizing agent, Ag(II), participates in the rate-determining step. Even such relatively strong oxidizing agents as $BrO_3^-$, $IO_3^-$, and $Cr_2O_7^{2-}$ utilize the disproportionation of $S_2O_6^{2-}$, independent of oxidizing agent, as the rate-determining step.[14] The rate law for the silver(II)–dithionate reaction is of the simple form

$$\frac{-d[Ag(II)]}{dt} = k[H^+][Ag(II)][S_2O_6^{2-}]$$

This rate law is open to more than one possible interpretation. The simplest of the possibilities arises if it is assumed that the predominant Ag(II) species present is the free aquo ion $Ag^{2+}$. In this case the composition of the activated complex would be $\{AgS_2O_6H^+\}^{\ddagger}$, aside from undetermined solvent participation. Even in this simple case the products formed in the rate-determining step are not uniquely determined, pro-

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[16] Material supplementary to this article has been deposited as Document No. 9250 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

vided that subsequent rapid reactions are such as to satisfy the stoichiometry of the over-all reaction, which requires the formation of one sulfate for every Ag(II) consumed. Perhaps the simplest mechanism that is consistent with the results is

$$H^+ + S_2O^2_6 \overset{K}{=} HS_2O_6^- \text{ (rapid)}$$

$$Ag^{2+} + HS_2O_6^- + H_2O \xrightarrow{k'} Ag^+ + HSO_3 + HSO_4^- + H^+$$

$$Ag^{2+} + HSO_3 + H_2O = Ag^+ + HSO_4^- + 2H^+ \text{ (rapid)}$$

Then the observed rate constant $k$ is given by $k = 2Kk'$. Another conceivable set of products in the rate-determining step could be $Ag + 2HSO_4^- + 3H^+$, provided a rapid completing reaction between Ag and Ag(II) follows. These two mechanistic possibilities differ in utilizing a one- or a two-electron change for silver, respectively. Other mechanisms arise as possibilities if one assumes that the predominant Ag(II) species in solution is not the free aquo ion $Ag^{2+}$, but rather a complex such as $Ag(S_2O_6)_n{}^{2-2n}$. Under this assumption, the composition of the activated complex would be $\{Ag(S_2O_6)_{n+1}H^{1-2n}\}^{\ddagger}$. The present data do not establish clearly which of these mechanisms is correct, since dithionate was usually present in excess over silver(II).

Within the concentration range for which the most reliable data are available ($[H^+] = 2.0$–$3.0\ M$, $[Ag^+] = 0.16$–$0.32\ M$, $[S_2O_6{}^{2-}] = 0.025$–$0.050\ M$, and $I = 3.4$–$3.5\ M$), it appears that participation of silver(III) in the mechanism is not required. However, this does not preclude the possibility that under different conditions of concentrations or temperature, a path involving silver(III) might become important. In any case the data establish the participation of the oxidizing agent, silver(II), in the rate-determining step, in contrast to previously known reactions of dithionate with other oxidizing agents.

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# The Crystal Structure of Lithium Aluminum Hydride

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The crystal structure of $LiAlH_4$ has been determined by single-crystal X-ray diffraction methods using counter detectors and filtered Cu K$\alpha$ radiation. The unit cell is monoclinic, $a = 4.845$, $b = 7.826$, and $c = 7.917$ A (all ±0.004 A). The space group is $P2_1/c$ and there are four formula weights per unit cell. Each aluminum atom is surrounded at an average distance of 1.55 A by four hydrogen atoms at the vertices of an almost regular tetrahedron. The lithium ions act as "bridges" between the tetrahydroaluminate ions; five hydrogen atoms surround the lithium ions, four at distances ranging from 1.88 to 2.00 A and one at 2.16 A.

## Introduction

Large numbers of crystalline phases containing $AlH_4^-$ and $BH_4^-$ groups have been synthesized and studied in recent years; these compounds are widely used, particularly in preparative organic chemistry, and are of considerable theoretical interest. The literature contains many references to the tetrahedral configuration of the aluminohydride and borohydride groups in these phases,[1] but only one serious X-ray diffraction structure analysis of any of these materials appears to have been attempted prior to the present investigation: a powder diffraction study of alkali borohydrides.[2] In that work, which is sometimes cited as having established the tetrahedral configuration of both groups in the solid state, no effort was made to locate the hydrogen atoms directly from the experimental data. Our survey of the literature of this subject revealed no other experimental basis for that admittedly reasonable expectation. This work was therefore undertaken to investigate the configuration and the dimensions of the tetrahydroaluminate ion by a single-crystal X-ray diffraction study of lithium aluminum hydride.

## Experimental Section

Lithium aluminum hydride crystallizes in the monoclinic system with $a = 4.845$, $b = 7.826$, and $c = 7.917$ A (all ±0.004 A) and $\beta = 112.5 \pm 0.2°$. The space group is $P2_1/c$ and there are four formula weights per unit cell: $d_{\text{calcd}} = 0.904$ g/cc and $d_{\text{measd}} = 0.92$ g/cc. The crystals grow in the form of rectangular parallelepipeds elongated along the $c$ axis when solutions in diethyl ether are evaporated slowly. Because the crystals are highly hygroscopic, the specimens used for intensity measurements were sealed into thin-walled glass capillary tubes. Intensity data were collected with a scintillation counter and filtered copper K$\alpha$ radiation, using the $\theta$–$2\theta$ scan technique. The usual Lorentz and polarization corrections were applied to the data; absorption corrections were considered unnecessary since the maximum dimension of the crystal was 0.2 mm. The intensities of 507 reflections were measured and used in the structure analysis.

## Structure Determination

Approximate positions of the aluminum atoms were obtained readily from the maxima on Patterson maps.

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