# REDUCTION OF SILVER(II) OXIDE BY THE SOLVENT IN ACID MEDIA

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Summary—The reaction of silver(II) oxide with water to yield silver(I) ions and oxygen is an important side-reaction in procedures which use silver(II) oxide as the oxidant. This reaction has been examined in solutions which were 0.01-1M in respect to sulphuric or perchloric acid. The rate of reduction varied directly with the amount of solid added and was a complex function of the concentrations of hydrogen ions, silver(I) ions and anions present. The kinetic results have been used to postulate a mechanism for the reaction.

### INTRODUCTION

SILVER(II) oxide is a powerful oxidant and studies have been made of its action on V(IV),<sup>1.2</sup> Cr(III),<sup>3-6</sup> Mn(II),<sup>3-7</sup> Ce(III),<sup>4.7.8</sup> NH<sub>3</sub><sup>9.10</sup> and NH<sub>4</sub><sup>+.11</sup> For chemical analysis<sup>1.3.4</sup> the published procedures recommend the addition of excess of solid reagent and it has been shown<sup>5.11</sup> that most of the added silver(II) oxide reacts with water to yield silver(I) and oxygen.

The reduction of silver(II) ions by the solvent has been examined in solutions (>4M) of perchloric,<sup>12,13</sup> sulphuric,<sup>14</sup> phosphoric<sup>15</sup> and nitric acids.<sup>16,17</sup> The rate of reaction is reported to be proportional to the square of the silver(II) ion concentration divided by the concentration of silver(I) ions. The proportionality constant can vary with the concentration of hydrogen ions and anions present. The tendency of silver(II) ions to form complexes with the anions in these strongly acid solutions has been clearly established<sup>13,14,15,18</sup> and these equilibria are partially responsible for the variable effect of hydrogen and anion concentrations on the rate.

The reaction mechanism is considered to involve a rapid equilibrium between the three oxidation states of silver  $[2Ag (II) \rightleftharpoons Ag (I) + Ag (III)]$ . This proposal is supported by an isotopic tracer study<sup>19</sup> made in 6*M* perchloric acid and the suggestion<sup>20</sup> that silver(II) oxide dissolves in nitric acid to give a mixture of silver(I) and silver(III) nitrates.

McMillan<sup>21</sup> has postulated that acid dissolution of silver(II) oxide leads to silver(II) ions in solution, and in a number of the reduction studies comparable results were obtained using silver(II) ions formed either electrolytically or by dissolution of silver(II) oxide. It therefore appears that the kinetics of oxygen formation due to reduction of silver(II) oxide are equivalent to those reported for silver(II) ions, in solutions which are more than 2M in respect to acid. The analytical significance of this knowledge has been indicated in a previous paper<sup>5</sup> where it was shown that the maximum efficiency for the oxidation of manganese and chromium ions occurred in 3M perchloric acid which corresponds to the acidity at which minimum reduction by the solvent occurs.<sup>12</sup>

Not all analytical reactions are carried out at acidities greater than 2M, and hence it appeared desirable to obtain detailed information on the reduction of silver(II)

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oxide in the pH range 0 to 3. This paper describes the results obtained in studies using perchloric and sulphuric acids.

#### EXPERIMENTAL

### Reagents

Silver(II) oxide was prepared by the method of Hammer and Kleinberg.<sup>22</sup> The total volume of oxygen liberated in acid solutions corresponded to a purity of 97%.

Solutions of perchloric or sulphuric acid of differing concentrations were prepared by dilution of analytical reagent grade concentrated acid. The solutions were checked titrimetrically against borax and the pH was measured with a Metrohm pH meter using a glass electrode standardised at pH 1.00.

Silver(I) perchlorate was prepared by adding a slight excess of freshly precipitated silver(I) oxide to concentrated perchloric acid. The filtered and diluted solution (pH 6-7) was standardised potentiometrically against pure dry sodium chloride.

#### Apparatus

The rate of oxygen evolution was measured in a water-jacketed gas burette which was connected to a jacketed reaction vessel by means of a short capillary tube. The reaction vessel had a second side-arm to which was attached a sealed tube containing a magnetic pusher rod and a small glass boat filled with the silver(II) oxide. The acid solutions were admitted through the side arm and were stirred at a constant rate with a magnetic stirrer. Temperature control was effected with the aid of a Braun Thermomix unit, used in conjunction with a refrigeration unit for the lower temperatures.

#### Procedure

After 50 ml aliquots of acid (0.03-1.2 M) had been placed in the reaction cell, centigram amounts of silver(II) oxide were weighed into the glass sample boat and placed in the sample introduction side tube. When all parts of the apparatus had reached thermal equilibrium, the silver oxide was added to the acid by movement of the pusher rod. The rate of oxygen evolution was measured in the gas burette.

The effects of variations in temperature, hydrogen ion concentration, silver(I) ion concentration and weight of oxide added were studied in different series of tests. The reaction with perchloric acid was investigated at temperatures from 0 to 30°, with most tests being made at 20°. The reaction with sulphuric acid was slower and the temperature range used was 45 to  $60^\circ$ .

Known amounts of the sodium salts of nitric, acetic and sulphuric acids were added to perchloric acid solutions to observe the effect of foreign ions on the rate of reactions.

### RESULTS

In most tests the reduction process resembled a pseudo first-order reaction and thus the effect of the different variables on both the initial rate and the apparent rate constant could be observed. Apparent rate constants were determined by plotting  $\log a/(a - x)$  against t where a was the maximum volume of oxygen evolved and x was the volume evolved at time t.

## The effect of weight of oxidant

As shown in Fig. 1, the initial rate of reaction varied linearly with the weight of oxide added. The apparent rate constant for the pseudo first-order reaction in perchloric acid solutions was independent of the amount of oxide added and at 20° and pH 1.08, k' was 0.011 sec<sup>-1</sup>. The initial rate of oxygen liberation (mole . sec<sup>-1</sup>) was 2.0 × 10<sup>-3</sup> × [AgO] where [AgO] is the number of moles of silver(II) oxide added. From the stoichiometry of the basic equation,  $-dAgO/dt = 4(dO_2/dt)$ , whence

 $-\left(\frac{\mathrm{dAgO}}{\mathrm{d}t}\right)_{\mathrm{initial}}$  is  $8.0 \times 10^{-3} \times [\mathrm{AgO}].$ 

With sulphuric acid solutions the pseudo first-order plots did not pass through the origin. Since preliminary tests indicated that the inhibitory effect of silver(I) ions was considerable in the presence of sulphate ions, the results were recalculated on the basis of a rate equation having the form  $-dAgO/dt = k[AgO]/[Ag^+]$ , the Ag<sup>+</sup> being formed in the reduction process. If a represents the number of moles of silver(II) oxide added and x the number of moles of silver(I) ion formed at time t, the integrated form of this rate equation becomes

$$a \ln a/(a - x) = k(t - t_0) + x.$$

This equation yielded straight lines passing directly through the origin. Five to ten different weights of oxide were used in each of the studies involving changes in pH or temperature and the mean values of the apparent rate constants, k'', derived from these "inhibition by-product" plots are recorded in Table I.



FIG. 1.—Dependence of initial reaction rate on weight of AgO added in (a)  $HClO_4$  at 20°, (b)  $H_2SO_4$  at 50°.

$\odot 0.1M$ HClO <sub>4</sub> , pH = 1.08	• $0.05M H_2SO_4$ , pH = $1.20$
$\bigcirc 0.0125M \text{ H}_2\text{SO}_4, \text{ pH} = 1.85$	$\oplus 0.38M$ H <sub>2</sub> SO <sub>4</sub> , pH = 0.55
$\otimes 0.025M$ H <sub>2</sub> SO <sub>4</sub> , pH = 1.50	$0 1.25M H_2 SO_4, pH = 0.00$

TABLE I.—APPARANT RATE	CONSTANTS	FOR TH	E REDUCTION
OF SILVER(II) OXIDE IN	SULPHURIC	ACID S	OLUTIONS
(15 to 75 mg of AgO ad	ded to 50 m	l of acid	l solution)

Temperature	рН	Silver ion inhibited $10^7 \times k''$ , mole. sec <sup>-1</sup>			
50	0.00	20.7			
50	0.55	15.5			
50	1.20	11.9			
50	1.85	7.8			
50	1.20	10.2			
45	1.20	8.1			
55	1.20	17.7			
60	1.20	32.4			



FIG. 2.—Effect of hydrogen ion concentration on the initial reaction rate in perchlorate media.  $4 \times 10^{-4}$  mole AgO.  $\odot$  at  $20^{\circ}$ ;  $\ominus$  at  $10^{\circ}$ .

## The effect of pH

The effect of pH on the initial rate of oxygen liberation in sulphuric acid solutions is shown in Fig. 1. Logarithmic plots of either the initial rate or apparent rate constant (k'') against pH indicated that the rate was proportional to  $[H^+]^{0.2}$ . Since sulphate ions inhibit the reaction this term could be a composite such as  $[H^+]^{0.5}/[$ sulphate species]<sup>0.3</sup>. In both cases, the fractional power term suggests the possibility of adsorption on the surface of the solid oxidant.

The results obtained in the sulphuric acid studies thus correspond to a rate equation such as

$$-dAgO/dt = 4(dO_2/dt) = \frac{k[AgO][H^+]^{0.5}}{[Ag^+][sulphates]^{0.3}}.$$

The specific rate constant, k, is  $2 \times 10^{-6}$  mole. sec<sup>-1</sup> at 50° if [AgO] and [Ag<sup>+</sup>] are expressed in the same units.

The effect of hydrogen ion concentration on the initial rate of oxygen liberation in perchloric acid solutions is shown in Fig. 2. The reaction has to be treated in two steps, since the effect of hydrogen ion activity on the rate indicates a change of mechanism at an intermediate concentration of acid.

At low acid concentrations (<0.1M at  $20^{\circ}$  and <0.3M at  $10^{\circ}$ ) the rate varied non-linearly with hydrogen ion activity. If it is assumed that the rate varies with the amount of hydrogen ion adsorbed, the results indicate a rate equation of the form

$$-dAgO/dt = k_1[AgO] \cdot \frac{A[H^+]}{1 + A[H^+]} \approx k_2[AgO][H^+]^{0.5}$$

where  $k_1$  is the rate constant, [AgO] is the number of moles of solid added, and the terms  $A[H^+]/(1 + A[H^+])$  or  $[H^+]^{0.5}$  are adsorption terms derived from either the Langmuir isotherm  $(x/m = A[H^+]/(1 + A[H^+]))$  or the Freundlich isotherm  $(x/m = b[H^+]^{1/n})$ . In these isotherms, x represents the amount of hydrogen ion adsorbed, m is the mass of solid adsorbent, and A, b and n are constants.

The dotted curves in Fig. 2 show the values obtained when  $k_1$  is  $1.2 \times 10^{-2} \text{ sec}^{-1}$ and A is 32 at 20° or 8 at 10°.

At higher acid concentrations the term  $A[H^+]/(1 + A[H^+])$  approaches a value of unity and the equation has to be modified by multiplying the numerator by [H<sup>+</sup>] since in this acid region the rate increases linearly with [H<sup>+</sup>]. The specific rate constant for this modified equation ( $k_3$ ) has a value of  $1.55 \times 10^{-2}$  mole<sup>-1</sup>.l.sec<sup>-1</sup> at 20° and  $6.3 \times 10^{-3}$  mole<sup>-1</sup>.l.sec<sup>-1</sup> at 10°.



FIG. 3.—Dependence of initial reaction rate on the concentration of added silver(I) ions in perchlorate media. At 20°,  $4 \times 10^{-4}$  mole. AgO.  $\bigcirc 0.1M$  HClO<sub>4</sub> (pH = 1.08);  $\bigcirc 0.2M$  HClO<sub>4</sub> (pH = 0.80);  $\bullet 0.5M$  HClO<sub>4</sub> (pH = 0.35).

## The effect of silver(I) ions

The significant effect of silver(I) ions on the rate of oxygen liberation in sulphuric acid solutions has been mentioned above. The addition of this species to perchloric acid reduced the rate as shown in Fig. 3. The inhibitory effect only became significant at 20° when the ratio of [Ag<sup>+</sup>] to [H<sup>+</sup>] exceeded 0.05. In the tests recorded in Figs. 1(a) and 2, the maximum concentration of silver(I) ions that developed in the initial stages was about  $10^{-3}M$ , and accordingly the retardation of initial rates by this ion could be ignored in acid concentrations greater than 0.02M. However, towards the end of the reaction the silver ion concentration exceeded  $5 \times 10^{-3}M$  and in acid solutions that were less than 0.1M this ratio was exceeded. This resulted in a distinct break in the pseudo first-order plots.

If silver ions are considered to compete with hydrogen ions for sites on the solid surface, the results shown in Fig. 3 correspond to an adsorption relationship of the form

$$x/m = \frac{32[H^+]}{1+32[H^+]+230[Ag^+]}$$

The addition of silver ions thus introduces a new term  $(+B[Ag^+])$  into the denominator of the rate equation. Because  $B \sim 7A$  at 20°, with low acidities the denominator approaches the value  $B[Ag^+]$  and the rate becomes approximately inversely proportional to the silver ion concentration as indicated by the sulphuric acid studies.

## The effect of anions

As shown in Fig. 4, the addition of small amounts of nitrate ion (<0.05M) had little influence on the initial rate of reduction. As the concentration was increased (*e.g.*, to 1*M*) the rate increased approximately in proportion to  $[NO_3^{-1}]^{0.3}$ . Higher concentrations of nitric acid (>3M) stabilise silver(II) ions through complex formation and this reduces the decomposition rate.<sup>16,17,22</sup>



FIG. 4.—Effect of addition of foreign anions on the initial reaction rate in perchlorate media. At 20°, pH = 1.00,  $4 \times 10^{-4}$  mole. AgO.  $\odot$  sulphate ions;  $\ominus$  acetate ions;  $\bullet$  nitrate ions.

Small amounts of acetate ion also had little influence but larger amounts greatly reduced the rate of reduction. The retarding effect of sulphate ions was far more pronounced and the results shown in Fig. 4 correspond to a term [sulphate added]<sup>-0.4</sup> in the rate equation. If sulphate ions are assumed to be adsorbed on the surface of the solid, the constant for use in a Langmuir isotherm is about 190, which is of the same order as that observed for silver(I) ions.

As silver species of all oxidation states have been shown to form complexes with many anions, it may be assumed that anions could be strongly adsorbed on the solid oxide and so inhibit attack by hydrogen ions. Accordingly, it may be suggested that the denominator of the rate equation should include an additional term for anions  $(e.g., + C[SO_4^{2-}])$ .

## The effect of temperature

The effect of temperature on the reaction rate is recorded in Tables I and II. Arrhenius plots of these results indicate an activation energy of 9 kcal.  $mole^{-1}$  for the initial reaction in perchloric acid and 6 kcal.  $mole^{-1}$  for the initial reaction in sulphuric acid. These values may be considered to represent the activation energy of the process when inhibition by silver ions is negligible. If the calculations are based on apparent rate constants, the perchloric acid values yield an answer of 7 kcal.  $mole^{-1}$  but the sulphuric acid value rises to 23 kcal.  $mole^{-1}$ . This high value indicates that temperature has a marked effect on the combined inhibitory influence of silver(I) and sulphate ions.

TABLE II.—INITIAL RATES AND APPARENT RATE CONSTANTS FOR THE REDUCTION OF SILVER(II) OXIDES IN 0.1M perchloric acid solutions (50 mg of AgO added to 50 ml of acid solution)

Temperature	1	5	10	15	20	25	30	35
Initial rate ( $\times 10^6$ , mole. sec <sup>-1</sup> )	0.27	0.43	0.48	0.62	0.77	1.25	1.37	2.01
Apparent rate constant ( $\times 10^{3}$ , sec <sup>-1</sup> )	0.37	0.62	0.69	0.92	1· <b>12</b>	1.25	1.67	1.95

## Mechanism

The dissolution of silver(II) oxide in acid media is said by McMillan<sup>21</sup> to proceed in the following steps:

$$Ag(I)-O-Ag(III) = O + H^{+} \stackrel{k_{1}}{\Longrightarrow} OH^{-} + Ag(I)-O-Ag(III)^{2+}$$
(1)

$$Ag(I) - O - Ag(III)^{2+} \stackrel{k_3}{\longrightarrow} + Ag(II) - O - Ag(II)^{+}$$
(2)

$$^{+}Ag(II) - O - Ag(II)^{+} + H^{+} \rightleftharpoons OH^{-} + 2Ag^{2+}$$
(3)

The kinetic data reported in this paper are consistent with this type of mechanism. At low acidities, or in the presence of foreign ions which are adsorbed on the solid surface, the rate controlling step appears to be diffusion of the species Ag(I)—O— $Ag(III)^{2+}$  from the surface (*i.e.*, step 1). The rate of diffusion of this species may be expressed by the equation (Fick's law)

rate of diffusion 
$$= \frac{S \cdot D}{\delta} (C - C_0)$$
 (4)

where S is the surface area, D is the diffusion coefficient of the species,  $\delta$  is the thickness of the diffusion layer,  $C_0$  is the concentration of the species in bulk solution and C is the concentration of the species at the solid surface. If it is postulated that the diffused material reacts rapidly,  $C_0 = 0$  and the rate becomes proportional to the concentration of the diffusing species.

In this particular system the amount of  $Ag_2O^{2+}$  formed will equal the amount of H<sup>+</sup> adsorbed, and the mass of adsorbent equals the mass of AgO taken. The adsorption isotherm may thus be written as

$$\{Ag_2O^{2+}\} = \{AgO\}A[H^+]/(1 + A[H^+])$$
(5)

where  $\{ \}$  represents the amount in g or moles. The amount of Ag<sub>2</sub>O<sup>2+</sup> can be converted into concentration C through multiplication by 10<sup>3</sup>/Sf where S is the surface area in cm<sup>2</sup> and f is the average thickness of the surface film in cm.

Combination of equations (4) and (5) yields the relationship,

rate of diffusion = 
$$\frac{10^3 \cdot D.A.[H^+]\{AgO\}}{f\delta(1 + A[H^+])}$$

which is of the same form as the rate equation derived by experiment.

At a given temperature the rate of diffusion tends towards a maximum as  $[H^+]$  is increased. The concentration of acid required to achieve this maximum becomes greater in the presence of other species which hinder adsorption of the hydrogen ions. Values for the constants A and D increase with temperature and thus an increase in temperature reduces the range of acidity over which this process is rate-controlling. Since the diffusion zone thickness can vary with the stirring rate and solution viscosity, these factors also influence the diffusion rate. The "effective" thickness also decreases with increased acidity and a point is reached where diffusion control is replaced by the next slowest process, which was found (Fig. 2) to be first order in hydrogen ions. Step 3 in the McMillan dissolution mechanism must therefore be the rate-controlling step in the presence of moderate concentrations of acid (e.g., 0.1 to 1M at 20°).

Studies of the decomposition of silver(II) ions indicate a further change in the rate-determining step as the acid concentration is increased beyond 1*M*. The kinetics of these systems are complicated by complex formation and the perchloric acid system has a distinct minimum in the rate vs. concentration curve, at 3*M* acid.<sup>12</sup> The results at higher concentrations correspond to a rate equation such as

$$-dAg^{2+}/dt = \frac{kK.K_1[Ag^{2+}]^2}{[Ag^+][H^+]^2}$$

which is based on the following mechanism:

$$2Ag^{2+} \xrightarrow{K} Ag^{+} + Ag^{3+} \text{ rapid}$$

$$Ag^{3+} + H_2O \xrightarrow{K_1} AgO^{+} + 2H^{+} \text{ rapid}$$

$$AgO^{+} \xrightarrow{k} Ag^{+} + \frac{1}{2}O_2 \text{ rate determining.}$$

**Résumé**—La réaction de l'oxyde d'argent (II) avec l'eau, donnant des ions argent (I) et de l'oxygène, est une réaction secondaire importante dans les méthodes qui utilisent l'oxyge d'argent (II) comme oxydant. On a examiné cette réaction dans des solution 0,01-1M en acide sulfurique ou perchlorique. La vitesse de réduction varie directement avec la quantité de solide ajoutée et est une fonction complexe des concentrations en ions hydrogène, ions argent (I) et anions présents. On a utilisé les résultats cinétiques pour supposer un mécanisme de la réaction.

**Zusammenfassung**—Die Reaktion von Silber(II) oxyd mit Wasser zu Silber(I) und Sauerstoff ist eine wichtige Nebenreaktion bei Vorschriften mit Silber(II) oxyd als Oxydans. Diese Reaktion wurde in 0,01-1MSchwefel- und Überchlorsäurelösungen untersucht. Die Reduktionsgeschwindigkeit anderte sich direkt mit der Menge an zugegebenem Feststoff und hing von den Konzentrationen von Wasserstoff-, Silber(I)ionen und Anionen in komplizierter Weise ab. An Hand der kinetischen Ergebnisse wurde ein Reaktionsmechanismus postuliert.

### REFERENCES

- 1. M. Tanaka, Bull. Chem. Soc. Japan, 1954, 27, 10.
- 2. D. M. Yost and W. H. Claussen, J. Am. Chem. Soc., 1931, 53, 3349.
- 3. M. Tanaka, Bull. Chem. Soc. Japan, 1953, 26, 299.
- 4. J. J. Lingane and D. G. Davis, Anal. Chim. Acta, 1956, 15, 201.
- 5. C. P. Lloyd and W. F. Pickering, Talanta, 1964, 11, 1409.
- 6. D. M. Yost, J. Am. Chem. Soc., 1926, 48, 152.
- 7. K. Kimura and Y. Murakimi, Mikrochemie Mikrochim. Acta, 1951, 36/37, 727.
- G. A. Barbieri, Atti. Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat., 1906, 5, 15, 508; Ber., 1907, 40, 3371.
- 9. C. V. King, J. Am. Chem. Soc., 1927, 49, 2689; 1928, 50, 2080; 1930, 52, 1439.
- 10. W. F. Pickering, Australian J. Chem., 1963, 16, 969.
- 11. Idem, ibid., 1964, 17, 731.
- 12. J. B. Kirwin, F. D. Peat, P. J. Proll and L. H. Sutcliff, J. Phys. Chem., 1963, 67, 1617.
- 13. G. A. Rechnitz and S. B. Zamochnick, *Talanta*, 1964, 11, 713.
- 14. Idem, ibid., 1964, 11, 1645.
- 15. Idem, ibid., 1965, 12, 479.
- 16. A. A. Noyes, J. L. Hoard and K. S. Pitzer, J. Am. Chem. Soc., 1935, 57, 1221.
- 17. A. A. Noyes, C. D. Coryell, F. Stitt and A. Kossiakoff, ibid., 1937, 59, 1316.
- 18. A. A. Noyes, D. De Vault, C. D. Coryell and T. J. Deahl, ibid., 1937, 59, 1326.
- 19. B. M. Gordon and A. C. Wahl, ibid., 1958, 80, 273.
- 20. G. A. Barbieri, Atti. Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat., 1931, 6, 13, 882.
- 21. J. A. McMillan, Nature, 1962, 195, 594.
- 22. R. N. Hammer and J. Kleinberg, Inorg. Syn., 1953, 4, 12.