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The kinetics of the silver (I)/silver (II) couple at a platinum electrode in perchloric and nitric acids

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The kinetics of the silver (I)/silver (II) couple have been studied in 3 M nitric acid and 3 M perchloric acid at a platinum electrode. It has been found that silver (II) can be produced in high current yields in a fast electrode reaction although the conversion of silver (I) to silver (II) is limited by the chemical reaction of silver (II) with water. It has also been shown that silver (I) can successfully be used as a catalyst or 'current carrier' in the anodic oxidation of organic and inorganic substrates.

At the present time there is considerable industrial interest in the electrochemical generation of powerful, ionic oxidants such as cobalt (III), manganese (III), manganese (IV), lead (IV), cerium (IV) and thallium (III) from their readily available, stable lower oxidation states and the subsequent reactions of these species with organic substrates. These subsequent reactions may be carried out either *in situ* in the electrochemical cell, when the metal ion may be considered to be a 'current carrier', or in a separate reactor. In the latter case, the electroactive ion may be recycled after the chemical reaction so that in each case the overall reaction sequence

$$M^{n+} \rightarrow M^{(n+1)+} + e$$
$$M^{(n+1)+} + \text{reactant} \rightarrow M^{n+} + \text{product}$$

uses the metal ion, $M^{(n+1)+}$, as the oxidation catalyst. It should also be noted that, particularly when the reaction is carried out *in situ* in the electrochemical cell, it is not necessary for the oxidizing cation to be completely stable provided the reaction with the substrate is faster than that with the solvent.

Silver (II) is known to be an even stronger oxidant than the ions listed above (the formal electrode potential for the silver (I)/silver (II) couple in 1 M nitric acid is reported to be +1·91 V versus the NHE[1]). Therefore it was decided to investigate whether the silver (I)/silver (II) couple could successfully be used in systems such as those previously described. The first part of this paper discusses the electrode kinetics of the silver (I)/silver (II) couple in aqueous perchloric and nitric acids; these relatively non-complexing media were chosen in order to maintain the highly oxidizing nature of the 'uncomplexed' silver (II) ion. The second part will illustrate the use of silver (II) as an intermediate in the electrochemical oxidation of organic and inorganic species.

No previous studies of the anodic oxidation of silver (I) in such acidic, non-complexing media have been reported. However, Syper [2] has reported the reaction of 'uncomplexed' silver (II) with a number of organic substrates. He prepared the solution free silver (II) by dissolution of silver (II) oxide in cold, aqueous acid; this method is inefficient, as is the ozonolysis of silver (I) solutions [3].

Experimental

Chemicals. The solutions for the electrochemical experiments were prepared from triply distilled water and 'Analar' perchloric acid and 'Reagent Grade' silver perchlorate or 'Analar' nitric acid and Johnson atthey M'pure recrystallized grade' silver nitrate. The organic

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compounds were the purest grades available and were used without purification. The chemicals used for the analysis of silver (II) were 'Analar' sodium chloride, hydrochloric acid and potassium bromate and 'Reagent Grade' thallous nitrate.

Cells and equipment. The electrochemical experiments were carried out with Chemical Electronics valve or transistorized (TR40-3A) potentiostats and pulse generator together with suitable recording equipment. The rotating disc experiments were performed with the aid of a Servomex Motor Controller Type MC 43.

Several electrochemical cells were used during this work. Except in a limited number of experiments where a pyrolytic graphite anode was employed, both the working and secondary electrodes were made from platinum and the reference electrode was a silver wire dipping into a solution of 10^{-2} M silver nitrate and 3 M potassium nitrate and it was separated from the working electrode by a tap and Luggin capillary. All potentials in this paper will be quoted versus this reference electrode which has a potential of +0·70 V versus a NHE. The design of the cell and particularly the working electrode depended on the actual experiment. The steady state curves were obtained using a rotating disc electrode rotating at 600 rpm.

Analysis. The silver (II) content of solutions were determined by a back titration method previously used by Noyes [1]. An aliquot of the silver (II) solution was pipetted into excess thallium (I) solution and the excess was determined by a titration with potassium bromate.

The organic analyses were carried out using a Pye 104 vapour phase chromatograph with ½-metre glass columns packed with 10% polyethyleneglycol adipate and 1% phosphoric acid on celite.

The kinetics of the silver (I)/silver (II) couple

Fig. 1 shows the concentration dependence of the steady state polarization curves for the oxidation at a platinum electrode of silver (I) in 3 M nitric acid. It may be confirmed from the slope of log *i*–log *c* plots such as those shown in Fig. 2, that over the potential range +1·0 V to 1·25 V and in the concentration range 10^{-2} M to 1 M, the current is first order with respect to the silver (I) concentration. At concentrations above 1 M, the current shows a tendency to deviate from this simple first order behaviour, possibly due to a double layer effect or adsorption of silver (I) on the electrode at these very high concentrations.

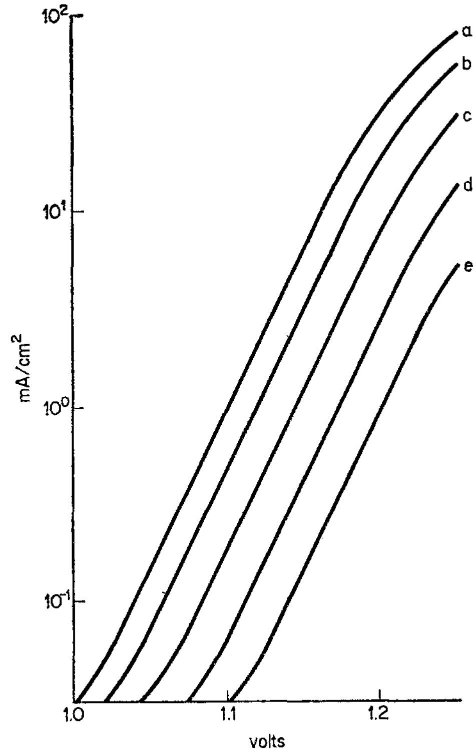


Fig. 1. Plots of steady state current versus potential for solutions containing 3 M HNO_3 and various concentrations of $AgNO_3$. Curve (a) 3·16 M (b) 1·00 M (c) 0·316 M (d) 0·10 M (e) 0·032 M. The curves were obtained at a disc electrode rotating at 600 rpm.

At potentials more positive than those shown in Fig. 1, growth of a solid phase, probably silver (II) oxide, occurs on the electrode surface; this process is characterized by rising *i–t* transients and catalytic oxygen evolution and, once initiated, only a minimal quantity of solution free silver (II) is produced. However, below the potential where initiation of the crystal growth process occurs, solution free silver (II) is the only silver containing product produced by the electrode reaction and oxygen evolution, although occurring, is a relatively slow and unimportant process.

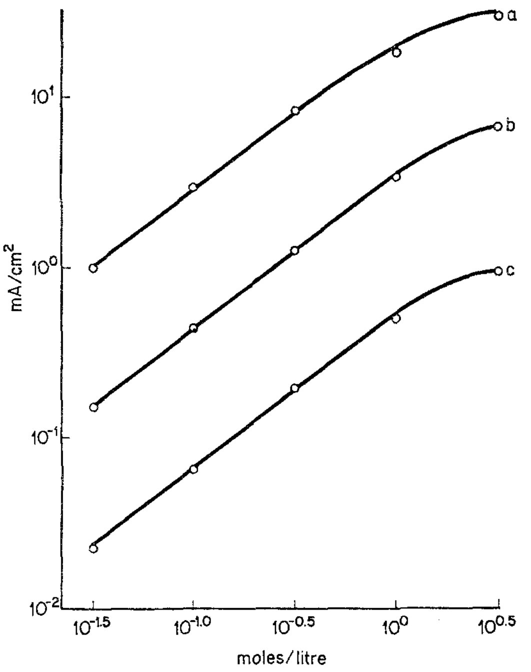


Fig. 2. Plots of current versus concentration of $AgNO_3$ at various potentials. Curve (a) 1·20 V (b) 1·15 V (c) 1·10 V.

The actual potential where growth of the surface oxide begins is dependent on the concentration of silver (I) as well as the pH of the solution and in a solution of 10^{-2} M silver (I) in 3 M nitric, it does not start below +1·4 V. Under these conditions a marked plateau is obtained on the log i–E curve. If the potential of the platinum anode is stepped from below +1·0 V to the potential range where this plateau occurs, falling i–t transients may be recorded and these data may be replotted in the form of i–$t^{-\frac{1}{2}}$ graphs. Since these plots are linear it can be concluded that the plateau is due to diffusion control and it may be calculated from the slope of these plots that a single electron is transferred during the electrode reaction [4], confirming that silver (II) is indeed the product.

Fig. 1 also shows that for all concentrations of silver (I), the polarization curves have linear portions with Tafel slopes of 60 mV^{-1}. Since only a single electron is transferred during the oxidation of silver (I), it is clear that these Tafel slopes indicate that the electrode process is controlled by diffusion of silver (I) to, and silver (II) away from, the electrode; that is, the current is controlled by the Nernst equation over the whole potential range.

A similar concentration dependence of the polarization curves for the oxidation of silver (I) in 3 M perchloric acid can be obtained, although the currents contain a larger contribution from oxygen evolution since the formal electrode potential of the couple in this acid is more positive than in nitric acid. This is because the nitrate ion is a stronger complexing agent for silver (II) than the perchlorate ion, a fact which is confirmed by a change in the solution colour; silver (II) is pale red in perchloric acid and dark brown in nitric acid.

In order to obtain the rate constant for the oxidation of silver (I) at a platinum electrode, a study was made using a rotating disc electrode. In Fig. 3, the results of a typical experiment are plotted in the form of $i-\omega^{\frac{1}{2}}$ plots (ω = angular velocity) for a number of potentials. It will readily be seen that there is considerable deviation from linearity at high rotation speeds, particularly at low potentials. These data were analysed by the treatment given by Jahn and

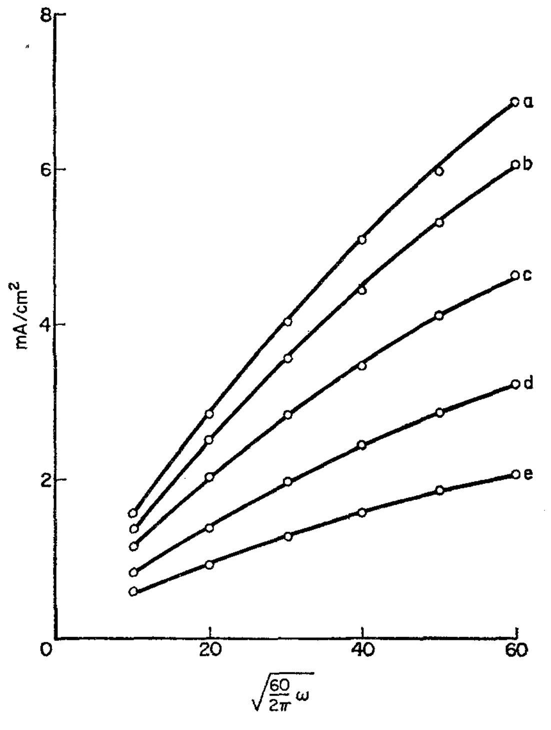


Fig. 3. Plots of i versus $\sqrt{(60/2\pi\ \omega)}$ at various potentials. Curve (a) 1·31 V (b) 1·29 V (c) 1·27 V (d) 1·25 V (e) 1·23 V. Solution contains 3·0 M HNO_3 and 10^{-2} M $AgNO_3$.

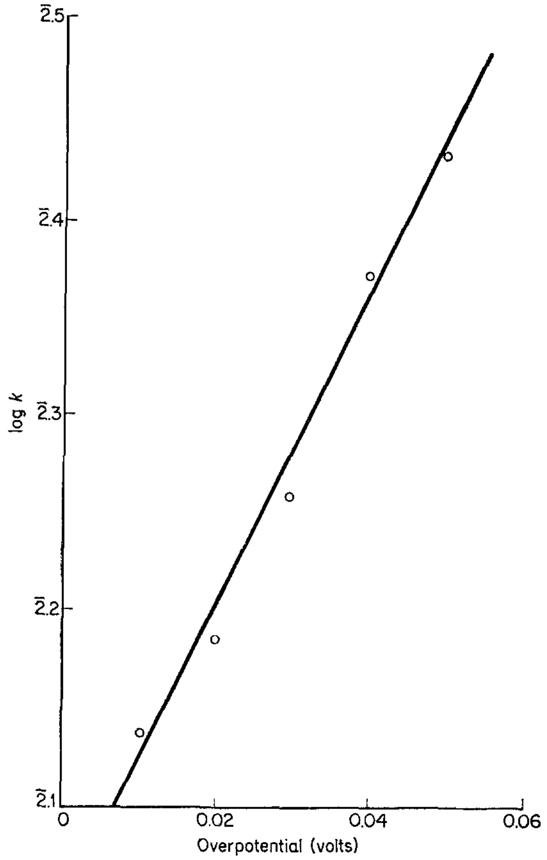
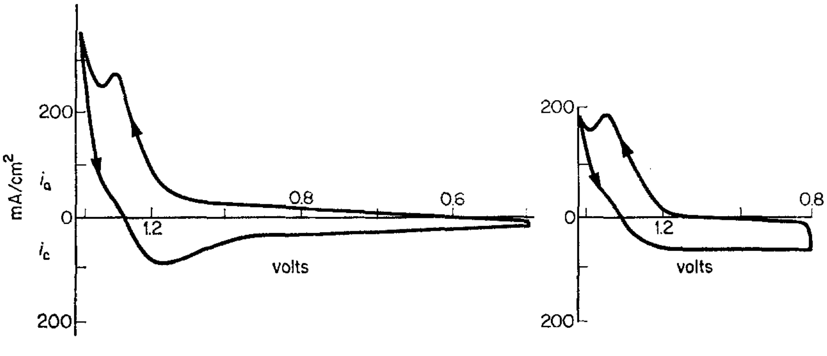


Fig. 4. Plot of log k versus potential. Solution contains 3 M HNO_3 and 10^{-2} M $AgNO_3$.

Vielstich [5], and the results are shown in the form of a log $k-E$ plot in Fig. 4 (k is the heterogeneous rate constant for the reaction $Ag^+ \rightarrow Ag^{2+} + e$). The rate constants obtained in these experiments are close to the limiting value obtainable by this technique so the accuracy of the measurements is not high. However, several runs were made at various concentrations and the mean standard rate constant for the electron transfer process was $1{\cdot}5 \times 10^{-2}$ cm/sec. The slope of the log $k-E$ plot is 125 mV^{-1}, indicating that the charge transfer coefficient, α, is a half. The formal electrode potential of the silver (I)/silver (II) couple in 3 M nitric acid is, of course, required in order to determine the standard rate constant. This was determined by a potentiometric technique using various silver (I)/silver (II) mixtures and was found to be $+1{\cdot}25$ V.

Thus it might be concluded from these steady state techniques that one is studying a simple, fast electron transfer reaction. However, it soon becomes clear from potentiodynamic experiments that the kinetics of the silver (I)/silver (II) system, and particularly the reduction of silver (II), is dependent on the immediate history of the platinum electrode.

For example, Fig. 5 shows two cyclic voltammograms run on a solution of silver (I) under identical conditions except for the length of the sweep towards negative potentials. This relatively minor change in the experimental conditions has a marked effect on the reduction of silver (II); the voltammogram using the longer sweep shows a peak for the reduction of silver (II) while no such peak is observed in the other case. The oxidation peak is affected less, although a slight shift in the peak potential to a more positive



(a) (b)

Fig. 5. Cyclic voltammograms of 10^{-2} M $AgNO_3$ in 3 M HNO_3 at a potential sweep rate of 100 V/sec. Curve (a) Potential sweep range $+0{\cdot}21$ V to $+1{\cdot}41$ V (b) Potential sweep range $+0{\cdot}81$ V to $+1{\cdot}41$ V.

value is observed as the sweep range is shortened. More generally, using the longer sweep range, it was found that the oxidation peak on the sweep in the anodic direction behaves in the way expected for an electrode process controlled by diffusion, i.e. a plot of peak current versus square root of potential sweep rate is linear and the peak potential is independent of sweep rate [13]. On the other hand, the reduction peak on the sweep in the cathodic direction does not give similar plots, is always markedly stretched out along the potential axis and its shape depends on the length of the sweep to negative potentials. In a further set of experiments using a linear potential sweep and a solution which contained 50% silver (II) and 50% silver (I), the shape of the current-potential curves for the reduction of silver (II) was found to depend on the direction of the potential sweep.

At the positive potentials required for the oxidation of silver (I), a platinum electrode is known to be covered with a layer of platinum oxide. Moreover, the thickness and nature of the oxide layer will depend on the electrode potential and will also be somewhat time dependent. Therefore, the potentiodynamic experiments would seem to indicate that the kinetics of the silver (I)/silver (II) couple and particularly the reduction of silver (II) are critically dependent on the oxide coverage, the reactions becoming slower as the oxide layer becomes thicker. The reason for the retardation of the reduction of the silver (II) on the oxide surface is not so clear although similar behaviour has been observed for the cobalt (II)/cobalt (III)[6], manganese (II)/manganese (III)[6] and cerium (III)/cerium (IV)[7] couples; in each of these examples the higher oxidation state can be produced on an oxide covered electrode while its reduction is complicated and rapid only at potentials where the oxide layer is removed. The cause may be the slow adsorption of the more highly charged species onto the electrode surface.

However, the complications indicated by the potentiodynamic experiments do not affect the fact that silver (II) can be produced in high yields and in a fast electrode reaction by oxidation of silver (I) in nitric or perchloric acids at a platinum anode, although it is essential that the electrode potential is carefully controlled. It has also been found that silver (II) may be prepared with equal success at an anode made from pyrolytic graphite.

Reactions of silver (II)

Unfortunately, 'uncomplexed' silver (II) is not completely stable in aqueous solution and the kinetics of the reaction between silver (II) and water have been studied by several authors[3, 8–12]. In the most recent paper, Po, Swinehart and Allen[11] have shown that in 2–6 M nitric acid, the reaction is second order with respect to the silver (II) concentration and that the pseudo-second order rate constant is 1·78 l mole^{-1} sec^{-1}. Under these circumstances, it is clear that it would not be possible to obtain complete conversion of silver (I) to silver (II) in an electrochemical reactor and in any practical system, any attempt to obtain a high conversion will lead to low current efficiencies. The exact conversion which may sensibly be attempted will depend on the design of the electrochemical cell but an example is shown in Fig. 6. In these experiments, 5 cm^3 of a 10^{-2} M silver solution in 3 M nitric acid were electrolysed at a rotating platinum electrode of area 1·8 cm^2 and the silver (II) content of the solution was determined after different quantities of charge had been passed; the anode potential was controlled at +1·29 V close to the optimum for silver (II) production under these conditions. The results are shown in the form of a graph of current yield versus percentage conversion to silver (II) and in this cell it would clearly be advisable to convert only 40% of the silver (I) to silver (II). Higher conversions than those shown in Fig. 6 can be working at higher electrode potentials but only at the cost of lower current efficiency. In any cell the optimum conversion is not likely to exceed 50%. This effect is unimportant when the silver (II) is used *in situ* in the electrochemical cell since the silver (II) concentration does not build up, but would have to be considered if the reaction were carried out in a separate reactor.

As has already been stated, silver (II) is a very powerful oxidant and undergoes rapid reactions with a wide range of inorganic and organic substrates. Thus silver (II) reacts rapidly with cobalt (II), manganese (II) and thallium (I) to

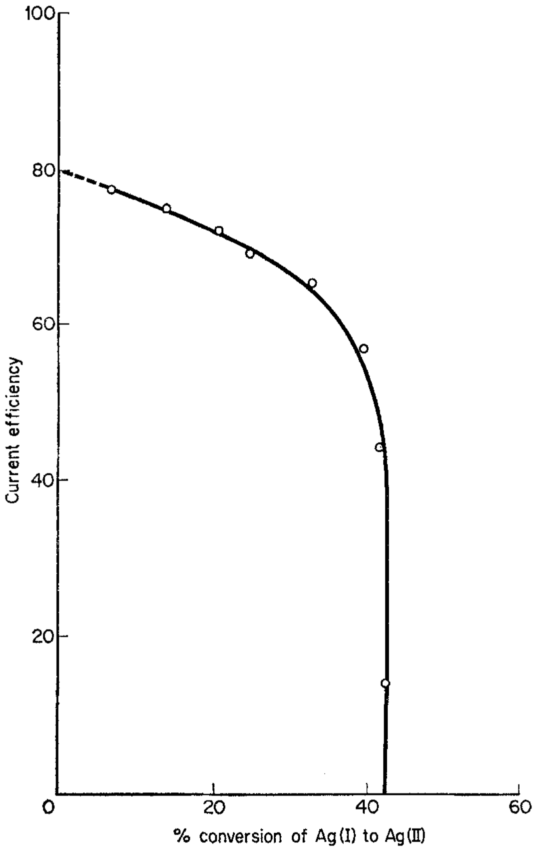


Fig. 6. Plot of current efficiency versus percentage conversion of silver (I) to silver (II). Starting solution contains 3 M HNO_3 and 10^{-2} M $AgNO_3$.

produce higher oxidation states of these metals although none of these species is oxidized rapidly at a platinum electrode prior to oxygen evolution in 3 M nitric acid. These reactions emphasize again the key advantage of silver (I) as a 'current carrier'; it is produced at a diffusion controlled rate at low overpotentials whereas many of the ions listed at the beginning of this paper can be prepared only at very high overpotential, e.g. cobalt (III), or by a kinetically controlled route at low current density, e.g. manganese (III).

Table 1

Substrate	*Product*	*Current yield* (%)
Benzene	*p*-quinone	33
Toluene	benzaldehyde	90
p-Xylene	*p*-tolualdehyde	60
Ethylbenzene	acetophenone	30
Tetralin	tetralone	60
Isopropanol	acetone	85

In the field of organic chemistry, silver (II) reacts with many substrates, for example with alcohols and with side chains of aromatic molecules[2]. In this work, the oxidation of a range of organic compounds has been carried out *in situ* in the electrochemical cell and the results of these experiments are shown in Table 1. With the exception of tetralin, the reactions were carried out in aqueous 3 M nitric acid; the isopropanol was 1 M and the other compounds were present as saturated solutions. The reaction medium for tetralin was 1 M nitric acid in 50% aqueous acetic acid. The yields of the products are similar to those found by Syper[2] although in several cases the reaction media are different. It should be stressed that we have not optimized the reaction conditions, e.g. solvent, pH, temperature, etc. We also found that in the case of organic compounds insoluble in water, similar yields could be obtained on a simple circulating system consisting of an electrochemical cell, a chemical reactor and pump.

Therefore, it can be concluded that silver (II) is a useful intermediate in electrode reactions and that it allows the oxidation of many organic and inorganic species which are not oxidized directly at a platinum anode at potentials less positive than those required for oxygen evolution. It has the advantage over the other powerful oxidizing ions in that it is produced in a rapid electrode reaction although its efficient use requires careful control of the anode potential because of the proximity of the potential of the silver (I)/silver (II) couple to that for oxygen evolution and to that for argentic oxide formation.

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