ELECTRO-OXIDATION OF SILVER (I) NITRATE AND SILVER (I) PERCHLORATE IN THE PRESENCE OF 2,2′-BIPYRIDYL IN ACETONITRILE*

M. A. A. Usmani

Department of Chemistry, University of Karachi, Karachi 32

D. B. Scaife

Department of Chemistry, The City University of London, London

(Received July 29, 1975)

Abstract. Detailed polarographic study of silver(I) nitrate and silver(I) perchlorate were performed in acetonitrile solvent in the presence of 2,2′-bipyridyl. Most interesting part of the present work, apart from preparation and isolation of bis(2,2′-bipyridyl)silver(II) nitrate–perchlorate and bis(2,2′-bipyridyl)silver(II) diperchlorate, has been the finding that the electroactive species is ML rather than ML_2.

The aim of the present work was to develop a method for the preparation of higher oxidation state complexes of transition metals using electro-oxidation techniques. Methods which have been employed successfully for electro-oxidation of organic compounds in nonaqueous solvents are reviewed by Weinberg and Weinberg,[1] these include controlled potential electrolysis at potentials corresponding to specific oxidation steps determined by anodic polarography. In the present work this technique has been applied to the oxidation of silver(I) nitrate and silver(I) perchlorate in the presence of 2,2′-bipyridyl (bipy).

Anodic polarography in the present work was carried out using a rotating platinum electrode (RPE) first described by Nernst and Merriam[2] and further investigated by Laitinen and Kolthoff.[3] A comparative study of platinum and graphite electrode has been reported by Lord and Rogers[4] where it was observed that graphite electrode generally gave less well-defined waves.

Experimental

Acetonitrile was chosen as a solvent for electro-oxidation work, since it is very resistant to oxidation in the presence of 0.1M tetra-n-butyl ammonium perchlorate (TBAP), the supporting electrolyte. Anodic limit was found to be of the order of 2.9 V vs S.C.E. The solvent supplied by Eastman-Kodak (spectro grade) was dried to 50 p.p.m. water-content from 600 p.p.m. using molecular sieve type 3A. Whereas S.C.E., the reference electrode was clamped so that the tip of the Agar–potassium chloride bridge, which was drawn to a fine capillary (about 0.5 mm dia) and packet with asbestos fibres, was kept at about 0.5–1.0 mm from the rotating platinum microelectrode (R.P.E.) during anodic polarography. Polarograms seems to be reproducible (i.e. no apparent potential drop effect) when maintaining the specified distance from S.C.E. to R.P.E. Water seepage was controlled to a greater extent by using such S.C.E. as mentioned above; the fact being manifested by the experiment that on dipping the tip of the S.C.E. in 100 cm^3 of acetonitrile for 3 hr gave only an increase of about 55 p.p.m. water. The complete polarographic cell assembly, including speed motor was housed in a nitrogen filled dry-box maintained at 5–8% R. H., at 20 ± 1°C. The dried solvent if left outside the dry box for 3 hr, the normal experimental period for each set, absorbed about 570 p.p.m. water. Water content determinations were made using Karl–Fischer method.

For polarographic work, a single compartment cell was employed with rotating platinum microelectrode as anode and a platinum strip of 2.5×2.5 cm acted as the cathode. While controlled potential electrolysis was performed in a three-compartment cell having anode and cathode compartments with a maximum capacity for 50 cm^3 acetonitrile bridged by third compartment having sintered discs of G-4 porosity on either side. Mercury pool was used as the cathode and its surface kept renewed with a magnetic stirrer, whereas the anode was a platinum electrode 50-cm long of 22 S.W.G. guage wire wound round a glass tube and rotated at 700 rev/min using constant speed motor.

The apparatus used for both the polarographic and controlled potential electrolysis work was basically the same and comprised a potentiostat, a reference voltage scanner, a potentiometric recorder and one of the two cells depending upon the mode of operation. The external circuit diagram is shown in Fig. 1.

Isolation and Analysis of Silver(II) *Complexes.* The small amount of solid which came out during controlled potential electrolysis of silver(I) nitrate in the presence of bipy was removed by decantation method and then silver(I) nitrate was gradually added with constant stirring until the dark red brown colour of anolyte disappeared, as almost all the complexes came out of solution. Crystals thus obtained were separated from the pale yellow supernatant liquid and purified by washing several times with acetone and dried in a vacuum oven at 40°C.
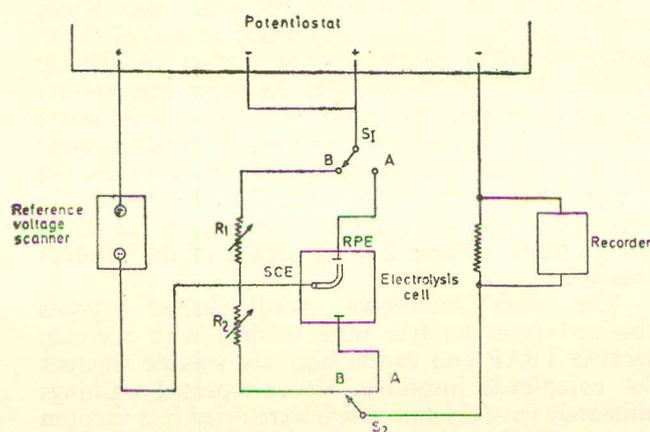
Fig. 1. External potentiostat circuit.

The C, H, N and Ag^{2+} analysis for the complex gave following values, alongwith theoretical values for $Ag(bipy)_2NO_3ClO_4$.

	$C(\%)$	$H(\%)$	$N(\%)$	$Ag^{2+}(\%)$
Theoretical	41.29	2.77	12.04	18.54
Found	40.9	2.8	11.9	17.8
Calcd	40.8	2.9	11.7	17.9

Evaporation of acetonitrile from anolyte, obtained from electrolysis of silver(I) perchlorate in the presence of bipy, was preferred where the concentration of ligand was very large compared to silver(I) perchlorate; and the residue thus obtained was washed several times with acetone to remove TBAP and excess bipy to seperate pure crystals of silver(II) complex. Whereas, the addition of silver(I) perchlorate was employed as in the case of [Ag(bipy)₂-]NO_3ClO_4 to obtain the product from anolyte in which the ligand was not taken in large excess compared to silver(I) perchlorate. Products, obtained via solvent evaporation method and via introduction of silver(I) perchlorate gave following C, H, N, and Ag^{2+} analysis.

	$C(\%)$	$H(\%)$	$N(\%)$	$Ag^{2+}(\%)$
Found (solvent evaporation)	38.75	2.69	9.16	16.8
Found (silver perchlorate)	38.54	2.58	9.01	15.9

The theoretical analysis for $[Ag(bipy)_2] (ClO_4)_2$ is as follows :

$C(\%)$	$H(\%)$	$N(\%)$	$Ag^{2+}(\%)$
38.80	2.60	9.05	17.42

Results and Discussion

Anodic Polarography and Coulometry of Silver(I) Nitrate Solutions. The oxidation of silver(I) to silver(II) within the anodic limit (2.9 V vs S.C.E.) of the solvent system would appear to be feasible. The strong solvation of silver(I) ions by acetonitrile has been demonstrated by Janz and his coworkers[5,6] who isolated $[Ag.(CH_3CN)]NO_3$ and $[Ag(CH_3CN)_2]$ NO_3 from solutions of silver nitrate in acetonitrile. That silver ions are more strongly solvated in acetonitrile than in water, is further indicated by the

fact that the standard reduction potential for the silver(I)–silver(0) couple in acetonitrile is some 0.4 V more negative than the corresponding value determined in an aqueous medium.[7]

Although the silver(I) ions are strongly solvated in acetonitrile [a factor which would tend to make the reduction potential of the silver(II)/silver(I) couple more positive] the dipositive ion might be expected to be even more strongly solvated as is usually found for ions of higher charges. Then it would be reasonable to expect that the standard reduction potential of silver(II)/silver(I) couple in acetonitrile would be of the same order as the value determined in an aqueous medium (2.16 V vs S.C.E.).[8] Since this value is well within the anodic limit of the solvent system (about 3.0 V), an oxidation wave would be expected to be observed within the experimental range available. Although a previous study[9] of the electrolytic oxidation of silver(I) nitrate solutions in acetonitrile did not indicate the oxidation of silver(I) ions, but suggested the oxidation of nitrate ion. This evidence was not considered to preclude the possiblity of the oxidation of silver(I) in acetonitrile, since the electrolysis were not carried out at a controlled anode potential and were not preceded by polarographic analysis.

Polarograms for silver(I) nitrate solutions in the concentrations ranging from 1 to 5 mM were recorded over the range 1.0–3.0 V at a scanning rate of 0.4 V/min. The lower limit of scanning range i.e. 0.0 V was changed to 1.0 V since a reduction wave was found to be present at 0.30 V (this wave was characterized by Kolthoff[10] and Larson and Iwamto[11] as the reduction wave of the silver(I)–silver(0) couple.

Half-wave potential for expected silver(II)-silver(I) couple was found to be about 2.00 ± 0.04V and the slope of i_L (limiting current) vs C (concentration) wave was found to be 1.8 ± 0.2 μA/mM, comparing favourably with the value of 1.8 ± 0.1μ A/mM obtained for one electron iodide ion oxidation wave used to calibrate the electrode system. Coulometric studies, further gave evidence in favour of a one-electron transfer. However, the process is irreversible since the plot of log i/i_L—i vs V gives a slope which corresponds to an electron change of about 0.5/ molecule. The attempt to isolate the product of silver(II) was not successful and no evidence for the existence of higher oxidation silver was manifested by any of the routine chemical tests. This leads to the belief that it was the nitrate ion rather than silver(I) which has been oxidised, and this belief was supported by the polarogram of silver perchlorate which gave no wave whatsoever in the entire anodic range available within the system, whilst the polarogram of tetra-n-butylammonium nitrate gave a wave similar to that of silver nitrate.

The polarographic and coulometric data for the oxidation of nitrate ion are not consistent with the scheme below, which is analogous to that proposed by Schmidt and Noack[12] for perchlorate ion oxidation in acetonitrile.

$$NO_3^- \longrightarrow NO_3^{\cdot} + e^- . \tag{1}$$
$$NO_3^{\cdot} + CH_3CN \longrightarrow HNO_3 + CH_2CN \tag{1a}$$
$$2 \cdot CH_2CN \longrightarrow CN-CH_2-CH_2-CN$$
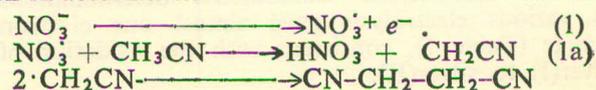
Since the nitrate ion is regenerated (1a), this scheme corresponds to the catalytic oxidation of the solvent rather than limiting current of the system.

The data are consistent, however, with the reaction scheme proposed by Schmidt and Stange[9] ot account for nitrate ion oxidation in acetonitrile viz.

$$NO_3^- \longrightarrow NO_3^{\cdot} + e^-$$
$$2NO_3^{\cdot} \longrightarrow N_2O_6$$
$$N_2O_6 \longrightarrow N_2O_5 + \tfrac{1}{2}O_2$$
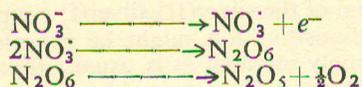
Although the above scheme is in agreement with the present data, a complete analytical investigation of the product and intermediates would be required before the mechanism could be more fully understood.

Electro-oxidation of Silver(I) *Nitrate in the Presence of 2,2′-Bipyridyl.* Initially, polarograms for a bipy wih 0.1M TBAP in acetonitrile were obtained and made sure that the ligand gives no wave within the anodic range. A very small wave($i_L \sim 0.3$ mA) is observed at a half-wave potential ($E_{\frac{1}{2}}$) of 2.1 V. Polarograms from 2 to 30 mM gave virtually constnat limiting current. It is difficult to account for this phenomenon, however, as far as the present work is concerned, it is clear that bipy wave will not interfere at potentials less than 2.0 V and at higher potentials a correction which is small can be made.

Polarograms for solutions of silver nitrate in the presence of bipy were obtained for various concentration ratios of metal to ligand at a scan rate of 0.4 V/min.

The silver nitrate–bipy system gives two well-defined the first of which corresponds to $E_{\frac{1}{2}}$ 1.44 ± 0.04V, the limiting current for this wave being much smaller than expected for a one-electron oxidation process; the second wave corresponding to $E_{\frac{1}{2}}$ about 2.0V, same as obtained for nitrate ion oxidation, but the limiting current is much greater compared to the system where bipy was absent. The limiting currents of both waves could be measured with a reproducibility of about 0.1 μA. An interesting feature of the system is that the limiting currents of both waves vary with the ligand concentration; that of the first wave reducing to zero when the bipy is present in large excess. The variation of the limiting current of the first wave of the silver nitrate–bipy system with ligand concentration was considered to be of particular interest to justify a more detailed investigation.

Electrolysis of Silver Nitrate/Bipy Solutions at 1.4–1.5 V. Coulometric determinations for the electrolysis of silver nitrate solutions in the presence of bipy were carried out at a constant potential in the vicinity of the half-wave potential (1.44 V). Initially, solutions having molecular ratios of ligand to metal salt of the order of 2:1 were electrolysed but it was found that dark red crystals separated from the solution and adhered to the rotating macroplatinum electrode giving a sharp reduction in current and preventing complete electrolysis. To overcome this problem the ligand to metal salt ratio was increased to 30:1 which enable smooth and complete electrolysis. Coulometric determinations on various electrolysis gave almost one electron change (Table 1), consistent with the oxidation of silver(I) to silver(II).

Subsequently, controlled potential electrolysis on a larger volume was performed in an effort to isolate silver(II) complex from almost completely oxidised dark brown anolyte. In these experiments the ligand to metal salt ratio were taken to be about 3:1. During electrolysis some of the product came out of solution and coated the electrode producing a rapid fall in current; when this happened the electrolysis was interrupted momentarily to clean the electrode. Table 2 gives details of the product obtained.

The dark red-brown needle-shaped crystals obtained from anolyte were washed with acetone, because TBAP and excess bipy are soluble whereas the complex is insoluble. Hence repeated washings ultimately gave crystals which were dried in a vacuum oven at 40°C, and they melted at 198–208°C. Expected silver(I) complex exhibited oxidising properties towards iodide and bromide in aqueous medium. The analysis of the product corresponded to the theoretical values for the complex with molecular formula $[Ag(bipy)_2]NO_3\ ClO_4$ for $[Ag(bipy)_2](NO_3)_2$ and $[Ag(bipy)_2](ClO_4)_2$ theoretical values of C, H, N and Ag^{2+} do not suggest any of these two formula to be true for the silver(II) complex isolated.

The compound had an effective magnetic moment of 1.9 B.M. at 20°C determined by Guoy balance, consistent with the d^9 configuration. The IR of the complex (in KBr disc) showed a very strong band at 1380 cm^{-1} indicating the presence of ionic nitrate and broad and very strong ionic perchlorate band was also observed at 1085–1145 cm^{-1}. The diffused reflectance spectrum gave a distinct absorption band at 18, 182 cm^{-1}, which compared with the single absorption band (for d^9 arrangment) at 19,048 cm^{-1} reported by Lake and Kennedy[13] for silver(II) in condensed phosphoric acid. Thorpe and Kochi[14] also reported an absorption band at 23,529 cm^{-1} for bis(bipy)silver(II) dinitrate in water. With all these supporting evidences, it may be suggested that the isolated complex is bis(bipy)silver(II) nitrate perchlorate.

TABLE 1. COULOMETRY OF SILVER(I) NITRATE/BIPY SOLUTIONS.

AgNO$_3$ (g)	Potential applied (V)	Initial current (mA)	Electrolysis time (min)	Current used (Coulombs)	Molecular ratio of bipy–AgNO$_3$	Electron per mole
0·0101	1·40	2·25	150	6·41	32:1	1·12
0·0109	1·45	3·1	118	6·09	30:1	0·98
0·0101	1·50	3·7	52	5·60	30:1	0·98

TABLE 2. PREPARATION OF BIS(BIPY)SILVER(II) NITRATE PERCHLORATE.

Silver nitrate (g)	Bipy–silver (I) (molecular ratio)	Anodic potential	Yield(%)
0·0212	3·0:1	1·50	44·1
0·0433	3·1:1	1·50	44·5
0·0630	3·2:1	1·45	39·0

Detailed Polarographic Study of Silver(I) *Nitrate in the Presence of 2,2'-Bipyridyl.* Anodic polarograms were obtained for solutions containing different total concentrations of silver(I) nitrate (C_M) and bipy (C_L) in 0.1M TBAP using 0.4 V/min scan rate. The data are recorded in Table 3 in which the values of the limiting current of the wave is denoted as i_L and half-wave potential as $E_{\frac{1}{2}}$; also includes the data of polarograms obtained for solution of bis-(bipy) silver(I) nitrate (these are indicated by an asterisk and in these cases C_L has been taken as equal to $2C_M$.)

The results of the coulometric experiments, and other evidences established that the anodic wave at $E_{\frac{1}{2}}$, i.e. 1.44 V corresponds to oxidation of silver(I) to silver(II). It is felt necessary to explore as to why the limiting value is much too smaller than would be expected.

The observation that for a given concentration of silver salt, the limiting current of the wave, i_L, at first increased and then decreased with increasing ligand concentration C_L, led to the suggestion that i_L might be related to the concentration of one of the complex species present. It is possible that the two complex species Ag(bipy)$^+$ and Ag(bipy)$_2^+$ are present having their concentration depending on the equilibrium constants of the following reactions :

$$Ag^+ + bipy \rightleftharpoons Ag(bipy)^+ \qquad (2)$$
$$Ag(bipy)^+ + bipy \rightleftharpoons Ag(bipy)_2^+ \qquad (2a)$$
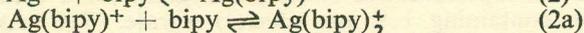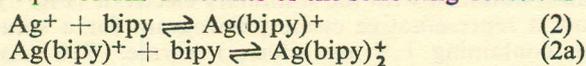
Since at constant C_M the concentration of Ag(bipy)$^+$ will first increase and then decrease as C_L increases, it seemed likely that there might exist a correlation between Ag(bipy)$^+$ and i_L. In order to test this hypothesis, calculations were made of the concentration of Ag(bipy)$^+$, in each of the solutions (of known C_M and C_L) used in the polarographic study. This was possible using values determined for the overall stability constants for the silver(I)–bipy system in acetonitrile.[15]

For the case in which a metal ion M forms two successive complexes ML and ML$_2$, the overall stability constants for the equilibria are defined as :

$$\beta_1 = [ML] / [M][L] \text{ and } \beta_2 = [ML_2] / [M][L_2]$$

Using the concept of the average ligand number, $\bar{n}$, defined by Bjerrum[16] as :

$$\bar{n} = C_L - [L] / C_M \qquad (3)$$

Where C_M and C_L are total concentrations of metal and ligand and L is the free ligand concentration; it follows that:

$$\bar{n} = [ML] + 2[ML_2] / [M] + [ML] + [ML_2]$$
whence $\bar{n} = \beta_1[L] + 2\beta_2[L]^2 / 1 + \beta_1[L] + \beta_2[L]^2 \qquad (4)$
and $[ML] = C_M \cdot \beta_1[L] / 1 + \beta_1[L] + \beta_2[L]^2 \qquad (5)$

The formation curve[16] of the system ($\bar{n}$ vs $p[L]$ constructed by substituting in equation (4) the values of β_1 and β_2 (determined as 9.37×10^2 mole^{-1} kg and 1.38×10^5 mole^{-2} kg^2 respectively) and calculated the values of $\bar{n}$ for different values of $[L]$. This curve is shown in Fig. 2.

For each experimental value of C_M used, a plot was made of C_L vs $[L]$ using equation (3) to calculate the value of C_L for given pairs of values $\bar{n}$, $[L]$

selected from the formation curves (two such curves are shown in Fig. 3, for $C_M = 1.76$ and 2.28 mM). Finally for each given set of experimental values of C_M and C_L, the value of $[L]$ was interpolated from the appropriate C_L vs $[L]$ curve and ML calculated from equation (5). Table 3 includes values of [Ag(bipy)$^+$] and Fig. 4 shows the relationship between [Ag(bipy)$^+$] and i_L. Within the experimental error of the limiting current values (± 0.15 μA) this relationship is linear.
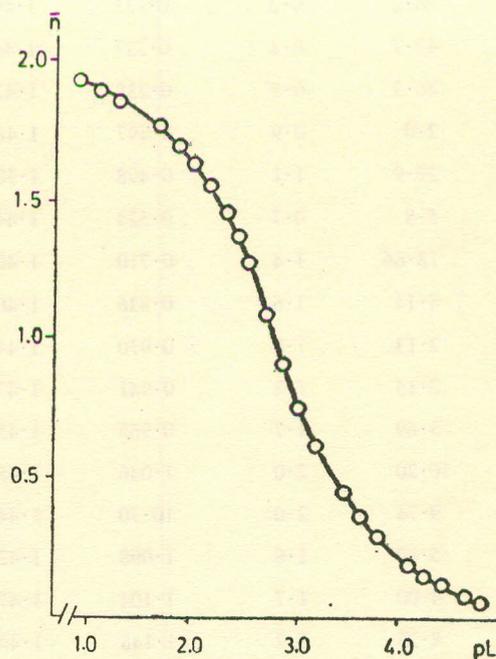
Fig. 2. Formation curve for Ag+/bipy system.
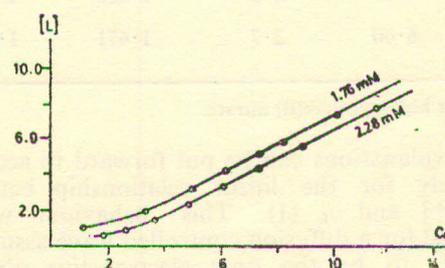
Fig. 3. C_L versus L for Ag+/bipy system.
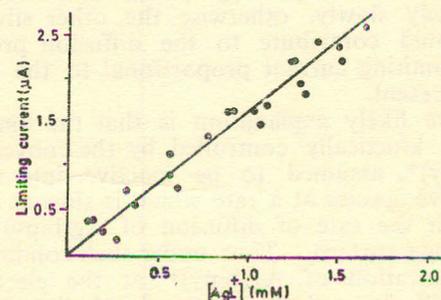
Fig. 4. Limiting current vs. concn of [Ag+(bipy)+].

TABLE 3. ANODIC POLAROGRAPHY OF THE SILVER(I) NITRATE/BIPY SOLUTIONS.

C_M (mM)	C_L (mM)	i_L (μA)	AgL^+ (mM)	$E_{\frac{1}{2}}$ (V)
0·62	31·5	0·3	0·113	1·44
1·66	93·7	0·3	0·116	1·44
1·76	86·2	0·2	0·133	1·46
1·66	43·7	0·4	0·237	1·44
1·76	46·3	0·5	0·238	1·42
1·00	2·0	0·9	0·497	1·48
2·28	27·9	1·1	0·498	1·38
1·00	5·8	0·7	0·524	1·44
2·28	18·66	1·4	0·710	1·40
1·50	4·14	1·6	0·836	1·40
1·76	7·13	1·6	0·970	1·44
2·28	2·15	1·4	0·941	1·47
1·76	3·69	1·7	0·968	1·45
2·28	10·20	2·0	1·046	1·45
2·28	9·74	2·0	10·70	1·44
2·00	5·80	1·8	1·098	1·42
2·00	4·00	1·7	1·104	1·47
2·28	8·25	2·2	1·148	1·44
2·28	6·30	2·2	1·244	1·44
2·28	4·15	2·0	1·253	1·40
3·00	6·00	2·7	1·671	1·40

·Data for bis(bipy)silver(II) nitrate.

Fig 5. Oscilloscope polarography of AgNO$_3$ with bipy.

Two explanations can be put forward to account qualitatively for the linear relationship between [Ag(bipy)$^+$] and i_L (1). This behaviour would be expected for a diffusion controlled wave assuming Ag(bipy)$^+$ to be the only electroactive silver(I) species present in solution. However, the important assumption would have to be made that the equilibria associated with silver(I)–bipy system were established extremely slowly, otherwise the other silver(I) species would contribute to the diffusion process giving a limiting current proportional to the total silver(I) present.

A more likely explanation is that the limiting current is kinetically controlled by the conversion of Ag(bipy)$^+$, assumed to be inactive, into some electroactive species at a rate which is slow as compared with the rate of diffusion of Ag(bipy)$^+$ to the electrode surface. Thus under such conditions, the concentration of Ag(bipy)$^+$ at the electrode surface will be maintained at the bulk solution concentration; the rate of conversion to the active form and hence the limiting current will be proportional to [Ag(bipy)$^+$] if the chemical reaction is first order or pseudo first order. This explanation is supported by the results of a series of cyclic voltammetry experiments on solutions containing silver(I) nitrate and bipyridyl in which the voltage was swept from 0.0 to 2.0V and back to 0.0 V in order to cover the voltage range of the first wave of the system. These data were obtained using the rapid sweep oscillographic polarograph in conjunction with the microplatinum electrode. Cyclic polarograms, obtained with the stationary electrode (Fig. 5), show a representative cyclic polarogram for a solution containing 1.9 mM silver(I) nitrate, 7.0 mM bipyridyl in 0.1M TBAP using a stationary electrode and sweep rate of 0.2 V/sec. The most striking feature of the polarogram is that the usual peaking characteristics of rapid sweep polarograms are absent; the wave appearing as a normal polarogram obtained with slow rate of scan. Another interesting feature is the almost complete absence of a reduction wave on the reversion scan. Further, the wave form and wave height were almost completely independent of scan rate even when rates as high as 4 V/sec were used. These characteristics are consistent with a kinetically controlled wave[17,18] and correspond to the case where the charge transfer process is preceded by a slow chemical reaction producing the depolariser. The depolariser will be formed at a constant rate at the electrode surface if the rate of diffusion of the inactive form is greater than its rate of conversion to the active form; under these conditions the surface layer would not be depleted in the inactive form and the current would remain constant. The absence of the reduction wave on the reverse sweep implies either that the charge transfer process is completely irreversible or that the oxidised form of the depolariser is rapidly converted into an inactive form.

The experimental data available for the silver(I) nitrate–bipy system do not, of course, enable the electroactive species to be identified and any theory put forward must be extremely speculative. It seems probable, however, that the complex species Ag(bipy)$^+$ is the precursor of the active form. Conversion to the active form may involve some change in the solvation sphere of the complex species, a process which has been suggested in the case of the reduction of aquated nickle(II) ions.[19] In the silver(I)

nitrate system a tentative suggestion is that the inactive species is in the form of an ion-pair, $Ag(bipy)^+$ NO_3^-; conversion to the active form involving the removal of nitrate ion. The rapid recombination of the nitrate ion with the oxidised form of $Ag(bipy)^{+2}$. would then account for the absence of a reduction wave in the reverse sweep of the cyclic polarogram. This idea is supported to some extent by published data[6] on the nature of acetonitrile solutions of silver(I) nitrate in which the presence of Ag^+, NO_3^- ion-pairs has been established.

$$Ag(bipy)^+NO_3^- \quad \xrightleftharpoons{\text{—NO}_3 \text{ (slow)}} \quad Ag(bipy)^+$$
ion-pair $-e \updownarrow \overset{\text{Charge}}{\text{transfer}}$
(inactive)

$$Ag(bipy)^{2+}NO_3^- \quad \xrightleftharpoons{+\text{NO}_3^- +\text{(fast)}} \quad Ag(bipy)^{2+}$$
ion-pair
(inactive)
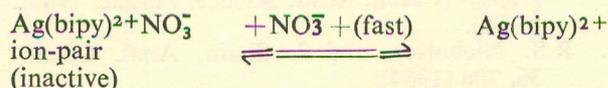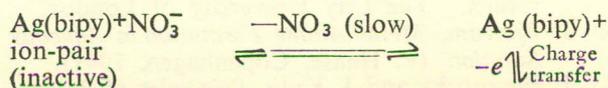
It must be emphasised that although such a scheme is consistent with the experimental data, it is highly speculative. A more detailed study will be required before the processes taking place are more fully understood. In this respect, a cyclic voltammetry study at a stationary planar electrode, for which the mathematical solutions of the electrode processes have been obtained,[18] would allow the electroactive intermediates to be detected and the rate constants of the reaction to be determined.

Electro–oxidation of Silver Perchlorate in the Presence of 2,2′-Bipyridyl. In contrast to the silver(I) nitrate–bipy system, the silver(I) perchlorate–bipy system shows a poorly-defined first wave which is followed by a pronounced maximum at higher potentials, the current falling to a low level before the anodic limit is reached. The first wave occurs at the same potential as that of the silver nitrate–bipy system (1.44 V); this wave and the maximum which follow it, disappear when the ligand is present in large excess.

Electrolysis of Silver Perchlorate–Bipy Solution at 1.4–1.5 V. Solutions of silver(I) perchlorate in the presence of bipy were electrolysed at controlled potential in the vicinity of the half wave potential of the first wave (1.4–1.5 V). For this system, coulometric determinations were incorporated in preparative scale electrolyses. Ligand was taken in large excess to avoid product covering the electrode. Coulometric determinations strongly supported one electron process for silver(I) to silver(II) change at first polarographic wave (Table 4).

Because of the large excess of bipy, evaporation of the solvent was preferred instead of adding of silver(I) salt, and washing with acetone enabled the removal of supporting electrolyte and large excess of bipy. The product was dried in a vacuum oven at 40°C. The dark red needle-shaped crystals had a m.p. of 231–236°C.

Two further preparative scale electrolyses were carried out using ratios of 5:1 of ligand to metal salt respectively, whereas the anode required to be recleaned. The silver(II) complex was precipitated by the addition of silver(I) perchlorate by the method used for bis(bipy)silver(II) nitrate perchlorate. The dark brown red needle-shaped crystals had a m.p.

TABLE 4. COULOMETRY OF SILVER (I) PERCHLORATE BIPY SOLUTIONS.

$AgClO_4$ (g)	Potential applied (V)	Initial current (mA)	Electrolysis time (min)	Current used (Coulombs)	Moelcular ratio of bipy–$AgClO_4$	Electron per mole
0·2011	1·45	40	204	107·73	11:1	1·15
0·0933	1·50	25	196	46·02	22·66:1	1·06

TABLE 5. PREPARATION OF BIS(BIPY) SILVER (II) DIPERCHLORATE.

Silver perchlorate (g)	Bipy-silver (I) (molecular ratio)	Anodic potential (V)	Yied (%)
0.0933	22:1	1.50	57.4
0.2011	11:1	1.45	65.1
0.2385	5:1	1.40	39.6

of 231–235°C. Table 5 gives details of the amounts of metal salt, ligand and the complex yield. The precipitation method had the advantage that only two or three washings were required whereas for the solvent evaporation method about eight washings were necessary.

Expected silver(II) complex exhibited oxidising properties towards iodide and bromide in aqueous medium. The analysis of the product isolated by two methods corresponded to the theoretical values for the complex with molecular formula $[Ag(bipy)_2](ClO_4)_2$.

The IR spectrum of the product gave a very strong broad band at 1085–1150 cm^{-1} corresponding to the absorption of the perchlorate ions. The data are in accordance with the diperchlorate silver(II) complex. The diffuse reflectance spectrum gave an absorption band at 20,408 cm^{-1} (490 nm) which is higher than that found for bis(bipy)silver(II) than that found for bis(bipy)silver(II) nitrate perchlorate.

The mass spectrum of the product gave a maximum mass number of 156.0687 corresponding to the mass of the 2,2′-bipyridyl molecule. It appears, therefore, that under the conditions for determining the mass spectrum (ion source temperature 300°C, electron energy 70 eV), the complex got decomposed. However, the mass spectrum is useful in demonstrating that the ligand remains unchanged during the electrochemical oxidation of silver(II) complex.

Conclusion

The preparation of bis(bipy)silver(II) complex is possible via electrooxidation of silver(I) salts in the presence of bipy. Various other ligands could also be attempted like bipy, provided they themselves do not get oxidised during electrolysis, and also these ligands should be capable of giving a strong chelation with silver(I) so that it is oxidisable within the anodic range. Ligands like, 4,4′-dimethyl-2,2′-bipyridyl; 2,2′,2″-terpyridyl; 5,5′-dibutyl and 2,2′-bipyridyl, may be chosen for further studies due to their characteristics which are expected to be very much close to 2,2′-bipyridyl.

References

1. N. L. Weinberg and H.R. Weinberg, Chem. Rev., **68**, 449 (1968).
2. W. Nernst and E.S. Merriam, Z. Physik. Chem., **52**, 235 (1905).
3. H.A. Laitinen and I.M. Kolthoff, J. Phys. Chem., **45**, 1079 (1941).
4. S.S. Lord Jr. and L.B. Rogers, Anal. Chem., **26**, 284 (1954).
5. C.B. Baddiel, M.J. Tait and G. J. Janz, J. Phys. Chem., **69**, 3634 (1965).
6. G.J. Janz, M.J. Tait and J. Meier, J. Phys. Chem., **71**, 963 (1967).
7. I.M. Kolthoff and F.G. Thomas, J. Phys. Chem., **69**, 3049 (1965).
8. A.A. Noyes and A. Kossiakoff, J. Am. Chem., Soc., **57**, 1238 (1935).
9. V.H. Schmidt and H. Stange, Z. Anorg. Chem., **293**, 274 (1958).
10. I.M. Kolthoff and J.F. Coetzee, J. Am. Chem. Soc., **79**, 1852 (1957).
11. R. C. Larson and R.T. Iwamoto, J. Am. Chem. Soc., **82**, 3526 (1960).
12. H. Schmidt and J. Noack, Z. Anorg. Chem., **296**, 262 (1958).
13. D.P. Lake and J.H. Kennedy, J. Electrochem. Soc., **117**, 1058 (1970).
14. W.G. Thorpe and J.K. Kochi, J. Inorg. Nucl. Chem., **33**, 3958 (1971).
15. A.G. Smeeth and M.N. Mahmood, unpublished results, The City University of London.
16. J. Bjerrum, *Metal Amine Formation in Aqueous Solution* (P. Haase, Copenhagen, 1941).
17. J. Heyrousky and J. Kuta, *Principles of Polarography* (Czech. Acad. Science, Prague, 1965), p. 506.
18. R.S. Nicholson and I. Shain, Anal. Chem **36**, 706 (1964).
19. J. Dandoy and L. Gierst, J. Electroanal. Chem. **2**, 116 (1961).