isomerization does not proceed to any great extent. However, in warm alkaline solutions, isomerization of the cis nitrosyl to the trans form is virtually complete. In addition, the characterization of these cis complexes has raised some interesting questions regarding the relative importance of cis ligands.

Registry No. *cis*-$[Ru(NH_3)_4(NO)Cl]Cl_2$, 38402-57-2; *cis*-$[Ru(NH_3)_4(NO)Br]Br_2$, 38402-58-3; *cis*-$[Ru(NH_3)_4(NO)I]I_2$, 38402-59-4; *cis*-$[Ru(NH_3)_4(NO)(OH)](ClO_4)_2$, 38402-60-7; *cis*-$[Ru(NH_3)_4(NO)OH_2](ClO_4)_3$, 38402-61-8; *cis*-$[Ru(ND_3)_4(NO)Br]Br_2$, 38402-62-9; *cis*-$[Ru(NH_3)_4(^{15}NO)Br]Br_2$, 38402-63-0; *cis*-$[Ru(NH_3)_4(NO)Cl]Br_2$, 38402-64-1; *cis*-$[Ru(NH_3)_4(NO)Cl]I_2$, 38402-65-2.

Acknowledgment. The authors wish to thank Professor R. Mann for his helpful advice on the interpretation of some of the infrared data. We would also like to acknowledge the encouragement of Professor H. Taube, in whose laboratories some very preliminary experiments were performed.

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Electrochemical Investigation of the Dichlorobis(2,2'-bipyridine)chromium(III) Complex[2]

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Received October 3, 1972

Electrochemical reduction of dichlorobis(2,2'-bipyridine)chromium(III) proceeds in a one-electron step and is followed by a fast ligand disproportionation and water substitution reactions that produce an equimolar mixture of $[Cr(bipy)_3]^{2+}$ and $[Cr(bipy)(H_2O)_4]^{2+}$. When the reduction is performed in the presence of an equivalent of 2,2'-bipyridine, $[Cr(bipy)_3]^{2+}$ is the sole product. Formation of the tris complex is highly sensitive to the solution pH below pH 4 owing to protonation of the transient free 2,2'-bipyridine. Slow chemical or electrochemical oxidation of reduced solutions produces diaquobis(2,2'-bipyridine)chromium(III). Rapid chemical oxidation carried out in such a way that the initial oxidation product does not mix appreciably with the yet unoxidized solution yields tris(2,2'-bipyridine)chromium(III). The mechanisms by which these oxidations are accomplished are discussed.

Introduction

There has been and continues to be substantial interest in the behavior of tris(2,2'-bipyridine)chromium(III) ion in solution.[4-9] Electrochemical studies of this complex ion in aqueous solutions have shown that under certain circumstances the attempted reduction of the complex resulted in the catalytic formation of a bis(2,2'-bipyridine)chromium(III) complex ion.[10,11] In a separate study of the tris-bipyridine complex, we reported briefly on the electrochemical behavior of a bis complex that was prepared *in situ via* the catalytic elimination of a bipyridine molecule.[12] From that brief study it appeared that the reduced complex was not behaving in a straightforward manner and that oxidation of the reduced solutions produced a substance quite different from the starting complex. We also noted some differences with the results of an earlier study of the bis complex that we were not able to satisfactorily resolve.[11]

This study was undertaken in an effort to gain a better understanding of the solution behavior of the bis complex and to resolve the apparent conflicts of earlier work with the preliminary results extending from our study of the tris complex. Our earlier success with the tris(2,2'-bipyridine)chromium(III) system[12] led us to believe that a similar electrochemical study of the bis complex would provide the answers and level of understanding we were seeking. The study is based on the polarographic and cyclic voltammetric behavior of the bis system at various stages of reduction, where the reductions were carried out by controlled-potential electrolysis at a mercury cathode.

Experimental Section

Apparatus. Electrochemical measurements were made with a Beckman Electroscan 30[13] equipped with an integrator. The integrator output was collected by and displayed on a Scallette pulse counter, Model SC-355.[13] Rapid (2–500 V/sec) cyclic voltammetric experiments were performed with a laboratory-constructed instrument employing operational amplifiers according to the basic design of Huntington and Davis.[14] Data were recorded on a Tektronix Type 564[13] storage oscilloscope.

A single cell was employed for the controlled-potential electrolysis, polarographic, and cyclic voltammetric experiments. The design of the cell has been described previously;[12] however, it is worthwhile to point out that exclusion of trace amounts of air is exceedingly important.

The open-circuit m and t values of the polarographic capillary were 1.46 mg/sec and 3.50 sec, respectively, in 0.1 M potassium chloride electrolyte at 25°. These gave a capillary constant of 1.59 $mg^{2/3}\ sec^{1/6}$.

Prepurified argon, used for deoxygenation and subsequent blanketing of the solution, was passed successively through a vanadium(II) sulfate solution, two chromium(II) chloride solutions, and a 0.1 M potassium chloride solution prior to passage through the sample in the cell. During the controlled-potential electrolysis experiments, after

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[1] One of the facilities of the Southern Region, Agricultural Research Service, U. S. Department of Agriculture.

[2] Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., 1971.

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[4] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 86, 1019 (1964).

[5] S. Herzog and W. Schon, *Z. Anorg. Allg. Chem.*, 297, 323 (1958).

[6] J. Josephesen and C. E. Schaffer, *Acta Chem. Scand.*, 24, 2929 (1970).

[7] E. Konig and S. Herzog, *J. Inorg. Nucl. Chem.*, 32, 585 (1970).

[8] Y. Sata and N. Tanaka, *Bull. Chem. Soc. Jap.*, 42, 1021 (1969).

[9] A. A. Vlcek, *Nature (London)*, 189, 393 (1961).

[10] B. R. Baker and B. D. Mehta, *Inorg. Chem.*, 4, 848 (1965).

[11] B. V. Tucker, J. M. Fitzgerald, L. G. Hargis, and L. B. Rogers, *J. Electroanal. Chem.*, 13, 400 (1967).

[12] D. M. Soignet and L. G. Hargis, *Inorg. Chem.*, 11, 2349 (1972).

[13] Use of a company or product name by this department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

[14] J. L. Huntington and D. G. Davis, *Chem. Instrum.*, 2, 83, (1969).

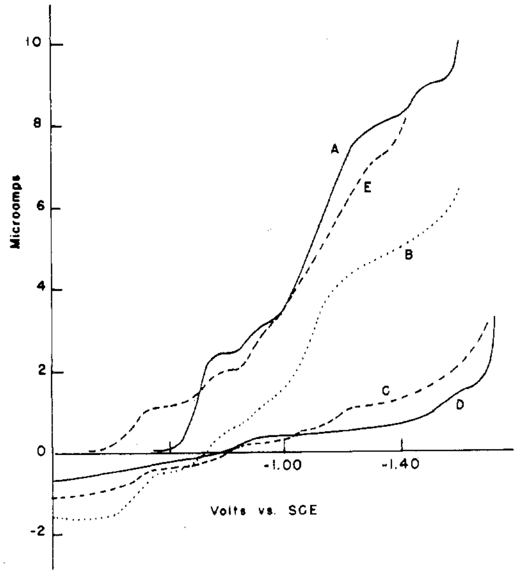

Figure 1. Polarograms of 1.16 × 10^{-3} *M* $[Cr(bipy)_2Cl_2]^+$ and of products of successive coulometric reductions in 0.1 *M* potassium chloride at 26° and pH 4.5: (A) unreduced complex; (B) complex reduced 1 electron/molecule at −0.78 V (*n* = 1); (C) complex reduced a second electron/molecule at −1.08 V (*n* = 2); (D) complex reduced an additional 0.60 electron/molecule at −1.13 V (*n* = 2.6); (E) complex reduced a total of 2.6 electrons/molecule and rapidly oxidized with oxygen gas.

initial purging, the gas flow was discontinued and the cell sealed.

Absorption spectra were obtained on a Beckman DBG recording spectrophotometer.

Solutions. Unless otherwise stated, the solutions employed were approximately 10^{-3} *M* with respect to the complex and 0.1 *M* in potassium chloride as the supporting electrolyte. All solutions contained 0.01% Triton X-100 as a maximum suppressor. The stability of the original solutions was checked by comparing their ultraviolet and visible absorption spectra and by examining chloroform extracts for the presence of free bipyridine periodically over a period of 1 month. No observable changes occurred during this period.

Since previous studies have shown that many buffer components, such as citrate and phosphate, may participate in catalytic electron-exchange reactions with chromium(II) to form chromium(III)[15a] and because polarographic behavior has been shown to differ in such buffers,[15b] unbuffered solutions were used throughout this study. Solution pH was adjusted to desired values by addition of HCl or NaOH. Solutions were checked occasionally after reductions or oxidations had been performed to make certain that no significant pH changes had occurred.

Dichlorobis(2,2′-bipyridine)chromium(III) Chloride Dihydrate. This cis complex[16] was prepared according to the procedure reported by Burstall and Nyholm.[17] After recrystallization from hot water, the solid product was suspended in chloroform to remove any unreacted 2,2′-bipyridine.

Anal. Calcd for $[Cr(C_{10}H_8N_2)Cl_2]Cl\cdot 2H_2O$: C, 47.40; H, 3.95; N, 11.06; total Cl, 20.99; ionic Cl, 6.99. Found: C, 47.83; H, 4.05; N, 10.91; total Cl, 20.76; ionic Cl, 6.96.

Procedures. In order to characterize adequately the behavior of $[Cr(bipy)_2Cl_2]^+$, controlled-potential coulometric electrolyses at a stirred mercury pool were planned at a suitable potential on the limiting-diffusion current plateau of each polarographic wave. In general, the various solutions were examined polarographically, cyclic voltammetrically, and spectrophotometrically.

Absorption spectra of the oxygen-sensitive reduction products were obtained by transferring the desired solution directly to a sealed absorption cell. The absorption cells were of a round-neck type that were fitted with rubber septums to make them airtight. The desired reduced solution was transferred from the electrolysis cell through a syringe needle to the deaerated absorption cell by applying a positive argon pressure to the electrolysis cell. The absorption cell was usually rinsed once or twice with the solution before the final filling to ensure that all traces of oxygen were removed. The absorption spectra were taken immediately after transfer.

For some experiments extraction of the reduced solutions with chloroform was used to remove any free bipyridine from the solution. The extraction was performed in a sealed absorption cell where the extract could be spectrophotometrically examined with a minimum of handling and with the knowledge that no oxidation of the complex could have occurred. The procedure was basically the same as described above except that a fixed amount of chloroform was added to the cell before purging and filling. Extraction was accomplished by vigorous shaking and the spectrum was obtained by positioning the cell in the spectrophotometer such that either the water or the chloroform solution alone was in the optical path.

Solutions of electrochemically reduced complexes were oxidized by a variety of methods which are described below.

Method 1. Rapid Oxidation with Oxygen Gas. One milliliter of 0.1 *M* KCl was placed on the fritted disk of a Buchner funnel. Oxygen gas was passed through the stem of the funnel and bubbled through the KCl solution. The solution to be oxidized was slowly transferred, under a positive argon gas atmosphere, into the Buchner funnel through which oxygen was continuously bubbling.

Method 2. Slow Oxidation with Oxygen Gas or Air. Oxygen gas or air was bubbled through the reduced solution in the electrolysis cell.

Method 3. Electrochemical Oxidation. The potential of a stirred mercury pool was adjusted so that oxidation of the reduced substance could proceed at the mercury electrode.

All reported voltages were measured *vs.* the saturated calomel electrode.

Results and Discussion

Figure 1 shows polarograms of the solution initially containing $[Cr(bipy)_2Cl_2]^+$ taken at various stages of the electrolysis. The polarogram of the unreduced complex, shown in Figure 1A, contains three important waves of approximately equal height with $E_{1/2}$ = −0.73, −1.06, and −1.22 V. These $E_{1/2}$ values and the relative wave heights correspond very closely to those reported by Tucker, *et al.*,[11] and Curtis.[18]

Tucker, *et al.*,[11] presented polarographic evidence that suggested a possible redox disproportionation of the complex resulting after a one-electron reduction of the bis complex. Our cyclic voltammetric study indicated somewhat different chemical behavior.

When a solution of $[Cr(bipy)_2Cl_2]^+$ was examined cyclic voltammetrically between −0.20 and −0.80 V at the fast scan rate of 500 V/sec, a single cathodic wave (1) near −0.8 V and a single anodic wave (2) near −0.6 V were observed on the first and subsequent scans (see Figure 2 for wave designations). When the scan rate was decreased to 200 V/sec, a second anodic wave (3) appeared near −0.2 V followed by a second cathodic wave (4) near −0.3 V. As the scan rate was further decreased to 20 V/sec and then to 2 V/sec, there occurred a cathodic shift in the position of anodic wave 3 from −0.2 to −0.42 V and an increase in the ratio (i_a/i_c) of the peak currents for anodic wave 3 and cathodic wave 1. Further decreases in scan rate produced no new effects and a typical voltammogram obtained using a sweep rate of 0.1 V/sec is shown in Figure 2. Similar voltammograms were obtained using K_2SO_4, NaCl, $NaClO_4$, KNO_3, and $NaNO_3$ as supporting electrolyte. This behavior is typical of a system in which the initial electron-transfer process (reduction) is followed by a chemical reaction which produces a new species capable of being oxidized in the potential range being examined. However, we do not believe that the following chemical reaction was a redox disproportionation as suggested by

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(15) (a) J. B. Hunt and J. E. Earley, *J. Amer. Chem. Soc.*, 82, 5312 (1960); (b) B. V. Tucker, Ph.D. Dissertation, Purdue University, 1964.

(16) P. Andersen, J. Josephsen, G. Nord, C. E. Schaffer, and R. L. Tranter, *J. Chem. Soc. D*, 408 (1969).

(17) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(18) K. Curtis, M.S. Thesis, Seton Hall University, 1968.

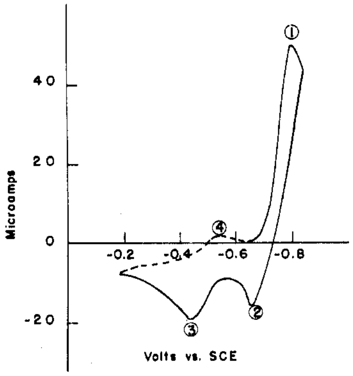

Figure 2. Cyclic voltammogram of 1.16×10^{-3} *M* $[Cr(bipy)_2Cl_2]^+$ in 0.1 *M* potassium chloride at a scan rate of 0.1 V/sec.

Tucker, *et al.*,[11] but that it was a ligand disproportionation which produced a tris-bipyridine complex. The evidence from which we drew our conclusion is presented below.

The position, on the potential axis, of the new cyclic voltammetric waves 3 and 4 (Figure 2) was the same as we had observed for waves corresponding to the reduction and oxidation of tris(2,2'-bipyridine)chromium(III) in a study of the tris complex.[12] At scan rates less than 1 V/sec the reaction which produced the substance oxidizable at −0.42 V was complete (at the electrode surface) as evidenced by the fact that the ratio of the current of wave 1 to that of wave 3 was constant for scan rates ranging from 1.0 to 0.02 V/sec. The current ratio i_3/i_1 was insensitive to temperature changes in the range of 5-40°; however, as seen in Figure 3, the ratio was very pH dependent. Although the actual current associated with wave 1 was relatively constant from pH 2 to 6, that of wave 3 decreased rapidly as the pH decreased below a value of 4. Our suspicion that the new species, formed chemically after the electrochemical reduction of the bis complex, was a tris complex is supported by the data presented in Figure 3. The pK_a for monoprotonated 2,2'-bipyridine is reported to be about 4.4.[19,20] Thus, in solutions of pH less than 4, the amount of free, unprotonated bipyridine in solution is small and reaction of the bis complex with bipyridine to produce the tris complex must necessarily be retarded, as is shown by the rapid decrease in wave 3 as the pH is lowered below 4 (Figure 3).

To obtain additional support for our belief that a tris chromium(II) complex was formed upon reduction of the bis chromium(III) complex, a 1 m*M* solution of $[Cr(bipy)_2Cl_2]^+$ at 26° and pH 4.5 was electrolyzed at a controlled potential of −0.80 V, a potential corresponding to the plateau of the first polarographic wave. A total of one electron per molecule of original $[Cr(bipy)_2Cl_2]^+$ could be added before current stopped flowing. The resulting solution was deep red, exhibiting visible absorption maxima at 562 and 467 nm. The ultraviolet absorption spectrum (Figure 4) contained a single maximum at 308 nm. A polarogram of the reduced solution, shown in Figure 1B, contained an anodic wave with $E_{1/2}$ of −0.49 V and a height approximately half that of the cathodic wave originally present at −0.72 V. The visible absorption spectrum with maxima at 562 and 467 nm and the anodic polarographic wave with $E_{1/2}$ of −0.49 V are characteristic of $[Cr(bipy)_3]^{2+}$ in aqueous solution.[9,12] Using a previously calculated diffusion current constant of 1.25 μA mM^{-1} mg$^{-2/3}$ sec$^{-1/2}$ for $[Cr(bipy)_3]^{2+}$ in solution,[12] the anodic polarographic wave was analyzed and it was determined that the concentration of tris complex was half that of the original bis complex.

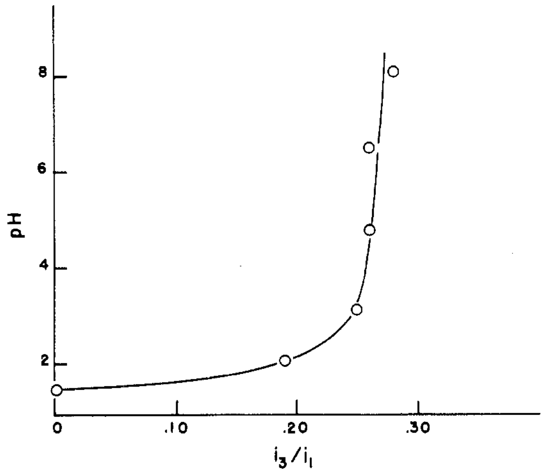

Figure 3. Ratio of anodic current of wave 3 (i_3) to cathodic current of wave 1 (i_1) for $[Cr(bipy)_2Cl_2]^+$ as a function of pH. Scan rate was 0.1 V/sec. Supporting electrolyte was 0.1 *M* potassium chloride.

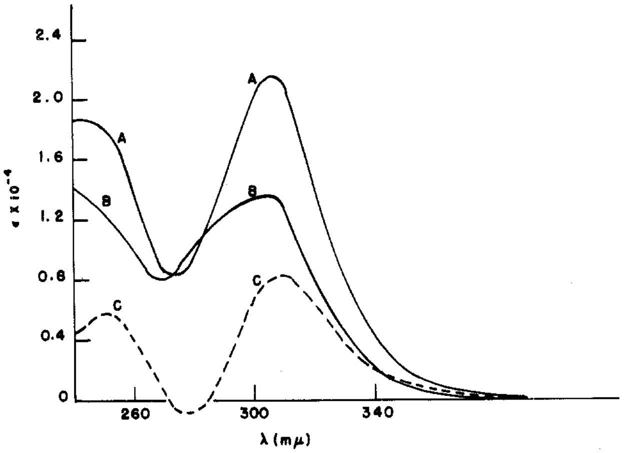

Figure 4. Ultraviolet spectra of chromium-bipyridine complexes: (A) solution of $[Cr(bipy)_2Cl_2]^+$ reduced 1 electron/molecule; (B) $[Cr(bipy)_3]^{2+}$; (C) difference spectrum of A − B.

One final experiment was performed to demonstrate conclusively that we had produced $[Cr(bipy)_3]^{2+}$ in solution. An electrochemically reduced solution was prepared and then rapidly oxidized with oxygen gas as described in the Experimental Section (method 1). The solution immediately turned yellow and the uv absorption spectrum contained a shoulder at 360 nm in addition to the peak at 308 nm, both properties characteristic of $[Cr(bipy)_3]^{3+}$. A polarogram, taken after removal of dissolved oxygen, displayed a cathodic wave at $E_{1/2} = -0.49$ V (Figure 5), and was essentially the same as that reported previously for a solution of $[Cr(bipy)_3]^{3+}$.[12] In addition, the cyclic voltammetric behavior was the same as that reported for the tris complex.[12]

It is now clear that reduction of $[Cr(bipy)_2Cl_2]^+$ to $[Cr(bipy)_2Cl_2]^0$ was followed by chemical reactions leading to the formation of $[Cr(bipy)_3]^{2+}$ in an amount half as great as the original amount of $[Cr(bipy)_2Cl_2]^+$. One further experiment was performed to determine the composition of the remaining component(s). The uv absorption spectrum of a one-electron reduced solution should be that of a mixture of $[Cr(bipy)_3]^{2+}$ plus the other reduced species. From the composite spectrum shown in Figure 4A the contribution due to $[Cr(bipy)_3]^{2+}$ (Figure 4B) was subtracted to yield the spectrum of the other reduced species (Figure 4C). The result-

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(19) J. H. Baxendale and P. George, *Nature (London)*, 163, 727 (1949).

(20) R. G. Inskeep and J. Bjerrum, *Acta Chem. Scand.*, 15, 62 (1961).

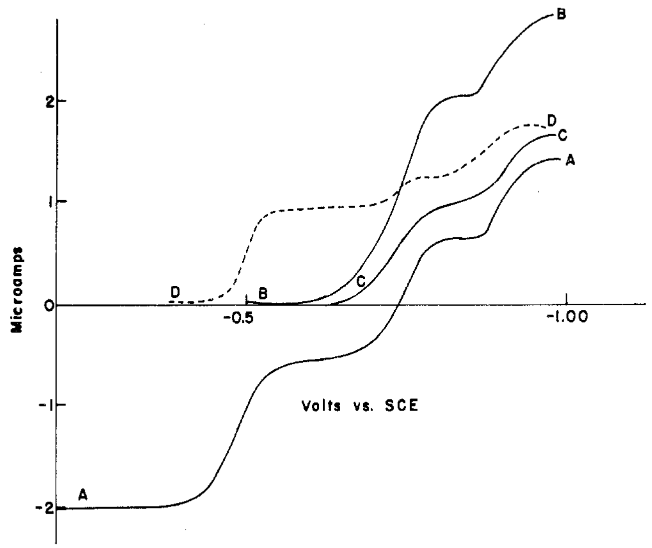

Figure 5. Polarograms of a 1.1 × 10^{-3} *M* solution of reduced [Cr(bipy)$_2$Cl$_2$]$^+$ and of products resulting from oxidation in 0.1 *M* potassium chloride at pH 4.5, 26°: (A) complex reduced 1 electron/molecule at −0.80 V; (B) reduced solution oxidized electrochemically at −0.35 V; (C) reduced solution oxidized slowly with air; (D) reduced solution oxidized rapidly with oxygen gas.

ant spectrum is not characteristic of Cr_{aq}^{2+}; neither did we observe any polarographic evidence of the presence of Cr_{aq}^{2+}. For these reasons we suggest the remaining species was a mono complex and that the process can be described by the reactions

$$[Cr(bipy)_2Cl_2]^+ + e^- \leftrightarrow [Cr(bipy)_2Cl_2]^0 \quad E_{1/2} = -0.73\ V \qquad (1)$$

$$[Cr(bipy)_2Cl_2]^0 + 4H_2O \rightleftharpoons [Cr(bipy)(H_2O)_4]^{2+} + 2Cl^- + bipy \qquad (2)$$

$$[Cr(bipy)_2Cl_2]^0 + bipy \rightleftharpoons [Cr(bipy)_3]^{2+} + 2Cl^- \qquad (3)$$

The symbol ↔ indicates a polarographically reversible reaction. Although we made no attempts to clarify the chloride situation, we suspect that the chlorides were rapidly replaced by water molecules in the chromium(II) complexes and we have written the reactions accordingly. It is indeed interesting that the stability of the tris complex is so great that it is formed even at the expense of a bis complex.

The above mechanism would predict that were excess free bipyridine available, then all of the starting [Cr(bipy)$_2$Cl$_2$]$^+$ would be converted to [Cr(bipy)$_3$]$^{2+}$ upon reduction. Accordingly, a solution containing equimolar amounts of 2,2-bipyridine and [Cr(bipy)$_2$Cl$_2$]$^+$ in 0.1 *M* KCl at pH 4.5 was prepared and reduced one electron per molecule at −0.80 V. The resultant solution was deep red with visible absorption maxima at 562 and 467 nm. A polarogram of the solution, shown in Figure 6A, contained a single anodic wave with $E_{1/2}$ = −0.49 V. The concentration of [Cr(bipy)$_3$]$^{2+}$ in the reduced solution, calculated from the uv spectrum or from the anodic polarographic wave at −0.49 V, indicated that more than 90% of the original [Cr(bipy)$_2$Cl$_2$]$^+$ was present as [Cr(bipy)$_3$]$^{2+}$. Rapid oxidation of the reduced solution with oxygen gas (method 1) produced the yellow [Cr(bipy)$_3$]$^{3+}$ complex. Again, the amount of this complex, determined from its uv spectrum or its first polarographic reduction wave, showed that better than 90% of the original bis complex now existed in the tris form.

The results of our study are not in complete agreement with results previously reported by Tucker, *et al.*,[11] in their study of the same complex. This latter study did not report on the existence of anodic polarographic waves for solutions that had been reduced by controlled-potential electrolysis. These authors reported that a total of 2 electrons per molecule could be added to a solution of [Cr(bipy)$_2$Cl$_2$]$^+$ at a potential of −0.80 V, with the second electron being added only slowly.

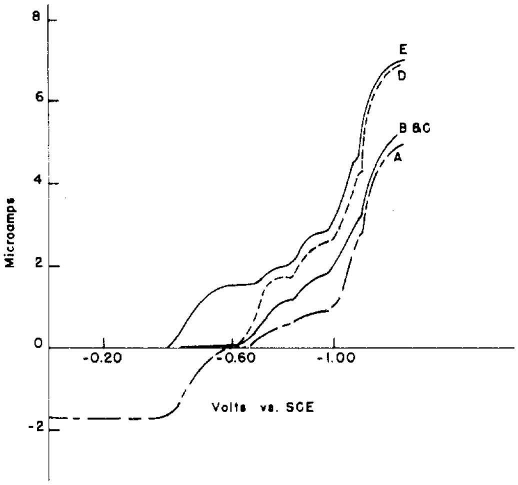

Figure 6. Polarograms of a 1.02 × 10^{-3} *M* solution of reduced [Cr(bipy)$_2$Cl$_2$]$^+$ and of products resulting from oxidation, all in the presence of an equimolar amount of 2,2′-bipyridine. Supporting electrolyte was 0.1 *M* potassium chloride, the pH 4.5, and temperature 26°: (A) reduced 1 electron/molecule at −0.80 V; (B) reduced solution oxidized slowly with air; (C) reduced solution through which oxygen gas was passed; (D) reduced solution oxidized electrochemically at −0.30 V; (E) reduced solution oxidized rapidly with oxygen gas.

The experimental procedures used to perform the controlled-potential electrolysis in both their studies and in ours were similar except for the cell construction and the method of purging and restricting air from the electrolysis cell. The cell employed by Tucker, *et al.*,[11] consisted of a beaker fitted with a large rubber stopper in which the electrodes, the purge gas inlet and outlet, and the salt bridge were mounted. Air was purged by continuous bubbling of deoxygenated nitrogen through the solution. The cell used in our study was completely glass. Electrodes and purge gas connections were made through airtight ground-glass or Teflon fittings. Air was purged from the solution with prepurified argon (preferable because of its higher density). During electrolysis, the cell was filled with argon and sealed in order to prevent even the smallest traces of air from entering the cell *via* backflow through the gas outlet. Although the differences are small, the conditions employed by Tucker, *et al.*,[11] provided a greater potential for air slowly to reach the reduced solutions than did our conditions.

Experiments were designed to evaluate the effect of air slowly entering the cell during an electrolysis. A solution of [Cr(bipy)$_2$Cl$_2$]$^+$ in our sealed cell was reduced at −0.80 V over a 24-hr period. One electron per molecule was added within 1 hr and an additional 0.1 electron per molecule in 23 hr. At the end of 24 hr no observable current was flowing. The purge gas inlet was opened and the solution stirred for 6 hr. Reduction at −0.80 V on the resulting solution was continued with 0.5 electron per molecule being added before current stopped flowing. When the process was repeated, 0.25 electron per molecule was added. This process continued until finally no current flowed at −0.80 V. By this process of alternating reduction and slow air oxidation, a total of 2 electrons per molecule was added to the solution at −0.80 V. The color and the polarogram of this solution were identical with those reported by Tucker, *et al.*,[11] for their two-electron reduced solution. Although this experiment does not unequivocally prove that the results reported by Tucker and coworkers were influenced by slow oxidation of the reduced materials, it does indicate that slow oxidation together with continual reduction can produce similar results.

Various methods of oxidation of the reduced bis complex produced startlingly different results. Four different methods of oxidation are described in the Experimental Section. It has already been shown that rapid, oxygen gas oxidation (method 1) produced 0.5 equiv of $[Cr(bipy)_3]^{3+}$ when no free bipyridine was present in the original solution and produced 1 full equiv of $[Cr(bipy)_3]^{3+}$ when 1 equiv of free bipyridine was present in the original solution.

Slower methods of oxidation (method 2) did not result in formation of a tris complex. Spectral and polarographic properties characteristic of the tris complex were noticeably absent. Polarograms of the oxidized solutions (Figures 5C, 6B, 6C) were similar to but not identical with a polarogram of the starting complex, $[Cr(bipy)_2Cl_2]^+$. We believe the product resulting from the slow oxidation methods was diaquobis(2,2′-bipyridine)chromium(III). The polarogram of our oxidation product was identical with the polarogram of this complex.[10,21] That this should be the case can be seen by examining reactions 1-3 described above and reaction 4

$$[Cr(bipy)_3]^{3+} + [Cr(bipy)_2(H_2O)_2]^{2+} \rightarrow [Cr(bipy)_3]^{2+} + [Cr(bipy)_2(H_2O)_2]^{3+} \qquad (4)$$

described in a previous electrochemical study[10,12] of $[Cr(bipy)_3]^{3+}$. According to reactions 1-3, reduction of the bis complex, $[Cr(bipy)_2Cl_2]^+$, ultimately produces some tris complex, $[Cr(bipy)_3]^{2+}$, which is in rapid equilibrium with a reduced bis complex, $[Cr(bipy)_2(H_2O)_2]^{2+}$. When oxidized slowly, any $[Cr(bipy)_3]^{3+}$ produced reacts with unoxidized $[Cr(bipy)_2(H_2O)_2]^{2+}$ according to reaction 4. The tris chromium(II) complex is regenerated and the final oxidation product is the diaquobis complex. There is, of course, the possibility of direct oxidation of the bis complex but this is not important since it is present only in very small amounts since the combined equilibrium constant for reactions 2 and 3 strongly favors the tris complex.[10,12] It can now be seen that $[Cr(bipy)_3]^{3+}$ will be the final oxidation product only when the oxidation is performed in such a way that little or no reduced solution is allowed to mix with the already oxidized solution. Oxidation method 1 meets this requirement.

Electrochemical oxidation at −0.35 V (method 3) in the absence of oxygen produced only $[Cr(bipy)_2(H_2O)_2]^{3+}$ (Figures 5B, 6D) in the same manner as described for the slow oxygen and air oxidations.

Further successive one-electron reductions were performed at −1.08 and −1.13 V. Polarograms of the solutions resulting after each of these reductions are shown in Figure 1. The second one-electron reduction at −1.08 V produced a black suspension. Very little electroactive material was dissolved as evidenced by the small polarographic response (Figure 1C). Additional reduction at −1.13 V was, as expected, accomplished only very slowly and proceeded only to 0.6 electron per molecule. Again, the product was a black suspension. The black suspension is probably the tris(2,2′-bipyridine)chromium(0) complex described by Herzog and Schon.[5] Rapid oxidation (method 1) produced almost quantitatively the tris complex $[Cr(bipy)_3]^{3+}$.

Registry No. Dichlorobis(2,2′-bipyridine)chromium(III) chloride dihydrate, 26154-79-0; $[Cr(bipy)_3]^{2+}$, 15276-15-0.

[21] D. M. Soignet, Ph.D. Dissertation, Louisiana State University in New Orleans, 1971.

Contribution from the Laboratoire de Chimi de Coordination,
Paris 5°, France

Low-Frequency Infrared and Raman Spectra of π-Cyclopentadienyl Compounds of Titanium, Zirconium, and Hafnium

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Received August 9, 1972

The infrared and Raman spectra in the region 600–50 cm^{-1} are reported for the series of compounds $CpTiX_3$ and Cp_2MX_2 (M = Ti, Zr, Hf; X = Hal, Me; Cp = C_5H_5 ring). A comparative study of these spectra allows assignments to be made for the metal–ring and metal–ligand stretching modes.

Introduction

Although the wedge-shaped transition metal bis(cyclopentadienyl) complexes and the "open-sandwich" mono(cyclopentadienyls) are compounds of continuing interest, their vibrational properties have not yet been investigated with the same thoroughness as those of the ferrocene-type sandwich compounds. Thus, the metallocene dihalides Cp_2MX_2 (M = Ti, Zr, Hf; X = F, Cl, Br, I)[1] and the mono(cyclopentadienyl) trihalides $CpTiX_3$ (X = Cl, Br, I)[2-4] have all been prepared, but no definite assignments of the metal–ring vibrations have as yet been made, partly as a result of the paucity of Raman data. The study of these compounds is particularly interesting in view of their importance in polymerization catalysis and nitrogen fixation.

The recent preparation of Cp_2MMe_2 (M = Zr, Hf; Me = CH_3)[5-7] has allowed us to study a series of compounds other than the halides, and this, together with new low-frequency

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[1] P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, *J. Chem. Soc. A*, 2106 (1969), and references therein.

[2] R. Gorsich, *J. Amer. Chem. Soc.*, **80**, 4744 (1958).

[3] C. L. Sloan and W. A. Barber, *J. Amer. Chem. Soc.*, **81**, 1364 (1959).

[4] A. Nesmeyanov, O. Nogina, B. Wokshin, and V. Dubovitsky, *Dokl. Akad. Nauk SSSR*, 182, 844 (1968).

[5] M. D. Rausch, paper presented at the 5th International Conference on Organometallic Chemistry, Moscow, 1971.

[6] E. Samuel and M. D. Rausch, to be submitted for publication.

[7] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, 34, 155 (1972).