POLAROGRAPHIC STUDY OF Sn(IV) CHLORIDE-PYRIDINE N-OXIDE COMPLEXES IN ACETONITRILE

A. DRTIL,[†] JAY MEUX,[†] J. W. MEUX, R. J. WILLIAMS and J. W. ROGERS* Department of Chemistry, Midwestern State University, Wichita Falls, TX 76308, U.S.A.

(Received 13 August 1982)

Abstract—Polarograms recorded of Sn(IV) chloride in acetonitrile in the presence of controlled quantities of each of nine substituted pyridine N-oxide ligands demonstrated the formation of stable and soluble complexes with a stoichiometry dependent upon the nature and position of the ring substituent. The polarographic data associated with each complex and the free ligands are used to substantiate a proposed bonding model which explains the dependency of the complex formula on the ligand structure.

The salt $SnCl_4$: SH_2O was employed as a source of Sn(IV) and the complete polarographic behaviour of this salt in acetonitrile is described as a basis for the interpretation of complex reduction behaviour.

Results of IR and proton magnetic resonance studies of complexes of substituted pyridine N-oxides with SnCl₄ in acetonitrile (ACN) solution have recently been reported.¹ Two types of behaviour were noted. Pyridine Noxide donors containing electron releasing substituents were generally found to form strong complexes with SnCl₄ and exhibited maxima in continuous variation plots at a 2:1 ligand-to-metal ratio. Pyridine N-oxide donors containing electron neutral to electron withdrawing substituents were found to form generally weaker complexes with SnCl₄ and exhibited maxima in continuous variation plots at a 1:1 ligand-to-metal ratio. Evidence for multi-nuclear and 2:1 or higher complexes was discussed and the results were rationalized in terms of an equilibrium model for this system.

The essential elements of the model include the assumption of octahedral geometry for all complexes of sterically unhindered N-oxide ligands and a consideration of the contribution of $d\pi p\pi$ backbonding to the coordinate bond and the effect of this bonding on the possible *cis-trans* isomerism in these complexes. The importance of $d\pi p\pi$ backbonding in these complexes should be dependent upon the degree of orbital energy matching between the d-orbitals of tin and the lowest unoccupied π^* orbital of the ligand. Electron releasing substituents on a pyridine N-oxide ring are expected to raise the energy of this π^* orbital so that it is too high in energy for effective overlap and, therefore, diminish the importance of $d\pi p\pi$ bonding in SnCl₄ complexes of these ligands. Complexes containing pyridine N-oxide ligands with electron releasing substituents were then expected to form stable, trans-2:1 complexes resulting in maxima in continuous variation plots at a 2:1 ligandto-metal ratio.

Electron withdrawing substituents on a pyridine Noxide ring are expected to lower the energy of the lowest unoccupied π^* orbital and enhance $d\pi p\pi$ backbonding. Assuming this backbonding is an important component of the coordinate bond, these ligands would be expected to form *cis*-2:1 complexes which were postulated subsequently to form stable, oxygen bridged dimers in solution. This would result in the observed maxima in continuous variation plots at a 1:1 ligand-to-metal ratio for these complexes.

Previously published UV spectrophotometric and electrochemical data demonstrate that tin (IV) chloride, SnCl₄ is a nonelectrolyte in ACN and that in this solvent the neutral complex acts as the Lewis acceptor.² The electrochemical reduction of SnCl₄ occurs *via* irreversible steps, not allowing the application of standard methods to the determination of thermodynamic properties. However, the polarographic studies have previously been shown to provide a straightforward means of specifying the electrolyte properties and stoichiometry of Sn(II) and Sn(IV) complexes in the low basicity solvent ACN.²⁻⁴

In an attempt to confirm the results of the IR and proton magnetic studies and to further test the proposed bonding model extensive polarographic data have been taken on solutions of SnCl₄ in ACN containing controlled quantities of a series of substituted pyridine Noxides. The polarographic behaviour of a metal complex is frequently dictated by properties of the metal moiety.⁵ In contrast, the data leading to the previously postulated bonding model are derived from physical properties directly associated with the ligand in complexed and noncomplexed states.

Polarographic data presented herein support the previously presented IR and proton magnetic data and the resulting conclusions and bonding model. Various substituted pyridine N-oxides are found to form complexes with SnCl₄ in ACN in a ligand-to-metal coordination ratio dependent on the electronic nature of the ring substituent. The polarographic test solutions were prepared from the solid pentahydrate of SnCl₄ as opposed to the liquid anhydrous form. The polarographic characteristics of the pentahydrate salt in ACN, not previously reported, are discussed in detail as a basis for interpretation of polarographic data relating to the complexation chemistry of Sn(IV) chloride acting as a Lewis acceptor.

EXPERIMENTAL

Chemicals. All pyridine N-oxide ligands (Aldrich Chemical Co.) were purified by sublimation or vacuum distillation before use. $SnCl_4$ · $5H_2O$ (Pfaltz and Bauer) was utilized without purification following confirmatory quantitative analysis. Spec-

^{*}Author to whom correspondence should be addressed. *Robert A. Welch Foundation Undergraduate Scholars.

troquality acetonitrile containing less than 0.03% water (Aldrich Chemical Co.), polarographic-grade tetrapropylammonium perchlorate and tetramethylammonium chloride (Southwestern Analytical Chemicals) were employed throughout. The supporting electrolyte, tetrapropylammonium perchlorate, was recrystallized from acetonitrile-water solutions and vacuum dried before use. All solutions were prepared and transferred under a nitrogen atmosphere.

Apparatus. The polarographic cell was of conventional design and has been described previously.⁶ The polarograms were recorded on a Houston Instruments Omnigraphic 2000 X-Y plotter using a Princeton Applied Research Model 173 potentiostat and Exact Model 7050 wave form generator for potential control.

RESULTS

Polarography of Sn(IV) chloride pentahydrate in ACN

Polarographic test solutions of ACN, containing 1.0 mM SnCl₄ prepared from the pentahydrate salt, SnCl₄·5H₂O and 1.0 M tetrapropylammonium perchlorate, exhibited two well-defined reduction current plateaus, Fig. 1(a). The lower potential plateau exhibiting a half-wave potential of -0.08 V vs saturated calomel (s.c.e.) does not exhibit the distortion or the maximum noted in the corresponding wave of similar test solutions prepared from anhydrous SnCl₄.² The higher potential wave is very broad and preceded by an adsorption maximum. The half-wave potential of the wave appears near 1 V vs s.c.e. The ratio of the total current of both waves to the square root of the corrected mercury column head height is constant signifying diffusion control. The current constants (Id) of the low and high potential waves measured at 25°C and at 1.0 mM con-



Fig. 1. Polarogram of (a) 1.0 mM SnCl₄·5H₂O in ACN (b) 1.0 mM SnCl₄·5H₂O in ACN containing 1.0 mM pno (c) 1.0 mM SnCl₄·5H₂O in ACN containing 2.0 mM pno.

centration are 4.01 and 9.43 respectively (DME characteristics at open circuit and 50 cm Hg head: m = 0.049 mg/sec, t = 6.50 sec). Both currents are apparently the result of irreversible electrochemical processes (slope of $\log[(\text{id} - i)/i]$ vs EDME for wave appearing at -0.08 V is 120 mV).

Addition of measured quantities of noncomplexed chloride ion in the form of tetramethylammonium chloride (TMACI) to the polarographic test solution resulted in a behaviour analogous to that exhibited by $SnCl_2$ and $SnCl_4$ solutions prepared from the anhydrous form of each.^{2,3} Increasing quantities of chloride up to 2.0 mM decreased the plateau current of the lower potential wave. The total polarographic current is unaltered. The lower potential wave is no longer detectable at concentrations of added chloride exceeding a ratio of 2:1 with respect to the metal. Only at concentrations of added chloride exceeding the 2:1 ratio is the characteristic oxidation of chloride observed at positive dropping mercury electrode potentials.

The observed behaviour of polarographic test solutions prepared from $SnCl_4 \cdot SH_2O$ in the presence of added chloride is consistent with the behaviour demonstrated by solutions prepared from anhydrous $SnCl_4$ even though the half-wave potential at the lower potential wave is significantly more negative and is not distorted. These data are consistent with an electrode reduction mechanism in which a water complex of $SnCl_4$ is reduced at the first polarographic wave, releasing free chloride thereby controlling the wave current by displacement of water and subsequent production of the hexachloro complex $SnCl_6^{2-}$, a species reducible only at potentials of the second polarographic wave.²⁻⁴ This sequence of events may be represented in the following manner:

Lower potential wave

$$\operatorname{SnCl}_4(\operatorname{H}_2O)_2 + \operatorname{Hg} + 4e^- \rightarrow \operatorname{Sn}(\operatorname{Hg}) + 2\operatorname{H}_2O + 4\operatorname{Cl}^-$$

 $\operatorname{SnCl}_4(\operatorname{H}_2O)_2 + 2\operatorname{Cl}^- \rightarrow \operatorname{SnCl}_2^{2-} + 2\operatorname{H}_2O.$

Higher potential wave

$$\operatorname{SnCl}_{6}^{2-} + \operatorname{Hg} + 4e^{-} \rightarrow \operatorname{Sn}(\operatorname{Hg}) + 6\operatorname{Cl}^{-}.$$

Polarography of Sn(IV) chloride pyridine N-oxide complexes

The stable physical properties of the pentahydrate form of Sn(IV) chloride and the lack of distortions in its polarograms in ACN made it a desirable source of the salt for polarographic studies dealing with the Lewis acceptor properties of SnCl₄ in a weakly coordinating solvent. Consistent with previous studies,¹ the effects of adding controlled quantities of substituted pyridine Noxides to polarographic test solutions prepared from SnCl₄·5H₂O in ACN containing TRAP supporting electrolyte reveal the production of complexes with stoichiometries that are dependent upon the nature and position of ring substituents.

Addition of the ligands pyridine N-oxide (pno), 3pyridine methanol N-oxide (3-pmno), 2-picoline N-oxide (2-picno), 4-phenylpyridine N-oxide (4-phenpno), 3picoline N-oxide (3-picno) and 4-picoline N-oxide (4picno) in sufficient quantities to bring test solutions of 1.0 mM SnCl₄·5H₂O to ligand-to-metal ratios of 1:2, 1:1, 2:1 and 2.5:1 bring about very similar changes in the structure of the resulting polarograms. Polarograms recorded in solutions containing 0.5 mM ligand (1:2 ratio) exhibit pronounced splitting of the lower potential wave resulting in a new polarographic plateau appearing near -0.3 V vs s.c.e., Figs. 1 and 2. It is reasonable to assume that the appearance of this wave signifies the existence and subsequent reduction of a SnCl₄-pyridine N-oxide complex. Increasing ligand to metal ratios bring about an increase in this complex reduction plateau current at the direct expense of the plateau current attributable to the reduction of the substrate complex, SnCl₄·2H₂O, Fig. 2. The ratio of the complex wave current to the metal chloride substrate wave current is 1.0 at a ligand-to-metal ratio of 1.0, Fig. 2. The plateau current associated with the reduction of SnCl₄·2H₂O is not detectable at a organic ligand to metal ratio of 2:1 or greater, Fig. 2. These data obviously suggest the formation of a stable SnCl -pno adduct with the stoichiometry SnCl₄·2L.

The properties of the polarographic wave associated with the reduction of each $SnCl_4 \cdot 2L$ complex are equivalent but at variance with those of the reduction wave of $SnCl_2 \cdot 2H_2O$. The polarographic $E_{1/2}$ of the reduction plateau of each complex is observed to be -0.33 V vs s.c.e. The complex wave deviates slightly from diffusion controlled behaviour and is significantly broadened relative to that of the Sn(IV) chloride reduction, Fig. 2. The current constant (Id) is found to be 3.64. The plateau current associated with the reduction of the $SnCl_6^{-2}$ complex is unperturbed by addition of organic ligands and subsequent complex formation, Fig. 1. Addition of the ligands 2,6-lutidine N-oxide (lno), 2pyridinemethanol N-oxide (2-pmno) and 4-chloropyridine N-oxide (4-Clpno) in sufficient quantities to bring test solutions of 1.0 mM SnCl₄·SH₂O to a ligand-to-metal ratio of 0.5:1 splits the lower potential polarographic plateau into two waves of equal current. Increasing the organic ligand-to-metal ratio to 1:1 brings about the complete replacement of the lower potential plateau by the complex reduction plateau suggesting the formation of a stable complex with the stoichiometry SnCl₄·L.

The characteristics of the plateau current associated with the reduction of each SnCl₄·L complex are equivalent. The polarographic $E_{1/2}$ is observed to be -0.29 V vs s.c.e. The wave is broadened relative to that of the reduction of SnCl₄·SH₂O and the observed current constant (Id) value of 3.26 is less than that of SnCl₄·2H₂O and the SnCl₄·2L complexes. The wave attributable to the reduction of SnCl₆²⁻ is characteristically unaltered.

Addition of noncomplexed chloride in the form of tetramethylammonium chloride (TMAC1) to test solutions containing ligand enhances the plateau current resulting from the reduction of $SnCl_6^{-}$ at the direct expense of the wave attributable to the reduction of the complex. For example, see Fig. 3. The complex reduction current is not detectable in test solutions containing equal molar volumes of pyridine N-oxide ligand TMAC1. The characteristic wave associated with the oxidation of chloride is observed only in test solutions containing TMAC1 in excess of the Sn(IV) chloride substrate.

Each of the nine substituted pyridine N-oxide ligands described herein exhibits a characteristic polarographic reduction plateau at potentials negative of the plateau

E vs SCE.

Fig. 2. Polarograms showing only lowest potential cathodic waves (expanded scale) of ACN solutions containing (a) 1.0 mM SnCl₄·5H₂O (b) 1.0 mM SnCl₄·5H₂O and 1.0 mM pno (c) 1.0 mM SnCl₄·5H₂O and 2.0 mM pno.



Fig. 3. Polarograms of (a) 1.0 mM SnCl₄·5H₂O in ACN and (b) 1.0 mM SnCl₄·5H₂O in ACN containing 2.0 mM pno and 2.0 mM TMAC1 (reduced scale).

currents associated with the reduction of all Sn(IV) species produced and described in ACN, Fig. 3. The compounds pno, 4-Clpno, 2-, 3- and 4-picno, lno and 4-phenpno each exhibit reversible one-electron reduction plateaus at -2.26, -1.88, -2.33, -2.30, -2.30, -2.43 and -2.00 V respectively. The compounds 2- and 3-methanolpyridine N-oxide exhibit a two-wave reduction process probably resulting from the reduction of the anion product.

The reduction plateau characteristic of each N-oxide is observed to be superimposed on the total current resulting from the reduction of all Sn(IV) species. The current associated with the reduction of the noncomplexed ligand varies in proportion to the concentration in the range 0.5-10 mM.

DISCUSSION

Data have been presented which demonstrate that in ACN the salt SnCl₄·5H₂O is reduced in two electrochemical steps resulting in well-defined polarographic current plateaus via a mechanism analogous to that previously reported for anhydrous SnCl4.² This information has been used as a basis for a polarographic study of SnCl₄-pno complex formation in ACN. Addition of each of the six ligands pno, 3-pmno, 2-picno, 4-phenpno, 3picno and 4-picno to test solutions containing SnCl₄ in a ligand to metal ratio of 2:1 brings about the replacement of the plateau associated with the reduction of the water complex of SnCL with a current plateau that may be reasonably associated with the reduction of a pyridine N-oxide SnCl₄ adduct having the formula SnCl₄·2L. Similarly conducted experiments employing the ligands Ino, 2-pmno and 4-Clpno reveal analogous behaviour but with the formation of adducts apparently having the forlula SnCL-L. The polarographic reduction current associated with the reduction of the stable SnCl₆²⁻ complex is unperturbed in all polarographic experiments conducted in this study.

The polarographic wave associated with the reduction of each 2:1 complex appears at an $E_{1/2}$ of -0.33 V and is irreversible. According to conventional criteria the wave current deviates slightly from diffusion control behaviour and the measured current constant value of 3.64 is small in comparison to most four-electron processes. Similar observations related to SnCl₄ electrochemistry have been discussed previously.^{2,7,8}

The polarographic wave associated with the reduction of each of the three 1:1 complexes studied appears at an $E_{1/2}$ of -0.29 V and is irreversible. The measured current deviates slightly from diffusion controlled behaviour and the current constant value of 3.26 is suppressed relative to that of SnCl₄·2H₂O as well as that of the 2:1 complexes.

The destruction of the 2:1 and the 1:1 complex reduction wave as well as that of $SnCl_4 2H_2O$ by the addition of TMACI and the concurrent enhancement of the wave associated with the reduction of the $SnCl_6^{-1}$ complex ion demonstrates the great stability of the hexachloro anion relative to each of the other complexes of Sn(IV). The unperturbable current wave and the predictably large current constant of the four-electron reduction of the $SnCl_6^{2-1}$ anion also signifies its great stability and diffusion controlled reduction.

These observations may be summarized with the fol-

lowing set of reactions: First Cathodic Wave (Lowest Cathodic Potential)

SnCl₄·2H₂O(s) + Hg + 4e⁻ → Sn(Hg) + 4Cl⁻(s) + 2H₂O
SnCl₄·2H₂O(s) + 2Cl⁻(s)
$$\Rightarrow$$
 SnCl₄²⁻(s) + 2H₂O.

Second Cathodic Wave (Complex Reduction)

$$\operatorname{SnCL}(s) + \operatorname{Hg} + 4e^{-} \rightarrow \operatorname{Sn}(\operatorname{Hg}) + 4\operatorname{Cl}(s) + \operatorname{nL}(s)$$

 $\operatorname{SnCL}(nL(s) + 2\operatorname{Cl}(s) \Rightarrow \operatorname{SnCl}(s) + \operatorname{nL}(s).$

Third Cathodic Wave

 $\operatorname{SnCl}_{6}^{2-}(s) + \operatorname{Hg} + 4e^{-} \rightarrow \operatorname{Sn}(\operatorname{Hg}) + 6\operatorname{Cl}^{-}(s).$

Fourth Cathodic Wave (Highest Cathodic Potential)

L+e⁻≠L⁻.

Where L is pno, 2, 3, and 4-picno, 4-phenpno and 4-Clpno.

In addition to these reactions describing the electrochemistry of SnCl₄ species in ACN and the current ratios which define the formulas of stable adducts, two other polarographic observations are central to the postulated bonding model¹ and its relationship to the nature of ring substituents. These are the polarographic $E_{1/2}$ values of the noncomplexed ligands and the diminished currents of the reduction waves of the 1:1 complexes relative to those of the 2:1 complexes and the SnCl₄·2H₂O complex.

It is postulated that the increased matching of metal d-orbitals with lowest π^* ligand orbitals through lowering of the π^* energy as a result of the electronic and mesomeric effects of electron withdrawing substituents enhances $d\pi p\pi$ backbonding promoting the formation of stable 1:1 complexes at the expense of the 2:1 form. The reported polarographic $E_{1/2}$ values of those ligands which undergo reversible one-electron reductions are, with the exception of lno¹, clearly consistent with the postulated substituent effect on the lowest π^* orbital. As an example, the $E_{1/2}$ values of 4-picno (2:1 complex) and 4-Clpno (1:1 complex) are -2.30 and -1.878 V respectively. It is well known that the value of the polarographic $E_{1/2}$ for a reversible electrochemical reaction is proportional to the Hückel (HMO) value of the lowest π^* energy.^{9,10,11} Employing the calculations of Streitwieser¹² in which the $E_{1/2}$ values of fifty aromatic substances undergoing reversible one-electron additions in aqueous dioxane (the dielectric effects of the solvent are found to be small) are correlated with the HMO value of the lowest π^* orbital, the difference in the E_{1/2} between 4-picno and 4-Clpno corresponds to a lowest π^* energy lowering by Cl-substitution of approx. 0.38 eV.

This observed sensitivity of the lowest π^* orbital of pyridine N-oxide to substituents in the 2- and 4-position is predicted by HMO calculations using generally accepted heteroatom parameters for nitrogen and oxygen exchange and Coulomb integrals.¹² Treating both 2- and 4-position substituents as Coulomb perturbations by varying the Coulomb parameter, h, of the 2- or 4-carbon in the conventional manner¹² over a range of 2.0 shifts the lowest π^* energy of 4-substituted pyridine N-oxides by 0.44 β_0 units and of 2-substituted pyridine N-oxides by 0.67 β_0 units. Treating a 3-position substituent perturbation in a similar manner does not alter the lowest π^* energy. The highest bonding π -orbital energy is unaltered by substitution in all calculations.

Empirical evidence presented in previous studies¹ in support of the proposed existence of 1:1 complexes in an oxygen-bridged dimeric form is indirect at best. Consequently the diminution of the 1:1 complex reduction current relative to that of the 2:1 complex reduction current appears to be quite significant but must be interpreted with caution owing to the complex nature of the electrochemical processes controlling the wave current. All polarographic wave currents are found to be proportional to the concentration of the reduced species in the range 1.0-10.0 mM and all wave currents are the result of four-electron processes. Additionally, the polarographic data suggests that the production of free chloride in the double layer and the concomitant production of SnCl₆²⁻ from all SnCl₄ complexes diffusing to the electrode surface is rapid and irreversible. This results in a constant, current-limiting effect, on each of the current waves resulting from the reduction of a SnCl₄ complex. Consequently the diminished current of the 1:1 complex may be explained in terms of a diminished diffusion coefficient. This, in turn, supports the existence of a 1:1 species of larger physical dimension than the 2:1 species, i.e. a dimeric complex.

Acknowledgements-The authors gratefully acknowledge the

financial support of the Robert A. Welch Foundation [R. J. Williams (AO-557), J. W. Rogers (AO-337)].

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