Formal Oxidation-Reduction Potentials and Indicator Characteristics of Some Cyanide and 2,2'-Bipyridine Complexes of Iron, Ruthenium, and Osmium

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► Formal oxidation-reduction potentials for $[Fe(bipy)_2(CN)_2]$, $[Ru(bipy)_2 (CN)_2$, $[Os(bipy)_2(CN)_2]$, $[Fe(bipy)_3]$ -SO₄, $[Ru(bipy)_3]SO_4$, and $[Os(bipy)_3]$ -SO₄ in sulfuric acid solutions ranging in concentration from 0.01 to 12M have been measured. Data for [Ru-(bipy)₂(CN₂)] in nitric acid solutions were also obtained. The neutral mixed ligand complexes all exhibit increasing formal potentials with increasing acid concentration; formal potentials of the simple tris complexes decrease markedly with increasing acid concentrations. Explanations are proposed for the observed trends. With the exception of $[Ru(bipy)_2]$ - $(CN)_2$, which behaves irreversibly on oxidation and reduction, the complexes show promise as indicators for a variety of oxidation-reduction titrations. By proper selection of complex and acid concentration, indication of redox potential in the range of 0.37 to 1.27 volts is possible.

VARIOUS METAL DERIVATIVES of 1,10-2,2'-bipyridine, phenanthroline, and related compounds have been proposed and demonstrated to be advantageous as high potential, reversible indicators in oxidation-reduction titra-The best known and most tions. widely used of these is the tris-(1,10phenanthroline)-iron(II) complex ion, commonly referred to as ferroin. The chemical literature on these various compounds and their applications, published prior to January 1, 1954, has been admirably reviewed by Brandt, Dwyer, and Gyarfas (2). Only one paper has appeared since 1953 that deals with oxidation-reduction characteristics of complexes of the ferroin type; in this, Dwyer and Gyarfas report formal potentials for the terpyridine complexes of iron, ruthenium, and osmium systems (7). At least two novel applications of ferroin type indicators have been described since the review article appeared. One involves the use of nitroferroin in conjunction with a slight excess of bromine as an indicator for the argentometric determination of bromide (9). Another demonstrates the applicability of ferroin as an indicator

for the cerimetric determination of hydroquinone in nonaqueous media, specifically acetonitrile and acetonitrileacetic acid mixtures (10).

Recently a number of new complexes of mixed ligand type involving cyanide, aromatic diimines, and the iron group metal ions have been synthesized that may prove to be suitable as oxidationreduction indicators (12, 13). An investigation of two of these, the neutral dicyano - bis - (1,10 - phenanthroline)-iron(II) complex and the analogous 2,2'-bipyridine derivative, revealed that they exhibit rather remarkable characteristics as indicators in comparison to the tris complexes (11). One objective of the present work is to extend the study to include the analogous neutral mixed ligand complexes of ruthenium(II) and osmium(II). Since comparisons are desired and the data available for the corresponding tris 2,2'-bipyridine complexes are somewhat meager, further measurements on the oxidation-reduction characteristics of the tris complexes over a broader range of acid concentrations are also of interest.

EXPERIMENTAL

Preparation of Neutral Complexes. Gram quantities of the neutral dicyano - bis - (2,2' - bipyridine) - metal (II) complexes were prepared following procedures previously described in the literature (12, 13). In all cases, analysis by potentiometric titration with standard cerium(IV) sulfate indicated purities of 98% or greater for the preparations.

Preparation of [Fe(bipy)₈]SO₄· 2H₂O. The solution obtained by adding 1.390 grams of FeSO₄· $7H_2O$ (0.05 mole) and 2.343 grams of 2,2'bipyridine (0.15 mole) to 25 ml. of distilled water was saturated with SO₂ and then evaporated to dryness. The resulting dark red solid, after recrystallization from 95% ethanol, was dried in vacuum over magnesium perchlorate. A purity of 99.9% for the product was found by potentiometric titration with standard cerium (IV) sulfate.

(IV) sulfate. **Preparation of** $[\mathbf{Ru}(\mathbf{bipy})_3]\mathbf{SO}_4$. **2H₂O.** The cyanide salt of this complex is obtainable as a by-product in the preparation of the neutral dicyanobis - (2,2' - bipyridine) - ruthenium(II) complex (13). It can also be readily obtained following the procedure of Dwyer (5) if sodium cyanide is used in place of sodium iodide as the precipitating agent. The sulfate salt was obtained by dissolving 3 grams of the cyanide salt in 15 ml. of 1M H₂SO₄, heating to drive off hydrogen cyanide, and cooling to induce crystallization. The orange-red crystalline product was collected by suction filtration, washed with acetone, and dried over magnesium perchlorate. Potentiometric titration with standard cerium(IV) sulfate indicated a purity of 99%.

with accelone, and dried over magnesidin perchlorate. Potentiometric titration with standard cerium(IV) sulfate indicated a purity of 99%. **Preparation of** $[Os(bipy)_3]SO_4$. **5H**₂**O**. The iodide salt of this complex can be obtained as a by-product in the preparation of the neutral dieyanobis - (2,2' - bipyridine) - osmium(II) complex (13), or it may be prepared more directly as described by Burstall, Dwyer, and Gyarfas (3). The sulfate form was prepared by metathesis of the iodide salt with an equimolar amount of silver sulfate. Silver iodide, after prolonged boiling to promote coagulation, was filtered from the reaction mixture and the sulfate salt was obtained from the filtrate by evaporation. The product was dried at room temperature over magnesium perchlorate. A purity of 98% was observed for the product on potentiometric titration with standard cerium(IV) sulfate.

Analysis of Complexes. Water of hydration was determined by loss in weight on drying at 196° C. in vacuo over magnesium perchlorate. In the case of tris-(2,2'-bipyridine)-iron(II) sulfate, bipyridine is also lost under these conditions; hence water was not determined. Purity of the various complexes was ascertained in conjunction with the potentiometric titrations carried out to determine formal redox potentials. Since the dicyano-bis-(2,2'-bipyridine) - ruthenium(II) complex could not be so titrated, its purity was established by spectrophotometric comparison with a sample available from earlier work that had been subjected to elemental analysis (13). Failure to observe absolute purity is believed to be a result of slightly indefinite water content rather than the presence of any objectionable contaminating substances. Note that the measurements of formal potentials are not subject to errors due to impurities or weighing of

		Table I.	Formal Re	dox Poten	tials at 25	° C. in H ₂ S	O ₄ Solutions	a		
Formal concentration of H_2SO_4 moles/liter										
Complex	0.01	0.05	0.11	0.50	1.0	2.0	4.0	6.0	10	12
$ \begin{array}{l} [Fe(bipy)_{3}]SO_{4}\\ [Fe(bipy)_{2}(CN)_{2}]\\ [Ru(bipy)_{3}]SO_{4}\\ [Ru(bipy)_{2}(CN)_{2}]\\ [Os(bipy)_{3}]SO_{4}\\ [Os(bipy)_{2}(CN)_{2}] \end{array} $	$1.069 \\ 0.781 \\ 1.274 \\ 1.12 \\ 0.858 \\ 0.778$	$0.777 \\ 1.273 \\ 1.11 \\ 0.783$	$\begin{array}{c} 1.062\\ 0.776\\ 1.262\\ 1.10\\ 0.841\\ 0.791 \end{array}$	0.776 1.12 0.804	1.026 1.236 0.803 0.810	$\begin{array}{c} 1.00\\ 0.79^{b}\\ 1.20\\ 1.13\\ 0.777\\ 0.836\end{array}$	$0.95 \\ 0.79^{b} \\ 1.15 \\ 1.16 \\ 0.723 \\ 0.89$	$\begin{array}{c} 0.88 \\ 0.82^b \\ 1.09 \\ 1.22 \\ 0.63 \\ 0.95 \end{array}$	$\begin{array}{c} 0.8 \\ 0.90^{b} \\ 0.88 \\ 1.26 \\ 0.44 \\ 1.01 \end{array}$	$\begin{array}{c} 0.98^{b} \\ 0.76 \\ 1.30 \\ 0.37 \\ 1.02 \end{array}$

^a Potentials are expressed in volts vs. the standard hydrogen electrode potential. Each value is the average of at least two determinations.

Taken from reference (11).

Table II.	Formal	Redox	Pote	ntials fo
[Ru(bipy) ₂	$(CN)_2$] in	Nitric	Acid	Solution
	at 2	25° C.		

Acid concentration, moles/liter	E°' vs. standard H2 electrode, volts
$ \begin{array}{c} 1.0\\ 2.0\\ 4.0\\ 5.0\\ 8.0\\ 16.0 \end{array} $	$1.10 \\ 1.13 \\ 1.14 \\ 1.18 \\ 1.24 \\ 1.40$

samples since the titration curves indicate the actual quantities of complex taken.

Reagents. STANDARD CERIUM(IV) Sulfate Solution. A solution $0.05\dot{M}$ in cerium(IV) and approximately 0.9M in H₂SO₄ was prepared using ceric hydroxide (G. Frederick Smith Chemical Co.) and the procedure described by Diehl and Smith (4). Arsenious oxide was employed for standardization.

STANDARD CERIUM(IV) NITRATE. A solution 0.05M in cerium(IV) was prepared by dissolving the requisite amount of $(NH_4)_2Ce(NO_3)_6$ in 1 liter of 1M HNO₃. Arsenious oxide was used for standardization.

Reagent grade chemicals were em-ployed for all tests and measurements. Solutions of acids were prepared in known concentrations, accurate to within 1 to 3%, by appropriate dilution of the concentrated acids, assayed by the manufacturers. The uranium(IV) solution was prepared by reducing a uranyl sulfate solution with a Jones reductor, then shaking it in air to oxidize any uranium(III) to the tetravalent state.

Apparatus. A Beckman Model G pH Meter equipped with a saturated calomel electrode and a platinum electrode was employed for the potentiometric titrations. Stirring was done with a magnetic stirrer; a 10-ml. microburet, graduated in 0.05-ml. divisions, was used.

Procedures. DETERMINATION OF FORMAL REDOX POTENTIALS. Weighed amounts (10 to 100 mg.) of the solid complexes were dissolved in known concentrations of acid solution (25 to 100 ml.) and titrated potentiometrically with standard cerium(IV) solution. Temperature was maintained at $25^{\circ} \pm$

0.5° C. by a water bath. The formal potential was taken as the potential of the platinum electrode at the halfway point in the titration as measured from the potentiometric end point rather than from the calculated theoretical equivalence point. In certain instances, potentiometric titrations were not practical. To determine formal potentials in such cases, a calculated amount of cerium(IV) (sufficient to oxidize exactly one half of the weighed complex) was added all at once to the acid solution of the complex and an immediate measurement of potential was made. This technique was necessary in the case of [Ru(bipy)2(CN)2] for all acid concentrations since potentials de-creased appreciably with time. It was also employed for $[Ru(bipy)_3]SO_4$ for acid concentrations approximately 1Mor less since poorly defined inflection points are observed in the titration curves.

A procedural modification was also necessary for measurement of formal potentials of [Fe(bipy)3]SO4 in acid concentrations greater than 0.1M since the complex undergoes dissociation at an appreciable rate in strong acid solutions. The rate of dissociation increases with increasing acid concentra-To minimize, as well as correct tion. for, the effect of dissociation on measurements of formal potential, the calcu-lated amount of cerium(IV) sulfate was added to the acid solution prior to addition of the complex. After the weighed complex and the prepared solution were mixed, potential measure-ments were made at 30-second intervals. The rate of potential decrease thus estimated was employed to calculate the redox potential at time of mixing. Dissolution was essentially complete within a few seconds after mixing. Initially, the rate of potential decrease in 10M H₂SO₄ was approximately 50 mv. per minute, and in 1M H₂SO₄ it was 2 mv. per minute. Since measurements could be made within 30 seconds after mixing, corrections to zero time were relatively small in all cases.

INDICATOR PROPERTIES, The behavior of complex after successive, repetitive treatments with cerium(IV) sulfate and various common reducing agents was examined. Solutions of the complex in 2M H₂SO₄ (1 to 3 mg. of complex in 20 to 30 ml. of acid) were treated first with a slight excess of cerium(IV) sulfate, then with a slight excess of reducing agent. To test for

reversibility of the color changes, the procedure was repeated at least 10 times using the same solution.

RESULTS AND DISCUSSION

Formal Potentials. The results obtained for sulfuric acid solutions of the complexes when cerium(IV) sulfate was used as the oxidant are compiled in Table I. In all cases in which titrations could be performed to evaluate formal potentials it was evident that cerium(IV) sulfate served as an effective oxidant: well defined potentiometric end points were observed, and the formal potentials exhibited by the cerium(IV)-cerium(III) couple ranged from 1.40 to 1.45 volts. Only in the case of $[Ru(bipy)_2(CN)_2]$, where rapidly changing electrode potentials precluded potentiometric titration, was there any doubt that $\operatorname{cerium}(IV)$ sulfate would react quantitatively with this more difficulty oxidizable complex. On the basis of observed formal potentials, cerium(IV) sulfate should be an effective oxidant for the ruthenium(II) complex. To test the validity of this contention, measurements were also performed in nitric acid solutions with the more potent cerium(IV) nitrate oxidant which exhibits formal potentials that range from 1.56 to 1.62 volts in 1 to 8M nitric acid solutions. The results are given in Table II. The use of the stronger oxidant and nitric acid solutions gives essentially the same results as when the formal potentials for $[Ru(bipy)_2(CN)_2]$ are measured in the sulfuric acid system.

Smith and Richter report formal potentials of 0.97 and 0.92 volt for $[Fe(bipy)_3]SO_4$ in 1 and 4M sulfuric acid, respectively (14). These values are lower than the corresponding ones reported here, perhaps because the necessity of minimizing or correcting for the effect of dissociation was overlooked. Similarly low values were obtained initially in the present study, until it was recognized that the rates of dissociation of the iron(II) and (III) species were appreciable in acid solutions of one molar or greater concentration and that time was thus an important variable to take into consideration.

Formal potentials for [Ru(bipy)₃] (NO₃)₂ at 0° C. in various concentrations of nitric acid have been determined by Dwver: 1.303, 1.288, 1.279, 1.270, 1.257, 1.240, and 1.222 volts for 0.002, 0.1, 0.3, 0.5, 1.0, 2.0, and 3.0 molar nitric acid, respectively (5). Considering the differences in temperatures and acids used in this and the present study, surprisingly minor differences are shown by the two sets of data. The pronounced decrease in formal potentials with increasing acid concentration, especially above 4M, is notable. A similar trend is evident for both [Fe(bipy)₃]SO₄ and [Os(bipy)₃]- SO_4 .

Dwyer and coworkers have measured formal potentials for $[Os(bipy)_3](ClO_4)_2$ in concentrations of perchloric acid up to 5M and observed values which decreased from 0.877 volt in neutral solution to 0.727 volt in 5M acid (6). When their results are compared with those in Table I, it is evident that nearly identical formal potentials are exhibited in sulfuric and perchloric acids of the same normalities, at least up to a concentration of 2N. Continuing close agreement at higher concentrations of course is not expected since HSO_4^- is only a moderately strong acid.

The influence of acid concentration on the formal potentials of the tris 2,2'bipyridine complexes of iron, ruthenium. and osmium is most striking. The present investigation reveals that the decreasing trends in potential continue at even more pronounced rates as the concentration of acid is increased bevond the moderate levels previously investigated. The decreases in formal potentials are such that very extensive and stable ion-pair formation between the complex cations and acid anions appears to be indicated. Any attempt at quantitative correlation of formal potentials with one or more solution variables, however, is quite impractical, at least for the concentrated solutions of this study. The difficulty stems from lack of reliable values for liquid junction potentials and activity coefficients, both of which vary with electrolyte concentration. Even under more amenable and nearly ideal conditions, Barnes, Dwyer, and Gyarfas found that the Debye-Huckel limiting law did not accurately predict experimental values obtained for the $[Os(bipy)_3](ClO_4)_3/$ $[Os(bipy)_3](ClO_4)_2$ system in various dilute electrolyte solutions (1). They suggested that the nature of the ligandmetal bonds may also change with ionic environment.

The trends in formal potentials with increasing acid concentration exhibited by the mixed ligand complexes of this study are just the opposite of those displayed by the simple tris complexes. Previous studies have revealed that the mixed ligand complexes of iron(II), ruthenium(II), and osmium(II) possess appreciable dibasic character and that each of the bound cyanide groups can be protonated (13). The corresponding iron(III) complex was found to be an extremely weak base; presumably, so also should be the analogous ruthenium (III) and osmium(III) mixed ligand complexes. With this information available, the influence of acid concentration on formal potentials is readily understood. As the acid concentration is increased, the extent of protonation of the metal(II) complexes increases; the reduced species take on greater positive charge; and the oxidation becomes increasingly more difficult. The oxidation process requires more positive potentials since removal of electrons from the positively charged species is more difficult than from the uncharged species. Also the process necessitates loss of protons to the medium, since the metal(III) complexes are too weakly basic to retain the protons formerly held by the metal(II) species. Thus, increased acidity, in discouraging loss of protons as well as loss of electrons, gives rise to more positive formal potentials.

Unfortunately, quantitative treatment of the results to determine the number of protons involved in the oxidation process and to evaluate basicity constants for the uncharged mixed ligand complexes proved unreliable. Liquid junction potentials and activity coefficients can neither be neglected nor assumed to be essentially constant. It is possible only to draw certain qualitative or semiguantitative conclusions from the data obtained. First, it is apparent from the changes in potentials that the metal(II) mixed ligand complexes are considerably stronger bases than the corresponding metal(III) complexes. Also, the order of increasing basicity in aqueous solution are [Fe- $(bipy)_2(CN)_2 < [Ru(bipy)_2(CN)_2] <$ $[Os(bipy)_2(CN)_2]$, as evidenced by the approximate acid concentration in which the formal potentials of each complex begins to show an appreciable increase [the sulfuric acid concentrations at such changes are 5, 3, and 1.5M, respectively. for the iron(II), ruthenium(II), and osmium(II) complexes]. Spectrophotometric measurements indicated this same trend in basicities for the complexes in glacial acetic acid (13).

Indicator Characteristics. Observations made in evaluating behavior and indicator properties of each complex in various simulated oxidationreduction titrations are reported in Table III. One of the six proved quite unsatisfactory as an indicator: [Ru(bipy)2(CN)2] does not exhibit reversible color changes on oxidation and reduction. The original yellow color of the ruthenium(II) complex in strong acid, once changed by an oxidant, cannot be restored by a reductant. Instead, an orange-brown color is produced. It appears likely that oxidation of the ruthenium(II) complex is accompanied by loss of coordinated cyanide, and that some ruthenium(IV)as well as ruthenium(III) species may be produced.

As a consequence of their dibasic character, the uncharged mixed ligand complexes exhibit colors in solution that are influenced by acid concentration. The colors of the oxidized complexes are

Table III. Indicator Characteristics in 2M H ₂ SO ₄									
Complex		Effect of various reductants on oxidized complex ^a							
	Color change on oxidation	FeSO4	Hydro- quinone	H ₃ AsO ₃	$H_2C_2O_4$	NaHSO3	$\mathrm{H}_{2}\mathrm{O}_{2}$	K. [Fe(CN)6]	UOSO₄
$\begin{array}{l} [Fe(bipy)_3]SO_4\\ [Fe(bipy)_2(CN)_2]\\ [Ru(bipy)_3]SO_4\\ [Ru(bipy)_2(CN)_2]\end{array}$	Red \rightarrow pale blue Orange \rightarrow pale violet Orange \rightarrow green Yellow \rightarrow pale green \rightarrow dark green \rightarrow orange	++++	++++++	0 0 8 -	0 0 8 -	+s+-	+0+-	+++++++++++++++++++++++++++++++++++++++	+s+
$[Os(bipy)_{2}]SO_{4}$ $[Os(bipy)_{2}(CN)_{2}]$	brown ^b Green \rightarrow pale pink Orange \rightarrow pale violet	+++++	+ +	O S	0 0	\mathbf{s}	0 0	+- +	$^{\mathrm{s}}_{+}$

^a Meaning of symbols: + = rapid and reversible color changes on alternately adding excess reductant and excess ceric sulfate; S = slow and reversible color changes; O = no color change; and - = irreversible color changes. ^b Colors observed on adding increasing amounts of ceric sulfate. not similarly affected. Changes in colors and changes in formal potentials are concomitant as acid concentration is changed. In dilute acid solutions the colors of [Fe(bipy)2(CN)2], [Ru(bipy)2 $(CN)_2$, and $[Os(bipy)_2(CN)_2]$ are red, yellow-orange, and red-brown, respectively; in concentrated acid solutions, the colors in the same order are vellow. pale vellow, and orange. Regardless of acid concentration, the color changes that accompany oxidation are distinct and discernible.

All of the reducing agents selected for the present study can be successfully titrated with ceric salts using ferroin as the indicator (8). A catalyst, usually osmic acid or iodine monochloride, is necessary to provide rapid reaction and indicator response in certain of these titrations. Presumably, use of suitable catalysts should also make practical the use of the complexes of this study as indicators in the same titrations-e.g., arsenic(III) or oxalic acid vs. cerium(IV).

With the exception of [Ru(bipy)₂ $(CN)_2$], all the complexes that were studied exhibit properties suitable for

their application as indicators. They should be appropriate in a great variety oxidation-reduction of titrations. Judicious selection of both indicator and acid concentration can provide redox potential indication over a broad range of 0.37 to 1.27 volts. Particularly inviting is the choice of the mixed ligand complexes of iron(II) and osmium (II), both of which exhibit increasing formal potentials with increasing acid concentration. Since certain titrantse.g., vanadium(V) and chromium(VI)also increase in oxidation strength with increasing acid concentration, use of an indicator which behaves similarly might eliminate the necessity of careful adjustment of acid concentration to ensure coincidence of indicator end point with the titration equivalence point.

Solution stability is favorable for all the complexes except [Fe(bipv)₃]SO₄ which dissociates rapidly into colorless species in concentrated solutions of strong acids. Intense absorption characteristics enable use of small quantities of the complexes; hence indicator titration blanks are minimal or negligible.

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Chronopotentiometric Oxidation of Hydrazine at a Platinum Electrode

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▶ The effect of electrode pretreatment on the anodic oxidation of hydrazine in sulfuric acid solutions was investigated. The reaction occurred with the smallest activation overpotential at a platinized electrode. An increase of $i\tau^{1/2}/C$ with increasing *i* and decreasing C, over a concentration range of 0.5 to 25mM hydrazine, was observed, and several possible mechanisms for this variation, involving adsorption of hydrazine, bubble formation, occurrence of an intermediate chemical reaction, and occurrence of catalytic decomposition of hydrazine at the electrode surface, are considered.

THE ELECTROOXIDATION OF HYDRA-**ZINE** is interesting both for its possible analytical applications and because hydrazine has been suggested as a possible fuel cell component. Recently Karp and Meites (12) examined the oxidation of hydrazine by voltammetry at mercury and platinum electrodes. They suggested that the oxidation proceeded more rapidly at oxide-coated than at reduced-platinum electrodes.

Anson and King (2), however, have demonstrated that increases in reversibility sometimes ascribed to oxide films may, in fact, be due to platinization of the electrode surface. The present study lends support to this idea, and examines the effect of various electrode pretreatments on the anodic oxidation of hydrazine. A variation of the chronopotentiometric constant, $i\tau^{1/2}/C$, with current density and concentration was also found, and some speculations concerning the source of this variation are considered.

EXPERIMENTAL

The experimental apparatus and (6). procedures have been described The working electrode was a plane shielded platinum disk, oriented horizontally for upward diffusion. The reference electrode was a mercury-mercurous sulfate electrode in contact with a saturated potassium sulfate solution (S.M.S.E.) with a potential of 0.40 volt vs. S.C.E. The reference electrode was positioned so that the tip of its salt bridge was very close to the surface of the platinum working electrode. All potentials given are referred to a S.M.S.E. The chronopotentiometric cell was thermostated at 25.0° C. The hydrazine solutions were prepared from reagent grade hydrazine sulfate, N₂H₄·H₂SO₄. Although acidic aqueous solutions of hydrazine are stable to air oxidation and autodecomposition (12), test solutions were usually freshly prepared.

RESULTS AND DISCUSSION

Effect of Electrode Pretreatment. The anodic oxidation of hydrazine occurs in acidic solution by the reaction

$$N_2H_5^+ - 4e \rightarrow N_2 + 5H^+$$
 (1)

Equation 1 represents only the overall reaction, and it is not meant to describe the detailed steps in the reaction. The potentials at which this oxidation occurs depend strongly upon the previous history of the platinum anode, and chronopotentiometric waves occurring at potentials separated by as much as 0.5 volt are observed. A chronopotentiogram of the anodic oxidation of hydrazine at an electrode which has been preoxidized by anodization in a 1M H₂SO₄ solution is shown in Figure 1. Also shown in Figure 1 are anodic