5131-95-3; $\cdot CH(CH_3)OCH_2CH_3$, 2229-06-3; ·diox, 4598-47-4; $\cdot CH_2CO_2H$, 2887-46-9; $\cdot CH(OH)CO_2H$, 3293-65-0; $\cdot C(CH_3)(OH)CO_2H$, 15552-92-8; $\cdot CH(CH_3)CO_2H$, 15671-30-4; $\cdot CH(CO_2H)_2$, 3247-02-7; $\cdot CH_2C(CH_3)_2OH$, 5723-74-0; $\cdot CH_2C(CH_3)_2CO_2H$, 26299-74-1; $\cdot C(O)NH_2$, 2858-51-7; $\cdot CH_2N(CH_3)CHO$, 17526-06-6; $Cr(H_2O)_6{}^{2+}$, 20574-26-9; $(H_2O)_5CrCH_2OH^{2+}$, 32108-95-5; $(H_2O)_5CrCH(OH)CH_3{}^{2+}$, 32108-94-4; $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 32108-93-3; $(H_2O)_5CrCH(CH_3)OCH_2CH_3{}^{2+}$, 32108-97-7; $(H_2O)_5Cr(diox)^{2+}$, 51965-43-6; $(H_2O)_5CrCH_2CO_2H^{2+}$, 52032-35-6; $(H_2O)_5CrCH(OH)CO_2H^{2+}$, 52109-46-3; $(H_2O)_5CrC(CH_3)(OH)CO_2H^{2+}$, 51965-44-7; $(H_2O)_5CrCH(CH_3)CO_2H^{2+}$, 51965-45-8; $(H_2O)_5CrCH(CO_2H)_2{}^{2+}$, 51965-46-9; $(H_2O)_5CrCH_2CH(OH)_2{}^{2+}$, 51965-47-0; $(H_2O)_5CrC(O)NH_2{}^{2+}$, 51965-48-1; $(H_2O)_5CrCH_2N(CH_3)CHO^{2+}$, 51965-49-2; $(H_2O)_5CrCH_2C(CH_3)_2OH^{2+}$, 51965-50-5; $(H_2O)_5CrCH_2C(CH_3)_2CO_2H^{2+}$, 51965-51-6.

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Electrochemical Reduction of Chromium(III) Complexes in the Presence of Nitrite Ion. Preparation of Nitrosyl Complexes[1]

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The electrochemical reduction of the ethylenediaminetetraacetatochromate(III), 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetatochromate(III), and hexacyanochromate(III) ions in the presence of nitrite ion have been studied by polarography and controlled-potential electrolysis. In each case, a chromium–nitrosyl complex was formed which was identified by direct synthesis. An interpretation of the unusual current–time behavior observed during the cpe is given and a mechanism of formation of the nitrosyls during electrolysis is proposed.

Introduction

Polarographic reduction of a reducible species in the presence of an electroinactive oxidant produces an increase in the observed limiting current provided the oxidant is kinetically capable of reacting with the reduced form at a sufficiently rapid rate. The experimental evaluation of such "catalytic" waves can lead to the extraction of reaction orders and rate constants in favorable cases.[3] This investigation was initiated to study the catalytic behavior produced by NO_2^- ions on the polarography of Cr(III) complexes as a convenient method of studying the oxidation of Cr(II) complexes.

Chromium(II) and chromium(II) complexes as reducing agents have been the subject of numerous kinetic, mechanistic, and stoichiometric investigations. Typical studies are those involving the reduction of coordination compounds[4] and organic compounds.[5] The reactions of Cr(II) and its complexes with oxy anions such as nitrate or nitrite have been less thoroughly studied but some results have been reported. Lingane and Pecsok[6] have reported a method for the determination of NO_3^- by Cr(II) which is most effective with titanium salts as catalysts. The terminal reduction product is NH_3. Ardon and Herman[7] have reported the preparation of $CrNO^{2+}$ by reduction of NO_3^- and NO with Cr(II). Armor and Buchbinder[8] have studied the reaction between Cr(II) and nitric oxide in detail. Several polarographic investigations of the catalytic behavior of nitrate ion on the reduction waves of Cr(III) complexes have been reported and analytical methods have been developed utilizing chromium(III) complexes of ethylenediaminetetraacetic acid,[9] glycine,[10] and other amino acids.[11] Very little work was found in which nitrite had been studied.

Preliminary investigation of the effect of NO_2^- on the polarographic reductions of a series of chromium(III) complexes showed that the catalytic wave enhancement of the reduction wave of the chromium(III) complex with ethylenediaminetetraacetic acid was significantly larger than the effect reported for nitrate. This work was then formulated to study the effect of NO_2^- on the ethylenediaminetetraacetatochromate(III) ion *via* polarography and controlled-potential electrolysis and expanded to include the complexes *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetatochromate(III) (CrCyDTA) and hexacyanochromate(III) ion.

Experimental Section

Reagents. Hydrogen ethylenediaminetetraacetatoaquochromate(III), $[CrH(EDTA)H_2O]$, was prepared according to the method of Hamm.[12] The pure product was identified by comparison with the reported visible spectrum[13] and polarographic data.[9] 1,2-Diaminocyclohexanetetraacetatoaquochromate(III) ion, $Cr(CyDTA)^-$, was prepared in aqueous solution by heating a mixture of $Cr(ClO_4)_3$ and CyDTA. The slight excess of Cr(III) was removed by ion exchange with a sodium counterion. The visible spectrum of the final product agreed well with the reported spectrum.[14] Pentaaquonitrosylchromium(I) ion, $Cr(NO)(H_2O)_5{}^{2+}$, was prepared in solution by the nitrite reoxidation of electrochemically reduced chromium(III) perchlorate. The reddish brown product was separated on an Amberlite 1R-120, 20-50 mesh, cation-exchange resin in the acid form. The product was eluted with 0.75 *M* $HClO_4$ and its visible spectrum was identical with the literature spectrum.[7] The *in situ* preparation of Cr(NO)EDTA and Cr(NO)CyDTA was accomplished by mixing of $CrNO^{2+}$ with the appropriate ligand followed by neutralization with Na_2CO_3. The reaction was complete in several minutes at room temperature when EDTA was the ligand but much slower with Cy-

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(1) Taken in part from the Ph.D dissertation of J. M. V., 1973.

(2) To whom correspondence should be addressed.

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DTA. However, after several hours significant amounts of Cr(NO)-CyDTA were obtained and could be separated.

Potassium hexacyanochromate(III), $K_3[Cr(CN)_6]$, was prepared according to the method of Bigelow.[15] After several recrystallizations from water, the product was identified by comparison with the literature values for the visible spectrum[16] and the polarographic half-wave potential.[17]

Potassium pentacyanonitrosylchromate(I), $K_3[Cr(CN)_5NO]$, was prepared by the method of Griffith.[18] The pure product was identified by comparison with the reported infrared spectrum[18] and polarographic half-wave potential.[19] Sodium ethylenediaminetetraacetatoaquoferrate(III), $Na[FeEDTA(H_2O)]$, was prepared by neutralization of an acidic solution of ferric perchlorate and the ligand with Na_2CO_3. At pH 5 the solution was heated to 60° until all the solid matter dissolved. Filtration followed by evaporation and cooling yielded large brown crystals. The purity of this compound was verified by controlled-potential coulometry.

Sodium perchlorate was prepared from perchloric acid and sodium carbonate. Hydrated chromic perchlorate was obtained from the G. Frederick Smith Co. *trans*-1,2-Diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid (CyDTA) was obtained from Aldrich Chemical Co., Inc. All other reagents were reagent grade.

All chromium solutions regardless of the ligand were standardized spectrophotometrically after alkaline oxidation with H_2O_2. The wavelength used for calibration and analysis was 373 nm. Solutions of Cr(II) complexes were prepared where possible by controlled-potential electrolysis and standardized by addition of an excess of known $FeEDTA^-$ solution followed by determination of the unreacted iron complex by controlled-potential coulometry at −0.4 V *vs.* Ag-AgCl reference electrode. Nitrite solutions were standarized by back-titration of a solution of excess standard permanganate with standard thiosulfate solution.

Stoichiometric Measurements. For solutions containing excess Cr(II) complex, the stoichiometry was determined by the polarographic method of Tanaka and Ito.[9] In addition, for solutions containing excess $Cr^{II}EDTA$ the unreacted chromium(II) complex remaining after reaction with NO_2^- was evaluated using $Fe^{III}EDTA$ and controlled-potential coulometry as in the standardization. For solutions containing excess NO_2^-, the unreacted nitrite was determined by the amperometric "dead-stop" method of Stone[20] using standardized sulfanilic acid as the titrant. With $Cr^{II}EDTA$ in excess, the $Cr^{II}:NO_2^-$ ratio was 6:1 corresponding to complete reduction to ammonia. Ammonia was verified by distillation and titrimeric analysis. The reverse addition produced a $Cr^{II}:NO_2^-$ of 1.5:1. When the stoichiometry of the $Cr^{II}CyDTA$ reaction with nitrite was determined polarographically with excess Cr(II) complex, a two-stage reaction was observed. The initial value was reproducibly 2. Long reaction times (*ca.* 30 min) produced a $Cr^{II}:NO_2^-$ ratio of 6:1. The stoichiometry of the chromous cyanide systems could not be determined. Similar difficulties were described by Fischerova and Fischer[17] for the chromous cyanide-hydroxylamine reaction.

Apparatus. All polarograms were obtained using a Heath Model EUA-19-2 polarographic or a Leeds and Northrup Type E electrochemograph. A standard H cell was used with a saturated KCl-3% agar bridge and an sce in one arm for solutions without perchlorate ion. When perchlorate was present, appropriate modification was made to prevent the precipitation of potassium perchlorate. The dme used for most of this work had a flow rate, *m*, of 1.88 mg sec^{-1} and a drop time, *t*, of 2.88 sec measured in 1.0 *M* $NaClO_4$ at −1.0 V *vs.* sce. The height of the reservoir was 52 cm. Oxygen was removed by bubbling nitrogen gas purified by passage through a series of vanadium(II) scrubbing towers prepared according to Meites.[21] An alkylaryl polyether alcohol maximum suppressor obtained from Southwestern Analytical Chemicals, Inc., Austin, Tex., was used when necessary. All polarographic measurements were obtained at 25 ± 0.1°.

Controlled-potential electrolysis were performed using an Anotrol Model 4700 potentiostat with an electrolysis cell of low resistance. The electrolysis cell was built to accommodate burets, the polarographic capillary, reference electrodes, and outgassing tubes. The counterelectrode was a platinum wire isolated from the solution by a fine sintered-glass disk. The reference electrode was a AgCl-Ag electrode. Electrolyte solutions were buffered with either sodium borate or acetic acid-sodium acetate and adjusted with NaCl, KCl, or $NaClO_4$ to the desired ionic strength. Integration of currents was accomplished by an electronic integrator build around a Philbrick USA-3 amplifier, a Model 7050 Fairchild digital voltmeter, and a mechanical counter. The integrator was calibrated using a precision constant-current source. Current-time curves were obtained using a digital data logger. Data were collected on paper tapes and processed using a PDP-8/1 computer with the MADCAP IV program from the Decus Program Library for scaling, smoothing, and plotting. Absorption spectra were obtained using a Cary Model 14 spectrophotometer. Analyses were performed using a Beckman DU spectrophotometer. Esr spectra were obtained using a Varian E-12 spectrometer with strong pitch as a standard for aqueous solutions at room temperature.

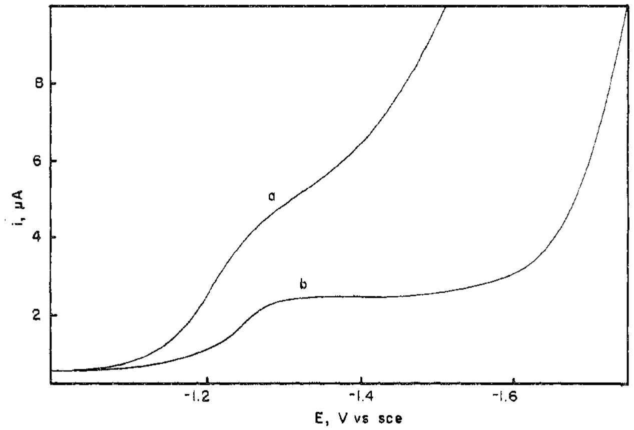

Figure 1. Polarograms for the $Cr^{III}EDTA$ complex at pH 5: a, $[Cr^{III}EDTA] = 5 \times 10^{-4}\,M$, $[NO_2^-] = 5 \times 10^{-4}\,M$; b, $[Cr^{III}EDTA] = 5 \times 10^{-4}\,M$.

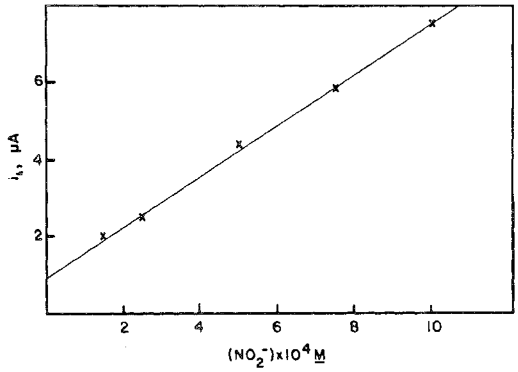

Figure 2. Polarographic limiting current as a function of nitrite ion concentration at pH 5; $[Cr^{III}EDTA] = 2.5 \times 10^{-4}\,M$.

Results

The $Cr^{III}EDTA$-NO_2^- System. Polarograms were obtained for solutions containing $Cr^{III}EDTA$ with and without NO_2^- as a function of pH. Typical polarograms are shown in Figure 1 for acetic acid-acetate buffers of pH 5. In Figure 2, the polarographic limiting currents obtained at pH 5 are plotted as a function of $[NO_2^-]$. At high concentration of nitrite the polarograms lost definition making reliable current measurements difficult. The limiting current at high $[NO_2^-]$ was found to be independent of the height of the mercury reservoir at this pH, establishing the expected kinetic character of this reaction. Although kinetic character was established at pH 5, these data were not analyzed for rate constants for two reasons: (1) the concentration of NO_2^-

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Table I. Polarographic Data for the $Cr^{III}EDTA-NO_2^-$ System at pH 8[a]

$10^2[NO_2^-]$, M	$\bar{i}_1$, μA	$\bar{i}_1/\bar{i}_d$	$10^2[NO_2^-]$, M	$\bar{i}_1$, μA	$\bar{i}_1/\bar{i}_d$
0.00	1.44 (i_d)		2.00	4.62	3.21
0.15	3.39	2.35	5.00	4.77	3.31
0.50	3.99	3.99	10.00	5.19	3.60

[a] $[Cr^{III}EDTA] = 8.07 \times 10^{-4}$ M, $\mu = 0.1$ M, $E = -1.40$ V *vs.* sce, and $t = 5.0$ sec.

which produced the waves was so low that correction must be made for the diffusion of NO_2^- and more seriously (2) there was the possibility of coreduction of nitrous acid. Polarograms obtained on blank solutions confirmed the coreduction of nitrous acid. In the pH 8 region, additional polarograms were obtained but the currents were much lower. These data are shown in Table I. The most significant feature of the polarography is the rapid leveling off of the limiting currents at high concentrations of NO_2^- in the more basic solutions. In the pH 8–9 region plots of the limiting current *vs.* $h^{1/2}$ at constant nitrite concentration were linear and parallel to the diffusion currents for the complex obtained in the absence of nitrite indicating no significant kinetic contribution to the enhanced wave.

Controlled-potential electrolyses were performed at pH 8 with a twofold molar excess of nitrite compared to the complex. At this pH, the $Cr^{III}EDTA$ complex exists as the blue monohydroxy dinegative anion $Cr(EDTA)OH^{2-}$. At a potential of -1.5 V *vs.* Ag-AgCl electrolysis was observed to produce a color change from blue to gray. Exhaustive electrolysis produced the light blue color expected for the formation of $Cr^{II}EDTA$. The production of the unusual intermediate color was studied in some detail. Figure 3 shows typical computer plotted current-time curves for two potentials, one on the plateau of the polarogram and the other 0.1 V more positive. In each case the curves are characterized by (1) rapid initial decay, (2) a region of high constant current, (3) a current surge, and (4) decay to background. Visual observations are as follows. In the initial region, the color changes from blue to gray. In the constant-current region, the color remains gray. The rapid rise in current is accompanied by a change to the original blue color followed by the current decrease to background and a change to the light blue color characteristic of the $Cr^{II}EDTA$ complex.

Figure 4 presents spectra obtained at pH 8 during the course of electrolysis of a solution containing excess nitrite and buffered with excess EDTA. These data correspond to the initial current decay portion of the electrolysis curve and reflect the formation of the intermediate. The product spectrum b was invariant with time since the electrolysis time was deliberately kept relatively short. The isosbestic points indicate only two absorbing species quantitatively account for all of the original Cr(III). All attempts to date to crystallize the intermediate have met with failure. In our hands, the direct reaction of $Cr^{II}EDTA$ with NO_2^- under the same conditions as those used during electrolysis did not yield the gray product regardless of order of mixing or rate of addition.

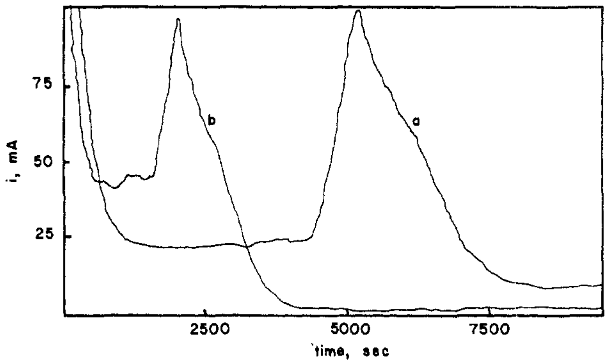

Figure 3. Current-time curves for the controlled-potential reduction of $Cr^{III}EDTA$ in the presence of a twofold excess of nitrite ion at pH 8: a, -1.4 V; b, -1.5 V.

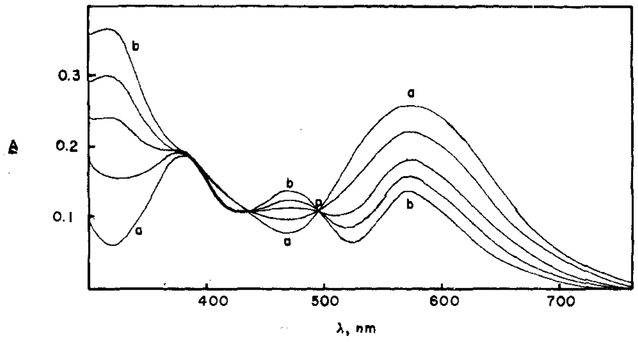

Figure 4. Visible spectra during the electrochemical reduction of $Cr^{III}EDTA$ in the presence of nitrite ion at pH 8: a, $Cr^{III}EDTA$; b, product; p, isosbestic point.

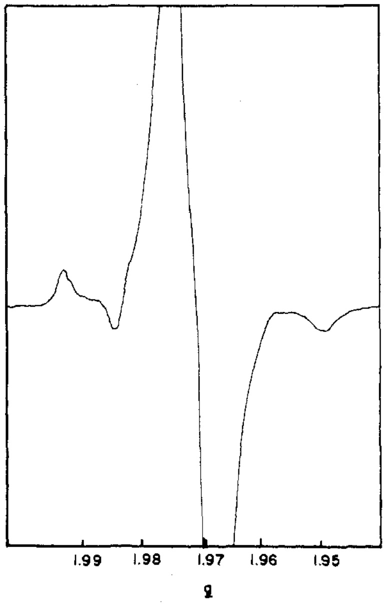

Figure 5. Esr espectrum for aqueous Cr(NO)EDTA.

The suspicion that the gray intermediate was a nitrosyl complex of chromium and EDTA was confirmed by the synthesis of the product by the direct reaction of $CrNO^{2+}$ and EDTA. The product prepared in this way had an absorption spectrum identical in detail with that obtained by electrolysis. The absorption maxima and estimated molar absorptivities for this product are 572 nm (ϵ 106), 474 nm (ϵ 107), and 313 nm (ϵ 280). Further characterization of the product was done by electron spin resonance and a typical esr spectrum is shown in Figure 5. A g value of 1.9727 was calculated using strong pitch as the standard. The esr spectra of the chemically and electrochemically prepared Cr(NO)-EDTA complex were identical. After complete removal of the nitrite excess, polarograms of both the chemical and electrochemically prepared products were the same. Figure 6 shows the polarograms obtained for equal concentrations of $Cr^{III}EDTA$ and Cr(NO)EDTA. The $E_{1/2}$ for Cr(NO)EDTA is -1.40 V *vs.* sce. It is evident that the half-wave po-

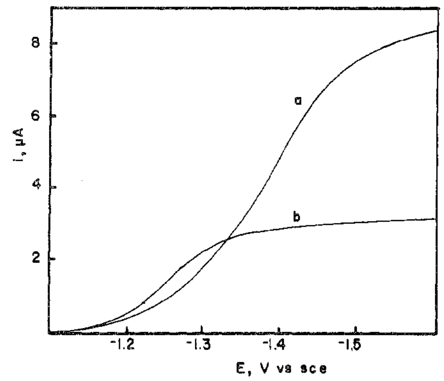

Figure 6. Comparison polarograms for Cr(NO)EDTA (a) and Cr^{III}-EDTA (b); pH 8; [complex] = 5 × 10^{-4} *M* in each case.

tentials are different and that the wave heights are significantly different. Slope analysis of the polarograms of Cr(NO)-EDTA indicated an irreversible one-electron reduction. The wave height was found to be relatively independent of the height of the mercury column indicating some kinetic character of the resulting wave. Chemical studies established that Cr^{II}EDTA reacted with Cr(NO)EDTA with a stoichiometric ratio of 3:1.

As expected, controlled-potential electrolysis of the Cr-(NO)EDTA complex produced a current-time curve corresponding to the latter stages of the controlled-potential electrolysis of Cr^{III}EDTA in the presence of NO_2^-; *i.e.*, the electrolysis current underwent an initial *increase*, passed through a maximum, and then decreased to background.

Detailed spectra as a function of pH showed no significant variation over the pH 2-9 region. In concentrated acid solution spectral changes occur which are coupled with the decomposition of the complex. Studies on the decomposition reaction in the absence of oxygen indicate that the ligand uncouples and the NO group is retained.

The Cr^{III}CyDTA-NO_2^- System. Typical polarograms obtained for the reduction of Cr^{III}CyDTA complex in the presence and absence of NO_2^- at two different pH values are shown in Figure 7. At pH 5 the presence of NO_2^- produces a two-stage wave which is not apparent at pH 8. The polarographic data for pH 8 are presented in Table II.

In agreement with Tanaka, *et al.*,[22] the Cr^{III}CyDTA system was found to be reversible in the absence of NO_2^- with $E_{1/2}$ = −1.21 V *vs.* sce. Spectra obtained during the electrolysis of Cr^{III}CyDTA in the presence of excess NO_2^- are similar to those shown in Figure 4 including isosbetic points. The absorption maxima and estimated molar absorptivities of the Cr(NO)CyDTA complex are 575 nm (ϵ 63) and 475 nm (ϵ 66). Typical polarograms of the Cr(NO)CyDTA complex and Cr^{III}CyDTA are shown in Figure 8. The same enhancement of the current is shown for the complex as for Cr(NO)-EDTA. The reduction is irreversible with $E_{1/2}$ = −1.52 V *vs.* sce. The appearance of the second wave in the polarography of the Cr^{III}CyDTA-NO_2 system can be attributed to the more negative half-wave potential of the nitrosyl complex compared to that formed from the Cr^{III}EDTA system. The esr spectrum of the electrolysis product is similar to that of the Cr(NO)EDTA with a *g* value of 1.9735.

Table II. Polarographic Data for the Cr^{III}CyDTA-NO_2^- System at pH 8[a]

$10^2[NO_2^-]$, *M*	$\bar{i}_l$, μA	$\bar{i}_l/\bar{i}_d$	$10^2[NO_2^-]$, *M*	$\bar{i}_l$, μA	$\bar{i}_l/\bar{i}_d$
0.00	1.44 (i_d)	1.0	2.00	2.80	1.94
0.10	1.87	1.23	5.00	3.35	2.33
0.20	2.12	1.47	10.0	4.28	3.0
0.50	2.32	1.61			

[a] $[Cr^{III}CyDTA] = 8.72 \times 10^{-4}$ *M*, $\mu = 0.1$ *M*, *E* = −1.40 V *vs.* sce, and *t* = 4.28 sec.

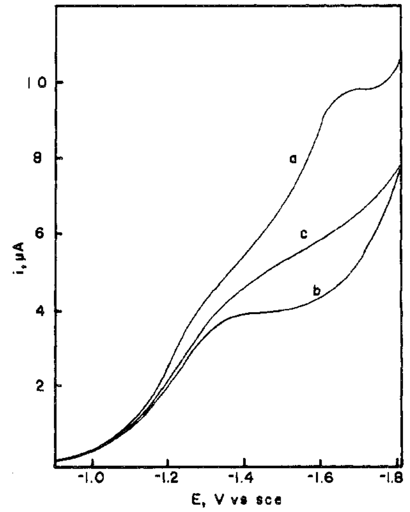

Figure 7. Polarograms of the Cr^{III}CyDTA complex; a, nitrite present, pH 5; b, no nitrite, pH 5; c, nitrite present, pH 8.

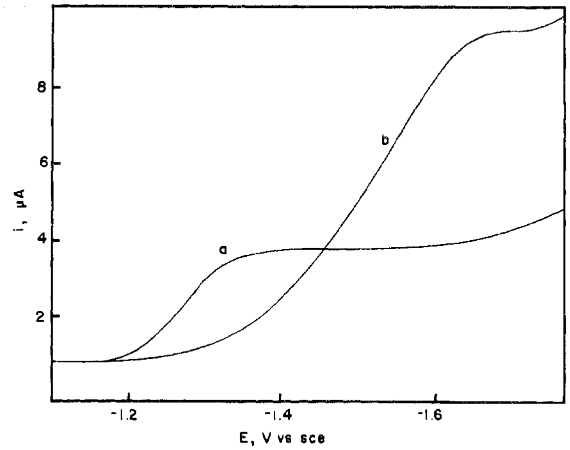

Figure 8. Comparison polarograms for Cr^{III}CyDTA (a) and Cr(NO)-CyDTA (b); [complex] = 5 × 10^{-4} *M*.

The $Cr(CN)_6^{3-}$-NO_2^- System. Typical polarograms are shown in Figure 9 for solutions containing OH^-, CN^-, and NO_2^-. Table III contains the observed currents under conditions of variable $[CN^-]$ and $[NO_2^-]$. The most obvious features of the observed currents are (1) at fixed $[CN^-]$ currents increase somewhat but tend toward limiting values as a function of $[NO_2^-]$, (2) at fixed $[NO_2^-]$, currents *decrease* with $[CN^-]$, (3) the most profound enhancement with NO_2^- occurs with low $[CN^-]$ and low $[NO_2^-]$, and (4) at high $[CN^-]$ and $[NO_2^-]$, the limiting-current values approach twice the limiting current for the complex alone. Controlled-potential electrolysis of the $Cr(CN)_6^{3-}$ ion in the presence of NO_2^- at −1.4 V *vs.* Ag-AgCl produced a bluish green solution. This reduction product was identified as the $Cr(CN)_5NO^{4-}$ ion by polarography, the visible spectrum, and esr spectroscopy. Coulometric data obtained during the cpe showed that the reduction required 2.0 ± 0.05 electrons/mol.

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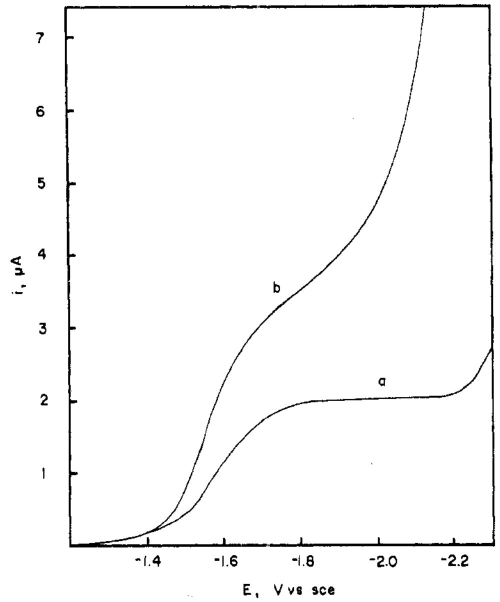

Figure 9. Polarograms of $Cr(CN)_6^{3-}$ in 0.1 *M* NaOH-0.05 *M* KCN; $[Cr(CN)_6^{3-}] = 2.8 \times 10^{-4}$ *M*: a, no nitrite; b, $[NO_2^-] = 0.1$ *M*.

Table III. Polarographic Data for the $Cr(CN)_6^{3-}$-NO_2^- System[a]

$[NO_2^-]$, *M*	$[CN^-]$, *M*	$\bar{i}_l$, μA	$\bar{i}_l/\bar{i}_d$
0.00	0.05	1.47	
0.10	0.05	2.50	1.7
0.20	0.05	3.10	2.11
0.30	0.05	3.39	2.3
0.00	0.10	1.55	
0.10	0.10	2.45	1.6
0.20	0.10	3.08	2.0
0.30	0.10	3.20	2.1
0.00	0.15	1.55	
0.10	0.15	2.37	1.5
0.20	0.15	2.70	1.7
0.30	0.15	2.95	1.9

[a] $[Cr(CN)_6]^{3-} = 2.78 \times 10^{-4}$ *M*, $\mu = 0.6$ *M*, $[OH^-] = 0.1$ *M*, and $E = -1.45$ V *vs.* sce.

Preliminary qualitative work on the $Cr(CN)_5OH^{3-}$ complex showed much more enhancement of the currents with nitrite.

Discussion

The electrochemical reduction of each of the three chromium(III) complexes in the presence of NO_2^- has been shown to lead to extensive formation of complexes which differ from the chromium(II) complexes of the respective parents. In the cases of the Cr^{III}EDTA and Cr^{III}CyDTA complexes, the electrochemical product can be synthesized from $CrNO^{2+}$ and the appropriate ligand. These syntheses support the idea that the electrochemical products are nitrosyls. In the case of the $Cr(CN)_6^{3-}$ reduction in the presence of nitrite, the product identification appears to be unequivocal. The polarographic behavior and the recorded spectrum agree with previously reported data for the complex $Cr(CN)_5NO^{4-}$.

The possibility of nitro rather than nitrosyl formation in the other two cases is real since the acid-base interconversion of these forms is well documented for ruthenium[23] and iron.[24] These conversions take place in solutions more alkaline than pH 8. However, in the complex designated as Cr(NO)EDTA no significant alteration of the visible spectrum was observed over the pH range 2-9. In electrochemical experiments conducted at pH 4, the same complex was obtained as at pH 8 but in low yield due to the concurrent electrolysis of nitrous acid. All indications are that the assignment of the $CrNO^{2+}$ entity as the nitrogen-containing function in these complexes is not incorrect. A detailed study of the esr spectra to resolve the oxidation state of the chromium has not been performed. However, the Cr(NO)-CyDTA and Cr(NO)EDTA complexes have esr spectra similar to that of $Cr(NH_3)_5NO^{2+}$.[25]

Since one condition for the measurement of rate constants by "catalytic" current enhancement is the reoxidation of the reduced form to its original form, such entrapment of the nitrosyl group precludes the measurement of meaningful rate constants by this technique. In fact, in the pH 8-9 region studied with Cr^{III}CyDTA and Cr^{III}EDTA no evidence of true kinetic behavior is observed. In the case of the $Cr(CN)_6^{3-}$-NO_2^- system, no evidence of kinetic behavior was obtained and the currents measured were quite small. For interpretation of the results, the $Cr(CN)_6^{3-}$-NO_2^- system provided the most significant results because of its apparent simplicity.

The $Cr(CN)_6^{3-}$-$Cr(CN)_6^{4-}$ system has been thoroughly studied and is established as electrochemically reversible. It has been recently demonstrated that the electrochemical behavior is complex[26,27] and that the Cr(II) product catalyzes the aquation of the parent $Cr(CN)_6^{3-}$ *via* a path involving $Cr(CN)_5OH^{4-}$ although significant quantities of this Cr(II) complex are not present. The results indicate that in both the polarography and controlled-potential electrolysis the appearance of $Cr(CN)_5OH^{3-}$ might be a mechanistic complication. In our experiments, no evidence was found of $Cr(CN)_5OH^{3-}$ and qualitative experiments indicated that the $Cr(CN)_5OH^{3-}$-NO_2^- system produced significantly higher current enhancements than those observed in the $Cr(CN)_6^{3-}$-NO_2^- system. The cpe resulted in the formation of the single product $Cr^0(CN)_5NO^{4-}$. This is the predicted result if $Cr^I(CN)_5NO^{3-}$ is the first product since at the potential used quantitative reduction of the Cr^I-NO complex to the Cr^0-NO complex takes place. The $Cr^0(CN)_5NO^{4-}$ complex is not oxidized by NO_2^- and its formation destroys the catalytic cycle. The effect of increasing $[CN^-]$ on the observed currents suggests that CN^- and NO_2^- are competing for a site in the Cr(II) coordination sphere.

These results while illuminating do not permit a detailed mechanism to be written. However, some comments can be presented and a partial mechanism proposed (eq 1 and 2).

$$Cr(CN)_6^{3-} + 1e^- \rightleftarrows Cr(CN)_6^{4-} \tag{1}$$

$$Cr(CN)_6^{4-} + NO_2^- \rightleftarrows Cr(CN)_5NO_2^{4-} + CN^- \tag{2}$$

There is little doubt about the nature of reaction 1 and reactions similar to (2) have been proposed by Fischerova and Fischer[17] to account for the effect of CN^- on the polarographic kinetic current in the $Cr(CN)_6^{3-}$-NH_2OH system and by Davies, Sutin, and Watkins,[28] for the denominator term in the rate law for the oxidation of $Cr(CN)_6^{4-}$ with H_2O_2.

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Alternate paths for this step can be written but the data at hand do not distinguish among the possibilities. The convergence of the polarographic limiting currents to a value of approximately twice the diffusion current at high NO_2^- and high CN^- suggests that only two electrochemical reduction steps are seen polarographically. The experimental finding that the reduction of $Cr(CN)_6^{3-}$ in the presence of nitrite to $Cr(CN)_5NO^{4-}$ is quantitatively a two-electron process strongly supports a reaction sequence in which only two electrons are transferred. This leads to the terminal step

$$Cr(CN)_5NO^{3-} + 1e^- = Cr(CN)_5NO^{4-}$$

which accounts for the second electron. The details of the chemical reactions involved after the substitution leading to the formation of $Cr(CN)_5NO^{3-}$ are obscure and are currently being investigated. However, it seems clear that this transformation is not electrochemical.

At low $[CN^-]$ and low $[NO_2^-]$, the higher currents could certainly be due to participation of $Cr(CN)_5OH^{4-}$. In the solutions of high $[NO_2^-]$ and high $[CN^-]$, the possibility of the direct substitution reaction

$$Cr(CN)_6^{4-} + NO_2^- \rightleftarrows Cr(CN)_5NO_2^{4-} + CN^-$$

occuring seems quite probable. While an outer-sphere reaction between $Cr(CN)_6^{4-}$ and NO_2^- without incorporation may take place, very little evidence exists for it from these data.

The CrCyDTA and CrEDTA systems can be rationalized in a similar way. In the pH 8-9 region, current enhancement was obtained but limited at high NO_2^- and no kinetic effect was observed. At pH 8 for 0.10 *M* nitrite, the $\bar{i}_l/\bar{i}_d$ ratio was 3.6 and 3 for the CrEDTA and CrCyDTA systems, respectively. In these cases, there is significant overlap of the reduction wave of the product nitrosyl with the parent, and a quantitative interpretation is not possible. The catalytic behavior of the reduction wave of the nitrosyl complex is a further complication. However, the fact that a limiting current enhancement is reached at high nitrite concentrations indicates that a substitution process is operative in these cases also.

The explanation for the unusual current-time behavior of the controlled-potential reduction of the $Cr^{III}EDTA$ system in the presence of NO_2^- is explicable in the following way. In the initial stages of the reduction the following reactions take place

$$Cr^{III}EDTA + 1e^- = Cr^{II}EDTA$$

$$Cr^{II}EDTA + NO_2^- \rightarrow Cr(NO)EDTA$$

In the presence of excess NO_2^-, the electrolysis product would be Cr(NO)EDTA if Cr(NO)EDTA were not reduced at the potential used and a normal current-time curve would be obtained. However, due to the overlap of the polarographic waves for Cr(NO)EDTA and $Cr^{III}EDTA$, a finite rate of reduction of the Cr(NO)EDTA complex exists. Since the ultimate reduction product of the nitrosyl complex is Cr^{II}-EDTA which is capable of reacting with NO_2^- producing the nitrosyl complex, the net effect is to keep a high steady-state concentration of nitrosyl complex as long as nitrite remains present. The current-time curve in this region appears normal except for the rather high background current. Upon the removal of all of the nitrate, the nitrosyl complex decomposes catalytically *via* the reactions

$$Cr(NO)EDTA + 1e^- = Cr^{II}EDTA + \text{products}$$

$$3Cr^{II}EDTA + Cr(NO)EDTA = xCr^{III}EDTA + yCr^{II}EDTA + \text{nitrogen products}$$

The reaction of $Cr^{II}EDTA$ with Cr(NO)EDTA has a stoichiometric ratio of 3:1 but neither the nitrogen products nor the product ratios were reliably determined. This sequence produces the current surge and accounts for the fact that at the maximum in the current-time curve only $Cr^{III}EDTA$ and $Cr^{II}EDTA$ were found. The subsequent course of the current-time curve is the reduction of the $Cr^{III}EDTA$ to Cr^{II}-EDTA. The effect of potential on the current-time curve is directly related to the polarogram of Cr(NO)EDTA. For potentials more positive than potentials on the plateau of the $Cr^{III}EDTA$ wave, the nitrosyl complex is reduced at a much slower rate which increases the time required for the current surge. The effect of nitrite concentration on the current-time curve is also readily explicable since the current surge does not occur until the nitrite has been consumed.

The electrochemical reaction studied here offers a simple direct method for the preparation of certain chromium-nitrosyl complexes. In addition these data strongly suggest that the nitrosyl complex results from an inner-sphere association of NO_2^- with the chromium(II) complex. Unfortunately, these studies do not provide detailed insight into the formation of the nitrosyl complexes after association. It is hoped that studies in progress will provide these details.

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Registry No. $Cr^{III}EDTA$, 16091-77-3; NO_2^-, 14797-65-0; Cr(NO)EDTA, 52165-23-8; $Cr^{III}CyDTA$, 28775-93-1; Cr(NO)CyDTA, 52165-24-9; $Cr(CN)_6^{3-}$, 14875-14-0.