Concluding Remarks

It is demonstrated that 2-(arylazo)pyridine ligands bind ruthenium(II) remarkably well. Two related groups of complexes of the *trans*-RuX$_2$ moiety are thoroughly characterized with use of spectroscopic and electrochemical methods. We wish to note that outside halocarbonyl chemistry[24] iodo complexes of ruthenium are limited in number,[15,18,25] and therefore well-characterized triads (X = Cl, Br, I) of dihaloruthenium complexes are relatively uncommon. Reports on the systematic identification of ν_{RuX} as X is varied are lacking.

The oxidation of the present complexes occur at high positive potentials, making the ruthenium(III) species strong oxidants and therefore quite reactive. In the synthesis of RuX$_2$L$_2$ from RuX$_3$ and L, it is quite likely that one or more unstable ruthenium(III) complexes are first formed which then undergo reduction (solvent oxidation?) to yield the final product. Snuff colored RuCl$_2$L$_2^+$ present in the coulometrically oxidized acetonitrile solution of RuCl$_2$L$_2$ is not particularly stable and is transformed to green (within 0.5 h) and then to blue (in 24

h) species which have not been fully characterized. A fresh solution of RuCl$_2$L$_2^+$ shows allowed electronic bands at $\sim$550 and $\sim$400 nm. The former may be of LMCT origin.[26] Attempts to isolate RuX$_2$L$_2^+$ as salts are under way.

The slow moving blue band remaining (see Experimental Section) on the silica gel column during chromatographic purification of green RuX$_2$L$_2$ (X = Cl, Br) yields small amounts of a crystalline blue complex after elution with acetonitrile–benzene mixture. Interestingly, the composition of this complex also corresponds exactly to RuX$_2$L$_2$. Evidently RuX$_2$L$_2$ (X = Cl, Br) exist as green and blue isomers. Preliminary IR and ^{1}H NMR data suggest that the blue complex has *cis*-RuX$_2$ and that it itself may actually be a mixture of more than one isomer differing in RuL$_2$ stereochemistry. Further studies are currently under way.

(24) Vancea, L.; Graham, W. A. G. *J. Organomet. Chem.* **1977,** *134,* 219. Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976,** 1861.
(25) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1979,** *18,* 549. Poddar, R. K.; Agarwala, U.; Monoharan, P. T. *J. Inorg. Nucl. Chem.* **1974,** *36,* 2275.

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Electrochemistry of the Intensely Green Complexes Formed by the Reaction of Cr^{2+} with Pyrazine ("Pyrazine Green"), Pyrazinecarboxamide, and Pyrazinecarboxylic Acid

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The electrochemical responses of "pyrazine green" and the "greens" formed by reaction of Cr^{2+} with pyrazinecarboxamide and pyrazinecarboxylic acid are described. Solutions of pyrazine green exhibit a single, composite polarographic wave which passes without inflection from anodic to cathodic currents. The anodic branch corresponds to the oxidation of the green by one electron to produce the pentaaquapyrazine complex of Cr(III). The cathodic branch corresponds to the reduction of the green by two electrons to produce Cr^{2+} and dihydropyrazinium ion. By contrast, the corresponding set of reactions for pyrazinecarboxylic acid green gives rise to separate oxidation and reduction waves. The more complex behavior of the green formed by pyrazinecarboxamide involves two isomers that can be interconverted by a reaction catalyzed by Cr^{2+}. The two isomers have very different electrochemical properties. One of the isomers of pyrazinecarboxamide green and the green formed from pyrazine carboxylic acid are believed to be chelates in which the organic reagent behaves as a bidentate ligand.

The rapid reaction of Cr^{2+} with pyrazines to form the intensely colored "pyrazine greens" has been observed repeatedly.[1-3] The product of the reaction seems best regarded as a complex of Cr(III) with a radical ligand.[3,4] As part of our continuing interest in the role of bridging ligands in catalyzing the oxidation of Cr^{2+} at mercury electrodes,[5] we have carried out electrochemical studies of three "pyrazine greens" and the corresponding products of their oxidation or reduction at

electrodes. No previous reports of the electrochemical behavior of these interesting complexes are available.

Experimental Section

Materials. Pyrazine, pyrazinecarboxylic acid, and pyrazinecarboxamide were commercially available reagents (Aldrich Chemical Co.) and were used as received. Chromium(III) perchlorate (G. F. Smith Chem. Co.) solutions were prepared in perchloric acid and were analyzed spectrophotometrically after oxidizing the Cr(III) to CrO$_4^{2-}$. Mercury(II) perchlorate solutions were prepared by dissolving mercuric oxide in perchloric acid. Sodium perchlorate solutions were prepared by neutralizing perchloric acid with sodium carbonate. Laboratory distilled water was further purified by passage through a Barnstead D2790 Nanopure purification train. Triply distilled mercury (Bethlemen Inst. Co.) was employed. Cation-exchange resins were Dowex 50W-X8 and Sephadex SPC 100-20.

Apparatus and Procedures. Conventional two-compartment electrochemical cells were employed for polarographic voltammetric measurements except when the PAR Model 303 automatic mercury electrode was employed. In those cases a single compartment cell

(1) Gould, E. S. *J. Am. Chem. Soc.* **1965,** *87,* 4730; **1967,** *89,* 5792. Dockal, E. R.; Gould, E. S. *Ibid.* **1972,** *94,* 6672.
(2) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y. T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978,** *17,* 326.
(3) Sprecker, H.; Wieghardt, K. *Inorg. Chem.* **1977,** *16,* 1290.
(4) (a) Dunne, T. G.; Hurst, J. K. *Inorg. Chem.* **1980,** *19,* 1152. (b) The equilibrium constant given in ref 4a was written as (Cr(pzH)$^{3+}$)/ (Cr^{2+})(pzH$^+$) = 1.5 × 10^4 M^{-1}; the value assigned to reaction 3 was calculated by taking K_a = (pz)(H$^+$)/(pzH$^+$) = 0.25.^{4a}
(5) Jones, J.; Anson, F. C. *Inorg. Chem.* **1969,** *8,* 195. Barclay, D. J.; Passeron, E.; Anson, F. C. *Ibid.* **1970,** *9,* 1024.
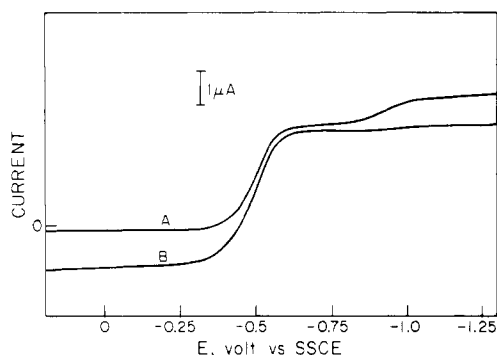
Figure 1. Sampled dc polarograms of solutions: A, 1 mM Cr(pz)$^{3+}$ prepared by electrolytic oxidation of the solution used to record polarogram B; B, A solution containing 1 mM Cr^{2+} and 1 mM pyrazine (supporting electrolyte 1 M NaClO$_4$ + 0.01 M HClO$_4$, drop time 0.5 s).

supplied by the manufacturer was utilized. Controlled-potential electrolyses were performed with conventional three-compartment cells.

Polarography (dc and pulse), cyclic voltammetry, and controlled-potential electrolyses were conducted with appropriate combinations of instruments from PAR (EG and G Industries, Princeton, NJ), including Models 173, 174, 175, 179, and 303. Polarographic drop times were mechanically controlled at 0.5 or 1 s. Mercury flow rates were 1 to 2 mg s^{-1}. Staircase voltammetry[6] was carried out by means of a computer-based signal generation and data acquisition system similar to one described previously[7] and a stationary mercury drop electrode (0.032 cm^2). Potentials were measured and are reported with respect to the sodium chloride saturated calomel reference electrode (SSCE) whose potential is 5 mV more negative than the standard SCE.
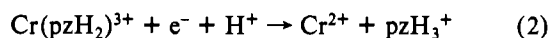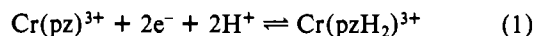
Spectra were recorded with Cary 219 or Hewlett-Packard 8450 spectrophotometers.

Solutions of Cr^{2+} were prepared by electrolytic reduction of Cr^{3+} at a stirred mercury pool or by reduction with amalgamated zinc in cases where the resulting Zn^{2+} did not interfere in subsequent electrochemical experiments. Solutions were deaerated with prepurified argon. Cr^{2+} was transferred anaerobically to reactant solutions by means of standard syringe procedures. Solutions of pyrazine green were prepared by mixing equimolar quantities of Cr^{2+} and pyrazine in thoroughly deaerated acidic supporting electrolytes. Solutions of Cr^{III}–pyrazine complexes were prepared from the corresponding greens by chemical (Hg(ClO$_4$)$_2$) or electrochemical oxidation followed by cation-exchange chromatography. So that the ratio of total chromium to pyrazine in such solutions could be determined, they were converted to hexaaquachromium(III) ion and the corresponding pyrazine by adjusting the solutions to a pH near 0 and heating to 90–110 °C for 60 min in a sealed tube. The use of less acidic media sometimes allowed the formation of oligomeric Cr(III) aquation products. The chromium concentration was determined spectrophotometrically after conversion to chromate (λ 375 nm; ϵ 4815), and the pyrazine was determined polarographically.

Results

(Pyrazine)pentaaquachromium(III) (Cr(pz)$^{3+}$). Before analyzing the electrochemical response obtained from solutions of "pyrazine green" ([H$_2$O)$_5$Cr(pzH)]$^{3+}$ = Cr(pzH·)$^{3+}$), it will be helpful to describe the more straightforward reduction of the simple monopyrazine complex of chromium(III), [(H$_2$O)$_5$Cr(pz)]$^{3+}$ ($\equiv$Cr(pz)$^{3+}$). Curve A in Figure 1 shows the dc polarogram for a solution of Cr(pz)$^{3+}$ prepared and purified as described in the Experimental Section (λ_{max} (ϵ) 565 (16) and 402 (19) nm). The heights of the two waves correspond to a two-electron reduction of pyrazine followed by

a one-electron reduction of Cr(III). (Separate experiments with pure solutions of pyrazine or chromium(III) showed that the diffusion coefficient of pyrazine is considerably larger than that for Cr(III).) Cyclic voltammetry shows the first wave with $E_{1/2}$ = –0.50 V to be reversible whereas the second reduction wave yields no anodic wave at potentials near its cathodic peak potential. Except for its pH dependence ($\sim$60 mV/pH unit), the first wave resembles the wave for the reduction of pyrazine itself and falls at nearly the same potential.[8,9] The behavior is readily interpreted by the pair of sequential reductions in eq 1 and 2. In reaction 1, the co-

$$Cr(pz)^{3+} + 2e^- + 2H^+ \rightleftharpoons Cr(pzH_2)^{3+} \qquad (1)$$

$$Cr(pzH_2)^{3+} + e^- + H^+ \rightarrow Cr^{2+} + pzH_3^+ \qquad (2)$$

ordinated pyrazine is reduced in a two-electron step to coordinated dihydropyrazine just as pyrazine itself is reduced dirrectly to dihydropyrazine except in quite acidic media. Reaction 2 represents the reduction of Cr(III) to Cr(II) accompanied by the rapid decoordination of the dihydropyrazine ligand. (It is known[8,9] that pyrazine is reduced to the dihydropyrazinium cation with the consumption of three protons.)

Controlled-potential electrolysis of a pH 2 solution of Cr(pz)$^{3+}$ at a potential between the first and second waves of Figure 1A consumes 2 electrons/mol of complex and removes the color from the initially red-violet solution; i.e., pyrazine green is not formed at any point during the electrolysis.

Pyrazine Green (Cr(pzH·)$^{3+}$). The polarographic response of a solution of pyrazine green, prepared by mixing equimolar quantities of Cr(OH$_2$)$_6^{2+}$ ($\equiv$Cr^{2+}) and pyrazine, is shown as curve B in Figure 1. The initially anodic current passes through 0 without inflection as the potential is made more negative to produce a single wave comprised of anodic (negative currents) and cathodic (positive currents) components. The anodic limiting current corresponds to a one-electron oxidation while the cathodic limiting current represents a two-electron reduction.

Controlled-potential electrolysis of a solution of pyrazine green at 0 V involved 1 electron/molecule of complex. The resulting oxidized solution exhibited a polarogram essentially identical with curve A in Figure 1. Two bands separated during ion-exchange chromatography of the electrolyzed solution. A minor band, eluting with 2.5 M NaClO$_4$–0.01 M HClO$_4$, gave a solution with a spectrum matching that of Cr(OH$_2$)$_6^{3+}$ ($\equiv$Cr^{3+}). A major, red-violet band was eluted with 3 M NaClO$_4$–0.01 M HClO$_4$ to produce a solution that was heated for 60 min at 90 °C to aquate the suspected Cr(pz)$^{3+}$ complex. Subsequent analysis confirmed the presence of equimolar quantities of Cr^{3+} and pyrazine in the resulting solution.

The production of both Cr^{3+} and Cr(pz)$^{3+}$ by oxidation of millimolar solutions of Cr(pzH·)$^{3+}$ at 0 V is consistent with the equilibrium constant for the formation of the green reported recently by Dunne and Hurst[4a,4b] (eq 3). At pH 2 with

$$Cr^{2+} + pz + H^+ \rightleftharpoons Cr(pzH·)^{3+} \qquad K = 6 \times 10^4 \ M^{-2} \qquad (3)$$
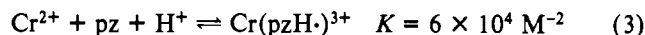
millimolar solutions of the green, over 70% of the chromium present remains as Cr^{2+} at equilibrium, and its direct oxidation to Cr^{3+} proceeds at 0 V. The relative quantities of Cr(pz)$^{3+}$ and Cr^{3+} produced during the electrooxidation will depend upon the heterogeneous electron-transfer kinetics for Cr^{2+} and Cr(pzH·)$^{3+}$ as well as the rate at which reaction 3 adjusts to perturbations from equilibrium, but the appearance of both

(6) Barker, G. C. *Adv. Polarogr., Proc. Inst. Congr., 2nd* **1960**, *1*, 144. Christie, J. H.; Ligane, P. J. *J. Electroanal. Chem.* **1965**, *10*, 176. Mann, C. K., *Anal. Chem.* **1961**, *33*, 1484; **1965**, *37*, 326. Zipper, J. J.; Perone, S. P. *Ibid.* **1973**, *45*, 452. Ferrier, D. R.; Schroeder, R. R. *J. Electroanal. Chem. Interfacial Chem.* **1973**, *45*, 343, 361. Ryan, M. D. *Ibid.* **1977**, *79*, 105.

(7) Lauer, G.; Abel, R.; Anson, F. C. *Anal. Chem.* **1967**, *39*, 765.

(8) (a) Moorhead, E. D.; Britton, D. *Anal. Lett.* **1968**, *1*, 541. (b) Klatt, L. N.; Rouseff, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 7295.

(9) Swartz, J.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *114*, 117.
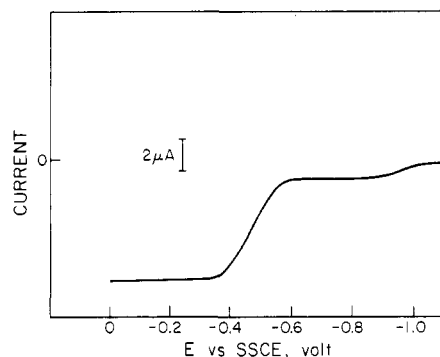
Figure 2. Reverse pulse polarogram for a solution containing 1 mM Cr^{3+} and 1 mM pyrazine. Initial potential was -1.1 V, and the potential was stepped progressively to increasingly positive values (supporting electrolyte 1 M $NaClO_4$ + 0.01 M $HClO_4$, drop time 0.5 s). The same curve was obtained with solutions of $Cr(pz)^{3+}$ or $Cr(pzH\cdot)^{3+}$.

oxidation products is not surprising.

The fact that the cathodic portion of the polarogram for pyrazine green in Figure 1 represents a two-electron rather than a one-electron process strongly suggests that reaction 4

$$Cr(pzH\cdot)^{3+} + 2e^- + 2H^+ = Cr^{2+} + pzH_3^+ \qquad (4)$$
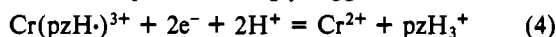
is responsible for the cathodic wave. The absence of any subsequent reduction wave, which would be expected if the chromium center had not been reduced, adds support to this suggestion.

Thus, curve B in Figure 1 is not a typical composite polarographic wave representing a single reaction that proceeds in one direction or the other at the electrode.[10] Such waves occur in the polarography of metal complexes that are thermodynamically unstable with respect to disproportionation. For example, Cu^+ in noncomplexing electrolytes yields a composite polarographic wave that passes through the 0 current axis without inflection to give equal anodic and cathodic limiting currents.[11] Exposure to metallic surfaces usually catalyzes the decomposition of such reactants because the oxidation and reduction reactions constituting the disproportionation can proceed simultaneously on the metal surface. However, the composite polarographic wave of pyrazine green (Figure 1B) must have a different origin because pyrazine green solutions are stable when stirred over mercury, and the inequality of the currents for the cathodic and anodic portions of the composite wave means that the two opposing electrode reactions responsible for the wave must be more complex than the simple pair of half reactions whose sum corresponds to a disproportionation reaction. We will defer to the Discussion our explanation of this unusual behavior.

Reverse Pulse Polarography. If solutions of $Cr(pz)^{3+}$, $Cr(pzH\cdot)^{3+}$, or Cr^{3+} + pz are examined by reverse pulse polarography[12] with the initial potential of the electrode at a value (-1.1 V) where Cr^{2+} and pzH_3^+ are formed, the response shown in Figure 2 results. The small wave near -0.95 V is also observed in solutions of Cr^{3+} alone and corresponds to the point where the diffusion-limited reduction of Cr(III) that proceeds at the initial potential no longer occurs at the pulse potential.[12] The larger wave near -0.5 V represents the pulse current for the two-electron oxidation of the pzH_3^+ formed at the initial potential. However, limiting currents exceeding those obtained in solutions of pyrazine alone result when the same concentrations of $Cr(pz)^{3+}$, $Cr(pzH\cdot)^{3+}$, or a mixture of Cr^{3+} and pyrazine are examined. The extra current must

(10) Kolthoff, I. M.; Lingane, J. J. "Polarography", 2nd ed.; Wiley-Interscience: New York, 1952; Chapter XII.
(11) Altermatt, J. A.; Manahan, S. E. *Anal. Chem.* **1968**, *40*, 655.
(12) Osteryoung, J.; Kirowa-Eisner, E. *Anal. Chem.* **1980**, *52*, 62.

Scheme I

At the Initial Potential (-1.1 V)

$$\left. \begin{array}{l} Cr(pz)^{3+} + 3e^- + 3H^+ \\ \text{or } Cr(pzH\cdot)^{3+} + 2e^- + 2H^+ \\ \text{or } Cr^{3+} + pz + 3e^- + 3H^+ \end{array} \right\} \rightarrow Cr^{2+} + pzH_3^+$$

At Pulse Potentials Positive of Ca. -0.6 V

at the electrode: $\quad pzH_3^+ - 2e^- \rightleftharpoons pz + 3H^+$
in solution: $\quad pz + Cr^{2+} + H^+ \rightleftharpoons Cr(pzH\cdot)^{3+}$
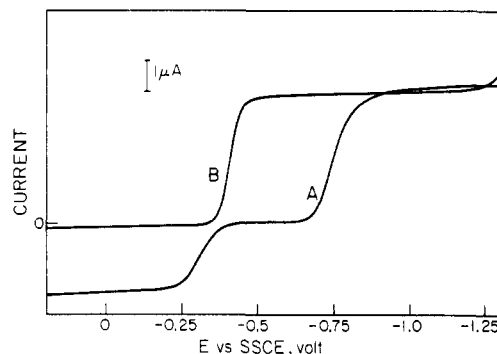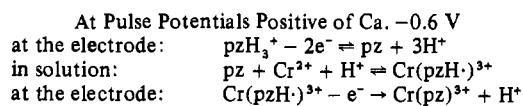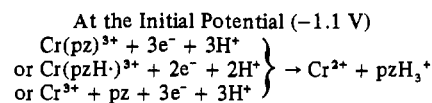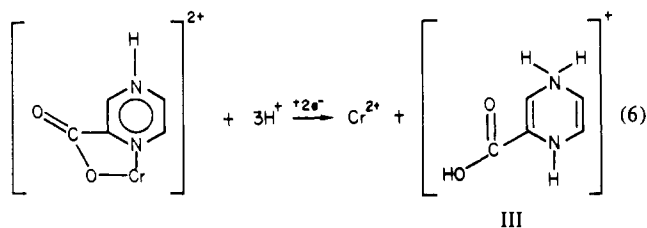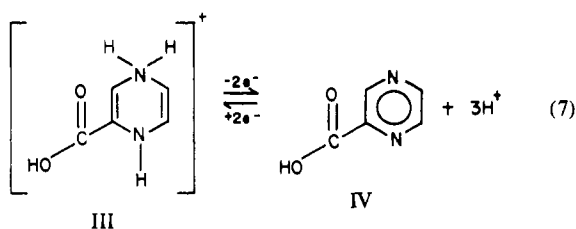at the electrode: $\quad Cr(pzH\cdot)^{3+} - e^- \rightarrow Cr(pz)^{3+} + H^+$

Figure 3. Sampled dc polarograms of solutions: A, 2 mM pyrazinecarboxylic acid + 2 mM Cr^{2+}; B, 2 mM pyrazinecarboxylic acid (supporting electrolyte 1 M $NaClO_4$ + 0.01 M $HClO_4$, drop time 0.5 s).

originate from the oxidation of Cr^{2+}, a process that proceeds much more slowly at these potentials in the supporting electrolyte alone but is evidently catalyzed by the presence of pyrazine. This catalyzed oxidation is likely to involve the intermediate formation of pyrazine green by reaction between the pyrazine generated at the electrode and Cr^{2+} as indicated in Scheme I.

The pyrazine is not acting as a true catalyst in Scheme I because it is consumed in the reaction, and the final Cr(III) product obtained, $Cr(pz)^{3+}$, differs from the species that is formed, albeit much more slowly, in the absence of pyrazine, i.e., Cr^{3+}. However, $Cr(pz)^{3+}$ does undergo slow, spontaneous aquation to give Cr^{3+} and pyrazine so that pyrazine could be employed in a catalytic cycle for the conversion of Cr^{2+} to Cr^{3+}.

Quantitative measurements of the catalytic efficiency of pyrazine were thwarted by the hydrolytic decomposition of pzH_3^+,[8b] and difficulties in measuring the catalytic currents at higher ratios of Cr^{2+} to pyrazine where the uncatalyzed oxidation of Cr^{2+} began to make more significant contributions to the total current at potentials on the limiting current plateau. However, with equal concentrations of Cr^{2+} and pzH_3^+, we estimated that at least 80% of the Cr^{2+} is oxidized to $Cr(pz)^{3+}$ via Scheme I at the same potential where pzH_3^+ is oxidized to pz.

Under some conditions, with ratios of Cr^{2+} to pyrazine somewhat greater than unity, we observed the pyrazine-catalyzed oxidation of more than an equimolar quantity of Cr^{2+}. We also observed the rapid formation of the color of pyrazine green when $Cr(pz)^{3+}$ was exposed to Cr^{2+} in the absence of uncoordinated pyrazine. Thus $Cr(pz)^{3+}$ appears to catalyze the electrooxidation of Cr^{2+} presumably by taking the role of pz in Scheme I. The behavior observed suggested that the binuclear, pyrazine-bridged ion, $CrpzCr^{6+}$ might be forming at the electrode surface, but attempts to prepare stable solutions of this ion by chemical or electrooxidation of solutions of Cr^{2+} and pyrazine were not successful. Similar binuclear complexes of Cr(III) and pyrazine have been proposed as intermediates in homogeneous reactions of $Cr(pz)^{3+}$ with Cr^{2+}.[3]

Pyrazinecarboxylic Acid Green. Solutions of the green complex formed when pyrazinecarboxylic acid reacts with Cr^{2+}

Scheme II

Anodic Polarographic Wave and Second
Anodic Peak in Cyclic Voltammetry of II

(5)
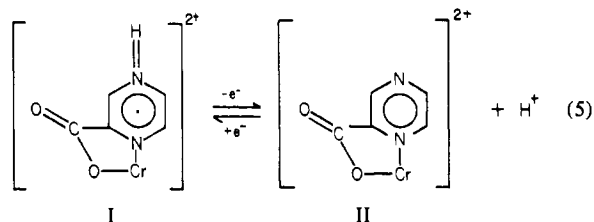
Cathodic Polarographic Wave

(6)

First Anodic Peak in Cyclic Voltammetry of III

(7)

Chemical Reaction following Reaction 7

(8)

Figure 4. Cyclic staircase voltammogram for an approximately 0.3 mM solution of the complex of Cr(III) with pyrazinecarboxylic acid, Cr(pzCOO)²⁺, prepared by chemical oxidation of the green and purified by ion exchange: supporting electrolyte 1 M NaClO₄ + 0.01 M HClO₄; effective scan rate 5 V s⁻¹. Initial potential was 0 V, and the initial scan was to more negative potentials.

Figure 5. Sampled dc polarograms of solutions: A, 2 mM pyrazinecarboxamide + 2 mM Cr²⁺; B, solution A after exhaustive oxidation at +0.15 V by controlled-potential electrolysis (supporting electrolyte 1 M HClO₄, drop time 0.5 s).
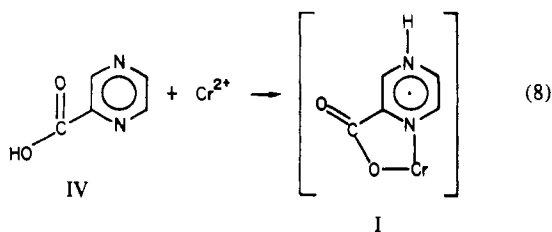
exhibit the simple polarographic response shown in Figure 3, curve A. Instead of the single composite wave obtained with pyrazine green (Figure 1B), two, well-separated waves are present. The anodic wave corresponds to a one-electron oxidation while the cathodic wave corresponds to a two-electron reduction. Both waves are shifted away from the potential where the free ligand undergoes its two-electron reduction (curve B, Figure 3) although the shift is small for the oxidation wave. Controlled-potential oxidation of the green solution at 0 removed the green color and consumed 1 mol of electrons/mol of chromium present. The resulting solution gave a two-wave polarogram essentially identical with curve A except that the first wave rose from 0 current rather than an anodic current plateau.

Chemical oxidation (with Hg(ClO₄)₂) of a more concentrated solution of pyrazinecarboxylic acid green produced a red solution which was subjected to ion-exchange chromatography. A red band containing most of the Cr(III) eluted with 2 M NaClO₄, suggesting a complex having a charge of 2+. Analysis of the eluted solutions showed the presence of 1 mol of pyrazinecarboxylic acid/mol of Cr(III). The spectrum of the complex: (λ_max(ε) 556 (30), 400 (sh), 277 (5900)) was in reasonable agreement with that previously assigned[3] to complex II (see Scheme II). A cyclic staircase voltammogram for a solution of II eluted from the cation-exchange column is shown in Figure 4. This voltammogram combined with the other observations suggests the electrode reaction
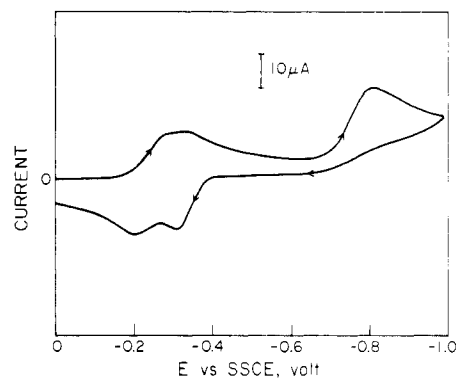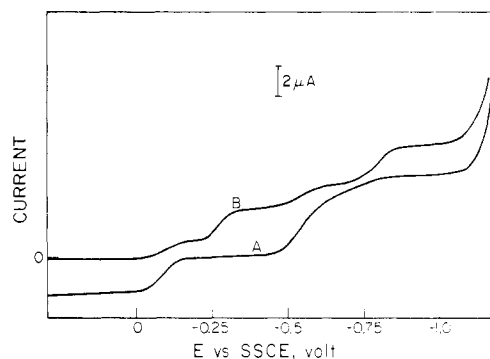
sequences shown in Scheme II for pyrazinecarboxylic acid green.

The rather broad peak near −0.3 V in Figure 4 corresponds to the reverse of reaction 5 of Scheme II, and the larger, irreversible wave near −0.8 V corresponds to reaction 6. The absence of a peak negative of −0.9 V confirms that all of the Cr(III) present in the initial reactant is reduced to Cr(II) as part of the wave to −0.8 V. During the return scan in the positive direction, no anodic current flows before the potential where the reduced, uncoordinated ligand, III, is oxidized to IV (reaction 7). The Cr²⁺ also present reacts rapidly with IV to form I, the "green" (reaction 8). However, in contrast with pyrazine itself, I is oxidized to II only at somewhat more positive potentials (reaction 5), so that a pair of waves appears in the anodic scan of the voltammogram. The most significant difference between the greens formed by pyrazine and its carboxylic acid is that the latter can be produced at the electrode surface by one-electron reduction of the chromium-(III)–pyrazinecarboxylato complex (the reverse of reaction 5) while the corresponding chromium(III)–pyrazine complex exhibits a two-electron reduction that bypasses the green.

Pyrazinecarboxamide Green. The green formed from reaction of pyrazinecarboxamide with Cr²⁺ yields a polarogram that has similarities to that for the carboxylic acid green (Figure 5, curve A). The distinct, one-electron oxidation wave is well separated from a reduction process consisting of two overlapping waves followed by a well-defined limiting current plateau that corresponds to an overall two-electron reduction. The reversible, two-electron reduction of free pyrazine-carboxamide occurs at a potential (−0.28 V in 1 M HClO₄)

between the oxidation and reduction waves for the green.

Electrolytic oxidation of the green at +0.15 V proceeds smoothly with the release of 1 electron/molecule of green to produce a solution that is free of its initial green color and retains only a faint red-violet color. The current during the oxidation decreases exponentially with time as expected for a diffusion-controlled process. However, the dc polarogram of the oxidized solution, curve B in Figure 5, contains four reduction waves! This large number of waves in the oxidized solution contrasts sharply with the behavior obtained with the greens of pyrazine (Figure 1) and pyrazinecarboxylic acid (Figure 3). When the oxidized solution was subjected to chromatography on a cation-exchange resin, a single, red-violet band was formed that eluted as a tripositive ion (3 M Na-ClO$_4$–0.01 M HClO$_4$). Polarography of the eluate produced a response essentially identical with that obtained before the chromatography; i.e., the four reduction waves remained. Analysis of the eluate after the complex had been aquated by heating to 90 °C showed the presence of equimolar quantities of chromium and pyrazinecarboxamide.

Cyclic voltammetry of an oxidized solution showed that the two polarographic waves at the most positive potentials correspond to reversible couples while the remaining two waves gave irreversible responses. The second wave matches that for uncoordinated pyrazinecarboxamide in the same solution, and the most negative wave appears at a potential typical for the reduction of Cr^{III}–amine complexes to Cr^{2+}.[13]

If the oxidized solution is rereduced by electrolysis at –0.18 V on the plateau of the first reduction wave, the current does not decrease exponentially as it did during the controlled-potential oxidation. Instead the current quickly falls to a low, steady value indicative of an electrode process limited by a chemical reaction instead of the diffusion-limited supply of reactant to the electrode surface. Nevertheless, if the electrolysis is continued until the current has decayed to background levels, the same amount of charge as was required for the oxidation is consumed and the green color of the original solution is restored. The resulting solution gives a polarographic response identical with that of the original solution of pyrazinecarboxamide green (curve A, Figure 5).

This superficially puzzling behavior becomes less so if the possible existence of two linkage isomers of pyrazinecarboxamide complexes of Cr(III) is recognized and the previously described behavior of the greens formed by pyrazine and pyrazinecarboxylic acid is recalled. Scheme III presents the combination of electrode and homogeneous reactions that we propose to account for the behavior of pyrazinecarboxamide green.

An essential ingredient in Scheme III is the isomeric equilibration of VI and VII by means of electron-exchange reactions with Cr^{2+} (reaction 10). These reactions are presumed to occur during the course of the electrolytic oxidation of the green, V. The Cr^{2+} is provided by the partial dissociation of V into Cr^{2+} and pyrazinecarboxamide, an equilibrium that has been shown to be rapidly established relative to the time scale of an electrolysis experiment.[2]

Reaction 10 also accounts for the observation that electrolytic reduction at –0.18 V of a solution containing a mixture of VI and VII leads to the complete reduction of both isomers to V: reduction of VI proceeds directly at –0.18 V to yield V which is in equilibrium with Cr^{2+}. The resulting Cr^{2+} catalyzes the isomerization of VII to VI to restore the equilibrium that is perturbed by the electrolytic removal of VI.

We convinced ourselves of the reliability of Scheme III by interrupting controlled-potential oxidations of solutions of V at various stages of the reaction to record polarograms of the

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(13) Weaver, M. J.; Satterberg, T. L. *J. Phys. Chem.* **1977**, *81*, 1772.
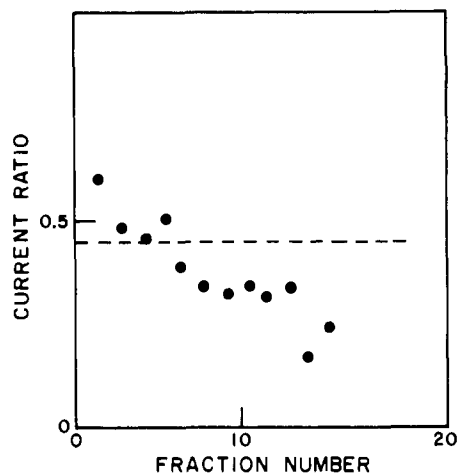
Scheme III
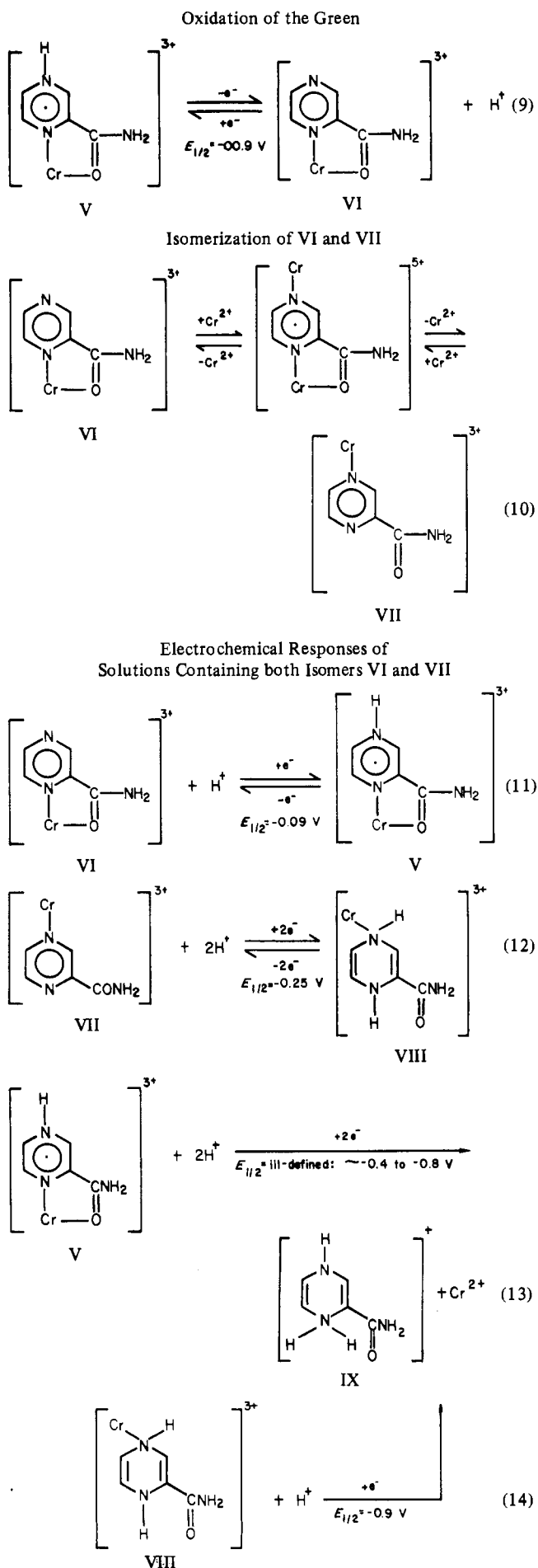
Figure 6. Ratio of limiting currents for the first two waves in curve B, Figure 5, as measured on successive fractions of a solution eluted from a Sephadex SPC 100-20 cation-exchange column that has been loaded with the product of the electrolytic oxidation of the solution used to record curve A, Figure 5. The eluting solution was 0.35 M $NaClO_4$ + 0.01 M $HClO_4$. The dashed line gives this current ratio before the chromatography.

resulting solutions. The four waves that appeared had magnitudes that could be predicted precisely on the basis of reactions 9–14, the total quantity of charge that had gone into the oxidation of each stage, and the equilibrium constant for the isomerization of VI and VII. The latter was taken as unity because the magnitudes of the four polarographic waves in curve B of Figure 5 correspond to the presence of approximately equal quantities of VI and VII in oxidized solutions.

Attempts to separate the two proposed tripositive isomers on a Dowex cation-exchange column were unsuccessful. However, evidence for partial separation on a Sephadex column is shown in Figure 6. The ratio of the limiting currents for the waves at $E_{1/2}$ = −0.09 and −0.25 V is greater for early fractions of the red-violet complex eluted from the column and smaller for later fractions than the corresponding ratio before the chromatography. The indication is that the species responsible for the two polarographic waves are being partially separated on the chromatographic column.

Oxidation of V with Hg(II) occurred more slowly ($t_{1/2} \approx$ 2 min) than the similar oxidation of the pyrazine and pyrazinecarboxylate greens, and the primary products were Cr^{3+} and free pyrazinecarboxamide. This behavior matches that reported by Gould et al.[2] who used pentaamminecobalt(III) complexes as oxidant. They concluded that the oxidation proceeded by dissociation of the green into Cr^{2+} and free ligand followed by oxidation of the Cr^{2+}. Hg(II) appears to employ this pathway for the oxidation of V but not for the other two greens studied.

Discussion

Behavior of Pyrazine Green. Table I contains a collection of formal potentials for the reversible couples encountered in this study. The first set is the result of direct measurements while the second set was calculated from combinations of measured values. All of these potentials are pH dependent, and some are susceptible to possible decomposition of the reactants during the measurements but they represent the only available values.

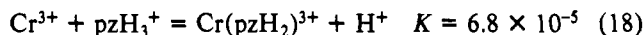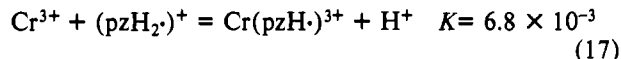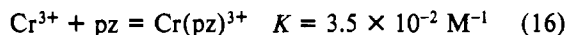In addition to that for reaction 3, Dunne and Hurst[4] also reported the equilibrium constant for reaction 15. When the

$$Cr(pzH\cdot)^{3+} + pz + H^+ = Cr(pz)^{3+} + (pzH_2\cdot)^+ \quad K = 5.2 \quad (15)$$
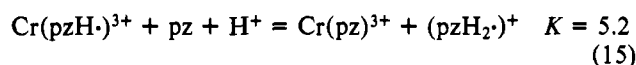
constants for thest two reactions are combined with formal

**Table I.** Formal Potentials for Some of the Half-Reactions Encountered in This Study

half-reaction[a]	$-E^f$, V vs. SSCE[b,c]	ref
A. Measured Values		
(1) $Cr(pz)^{3+} + 2e^- + 2H^+ = Cr(pzH_2)^{3+}$	0.38	d
(2) $pz + 2e^- + 3H^+ = pzH_3^+$	0.30	e, f
(3) $pz + e^- + 2H^+ = (pzH_2\cdot)^+$	0.24	g
(4) $Cr(pzCOO)^{2+} + e^- + H^+ = Cr(pzHCOO\cdot)^{2+}$	0.18	d, h
(5) $pzCOOH + 2e^- + 3H^+ = (pzH_3COOH)^+$	0.23	e
(6) $Cr(pzCONH_2)^{3+} + e^- + H^+ = Cr(pzHCONH_2\cdot)^{3+}$ (chelated isomer)	0.09	d
(7) $Cr(pzCONH_2)^{3+} + 2e^- + 2H^+ = Cr(pzH_2CONH_2)^{3+}$ (nonchelated isomer)	0.25	e
(8) $pzCONH_2 + 2e^- + 3H^+ = (pzH_3CONH_2)^+$	0.28	e
B. Calculated Values		
(9) $Cr(pz)^{3+} + e^- + H^+ = Cr(pzH\cdot)^{3+}$	0.28	d
(10) $Cr(pzH\cdot)^{3+} + 2e^- + 2H^+ = Cr^{2+} + pzH_3^+$	0.44	d
(11) $Cr(pzH\cdot)^{3+} + e^- + H^+ = Cr(pzH_2)^{3+}$	0.48	d

[a] For half-reactions 1, 2, 5, and 8, the proton stoichiometry has been verified from the pH dependence of E^f. For the other cases the proton stoichiometry shown is assumed. [b] Values apply to 1 M $HClO_4$. [c] Based on half-wave potentials of sampled dc polarograms (except for half-reaction 3); the values for the free ligand are ±0.02 V. For the other cases uncertainties up to ±0.05 V may be involved. [d] This work. [e] Reference 9. [f] Reference 8. [g] Reference 8a. [h] Calculated from the value measured at pH 2.

potentials of the $Cr^{3+/2+}$ couple (−0.65 V vs. SCE) and the first three couples listed in Table I, the affinities of Cr^{3+} for pz, pzH_2^+, and pzH_3^+ can be compared (eq 16–18). Unfortunately,

$$Cr^{3+} + pz = Cr(pz)^{3+} \quad K = 3.5 \times 10^{-2} \text{ M}^{-1} \quad (16)$$

$$Cr^{3+} + (pzH_2\cdot)^+ = Cr(pzH\cdot)^{3+} + H^+ \quad K = 6.8 \times 10^{-3} \quad (17)$$

$$Cr^{3+} + pzH_3^+ = Cr(pzH_2)^{3+} + H^+ \quad K = 6.8 \times 10^{-5} \quad (18)$$

fortunately, no pK_a values have been reported for $(pzH_2\cdot)^+$ or pzH_3^+ so that the affinities of Cr^{3+} for the three bases, pz, $pzH\cdot$, and pzH_2 cannot be compared. However, the linear pH dependence of the formal potential for the pz–pzH_3^+ couple[8,9] up to pH 7 requires tha the pK_a of pzH_3^+ be greater than ca. 7.5. This allows a lower limit to be placed on the equilibrium constant for reaction 19. Thus, the much more basic di-

$$Cr^{3+} + pzH_2 = Cr(pzH_2)^{3+} \quad K > 2 \times 10^3 \text{ M}^{-1} \quad (19)$$
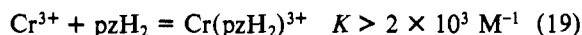
hydropyrazine ligand forms a far more stable complex with Cr(III) than does pyrazine. The same may well be true for the neutral radical, $pzH\cdot$, but data to support quantitative estimates are not available.

The formal potential for the one-electron reduction of pyrazine green can be estimated by combining the equilibrium constant for reactions 17 and 18 with the formal potentials for half-reactions 2 and 3 in Table I

$$Cr(pzH\cdot)^{3+} + e^- + H^+ = Cr(pzH_2)^{3+} \quad E = -0.48 \text{ V} \quad (20)$$
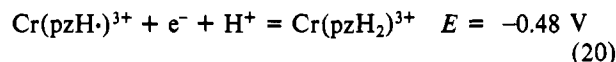
When the reverse of equilibrium 3 is combined with the second half-reaction in Table I, the formal potential for the two-electron reduction of pyrazine green according to reaction 4 can be calculated to be −0.44 V. The relative values of these formal potentials for half-reactions 4 and 20 provide an explanation for the observed behavior of pyrazine green. Thus, the composite polarographic wave in Figure 1, curve B, involves a two-electron rather than a one-electron reduction process because the products of the two-electron process, Cr^{2+} and pzH_3^+, are thermodynamically more stable than the one-electron reduction product, $Cr(pzH_2)^{3+}$. Since half-reactions

4 and 20 both involve the same number of protons per electron, this conclusion should not depend on the pH of the solution in which the polarogram for pyrazine green is recorded.

There is a quantitative flaw in this interpretation because the numerical values of the calculated formal potentials for half-reactions 9 and 10 in Table I predict that the oxidation and reduction waves of pyrazine green should be separated by about 160 mV so that a polarographic wave consisting of two, closely spaced portions is to be expected instead of the observed single, composite wave. However the uncertainties in the numerical values of the equilibrium constants and formal potentials that were utilized in the analysis are certainly great enough to account for this discrepancy. The relative values of the formal potentials for reactions 4 and 20, which account for the magnitudes of the two portions of the composite polarogram of pyrazine green (Figure 1, curve B), are believed to be reliable.

At the point where curve B in Figure 1 crosses the zero-current axis, i.e., at the equilibrium potential assumed by the electrode in solutions of $Cr(pzH\cdot)^{3+}$, the anodic current arising from half-reaction 21 (taken twice) is matched by an equal

$$Cr(pzH\cdot)^{3+} = Cr(pz)^{3+} + H^+ + e^- \qquad (21)$$
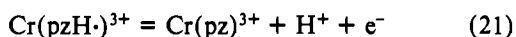
cathodic current provided by half-reaction 4. If the pzH_3^+ and Cr^{2+} produced in half-reaction 4 and the $Cr(pz)^{3+}$ produced in half-reaction 21 react with each other to form $Cr(pzH\cdot)^{3+}$, no net chemical change would result from the simultaneous occurrence of half-reactions 4 and 21. This would account for the observation that stirring solutions of pyrazine green over mercury pool electrodes does not affect their composition.

An alternative conceivable pathway for the electroreduction of pyrazine green is half-reaction 22, for which a formal po-

$$Cr(pzH\cdot)^{3+} + e^- + 2H^+ = Cr^{3+} + pzH_3^+ \qquad (22)$$
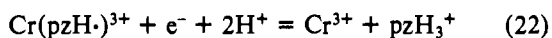
tential of -0.13 V vs. SCE can be calculated. This potential indicates that half-reaction 22 is thermodynamically much more favorable than reaction 4, the half-reaction that actually proceeds. The failure of the electroreduction to follow this lowest energy pathway doubtless reflects the great kinetic stability of the bond between Cr(III) and the nitrogen atom of the ligand in pyrazine green.

According to reaction 4, Cr^{2+} is formed on the cathodic portion of curve B in Figure 1 even though the wave appears at potentials substantially more positive than the standard potential of the $Cr^{3+/2+}$ couple (-0.65 V vs. SCE). This result is a direct consequence of the thermodynamic instability of pyrazine green with respect to dissociation into Cr^{3+} and $(pzH_2\cdot)^+$ (the inverse of reaction 17). This dissociation is blocked by substitutional inertness of Cr(III), but since it is a thermodynamically favored reaction, the reduction of $Cr(pzH\cdot)^{3+}$ to Cr^{2+} can proceed at potentials more positive than those where Cr^{3+} can be reduced to Cr^{2+}.

It is interesting to note the difference in the way that equilibrium 3 affects the course of the anodic and cathodic electrode reactions of pyrazine green. The oxidation of pyrazine green and dihydropyrazine proceed at the same potentials. The only component of equilibrium 3 that is oxidized at an appreciable rate at this potential is $Cr(pzH\cdot)^{3+}$. Since a large fraction of the reactants are present as Cr^{2+} and pz, these must combine with each other to form $Cr(pzH\cdot)^{3+}$ before any oxidation reaction can proceed. This is the reason that the oxidation produces only $Cr(pz)^{3+}$ when it is carried out at potentials where Cr^{2+} is not oxidizable. By contrast, the only component of equilibrium 3 that can be reduced at potentials where pyrazine green reduction commences is pz. Thus, the dissociation of pyrazine green precedes its reduction while the association of Cr^{2+} and pz to form pyrazine green precedes its oxidation.

Electrochemistry of Pyrazinecarboxylic Acid Green (Cr-(pzHCOO·)²⁺). The pair of separated polarographic waves exhibited by $Cr(pzHCOO\cdot)^{2+}$ points to a greater stability with respect to disproportionation for the green formed with this ligand than is true for pyrazine. The formulation of the green as a chelate (Scheme II) was based on the behavior of the oxidized complex on a cation-exchange column as well as its spectrum which is quite close to that of the complex of Cr(III) with pyrazinecarboxylate obtained from the reaction of Cr^{2+} with the pentaammine cobalt(III) complex of this ligand to which the same chelate structure was assigned.[3] This formulation would also account for the greater stability of the green as reflected in the more positive potential at which it is oxidized compared with pyrazine green (presuming, as seems reasonable, that the chelated form of the oxidized chromium-(III) complex, $Cr(pzCOO)^{2+}$ is at least as stable as $Cr(pz)^{3+}$).

The greater stability of $Cr(pzHCOO\cdot)^{2+}$ compared with $Cr(pzH\cdot)^{3+}$ is also the reason that only the former can be generated from its oxidized Cr(III) precursor by a one-electron reduction at the electrode. The potential at which $Cr(pzCOO)^{2+}$ and $Cr(pzHCOO\cdot)^{2+}$ are reversibly interconvertable (-0.18 V; Table I) is sufficiently positive of the potential where the ligand is reduced (-0.23 V[9]) that the two processes can be observed separately.

The fact that both $Cr(pzH\cdot)^{3+}$ and $Cr(pzHCOO\cdot)^{2+}$ exhibit disruptive, two-electron reductions to Cr^{2+} and the corresponding dihydropyrazinium cations rather than one-electron reductions to the Cr(III) complexes of the reduced ligands reflects the high stability of the uncoordinated, protonated, reduced ligands rather than special instabilities built into the two greens.

Electrochemistry of Pyrazinecarboxamide Green (Cr-(pzHCONH₂·)³⁺). This green, consisting of two isomers, exhibits a more complex electrochemical response that can be viewed as the combination of the two contrasting behavioral patterns of the greens formed by pyrazine and pyrazinecarboxylate. One isomer (VI in Scheme III) is believed to have a chelate structure similar to that proposed for the pyrazinecarboxylate green. It shows the same pattern of a separated pair of polarographic waves: one corresponding to the reversible interconversion of the green and its one-electron oxidation product, and the other corresponding to the two-electron dissociative reduction to Cr^{2+} and the dihydropyrazine derivative. The second isomer (VII in Scheme III), thought to contain the chromium(III) center bound only to the heterocyclic nitrogen atom, behaves like pyrazine green with a single, composite polarographic wave. The four reduction waves encountered in oxidized solutions of pyrazinecarboxyamide green are thus identified with the successive reductions of species VI, VII, V, and VIII in Scheme III. Thus, the rather complex behavior exhibited by pyrazinecarboxyamide green can be understood on the basis of the interpretations given to the behavior of the other two greens.

The homogeneous oxidation of pyrazinecarboxamide green by halopentaamminecobalt(III) complexes proceeds by dissociation of the $Cr(pzHCONH_2\cdot)^{3+}$ complex followed by reaction of the resulting Cr^{2+} with $Co(NH_3)_5X^{2+}$ to form halopentaaquachromium(III).[2] By contrast, the corresponding electrooxidation can be carried out so as to form $Cr(pzCONH_2)^{3+}$ exclusively, thus demonstrating that dissociation of $Cr(pzHCONH_2\cdot)^{3+}$ is not a prerequisite for its oxidation. This difference in behavior is probably a reflection of the relatively small rate constant governing the heterogeneous oxidation of Cr^{2+} to Cr^{3+} at mercury electrodes in perchlorate supporting electrolytes.[14] Cyclic voltammetry showed the standard-electrode reaction rate constant for the Cr-

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(14) Weaver, M. J.; Anson, F. C. *J. Electroanal. Chem. Interfacial Chem.* **1975**, *65*, 711.

$(pzHCONH_2 \cdot)^{3+}/Cr(pzCONH_2)^{3+}$ couple to be at least 10^3 times greater than the corresponding constant for the $Cr^{3+/2+}$ couple. This difference, coupled with the small transfer coefficient for the oxidation of Cr^{2+},[14] is large enough to account for the observed oxidation of $Cr(pzHCONH_2 \cdot)^{3+}$ instead of Cr^{2+} despite the difference in formal potentials that produces a large driving force favoring the oxidation of Cr^{2+} at +0.15 V ($E^f(Cr^{3+/2+}) = -0.65$ V; $E^f(Cr(pzHCONH_2 \cdot)^{3+}/Cr-(pzCONH_2)^{3+}) = -0.09$ V). If the electrooxidation were carried out in halide-supporting electrolytes where inner-sphere oxidation of Cr^{2+} can proceed,[5] it seems likely that the reaction might follow a pathway similar to that described by Gould et al.[2]

Effects of Pyrazine Reduction Potentials. The formation constants for greens derived from substituted pyrazines appear to become greater as the reduction potential for the pyrazine becomes more positive. For example, Gould et al. estimated a formation constant for pyrazinecarboxamide (at pH 0) that is about 10^3 times greater than the corresponding constant for pyrazine,[2] and the reduction of the carboxamide occurs at a potential slightly positive of that for pyrazine.[9] Similarly, chloropyrazine is reduced at much more negative potentials than pyrazine,[9] and no intensely green complex forms when Cr^{2+} is mixed with chloropyrazine at pH 2 with millimolar concentrations (although the formation of a chloropyrazine green was reported[2] in 1.2 M $HClO_4$ with chloropyrazine concentrations exceeding 20 M).

Conclusions

The electrochemistry of pyrazine green can be understood in terms of the known homogeneous redox and coordination chemistry it exhibits. With the carboxylate and carboxamide derivatives, chelated greens are apparently formed, and these undergo reversible, one-electron oxidations to the corresponding chromium(III) complexes of the unreduced ligands. When a chelate is not formed, as with pyrazine and one isomer of the carboxamide, the resulting greens undergo irreversible one-electron oxidations to yield complexes that are reduced directly to the corresponding chromium(III)–dihydropyrazine complexes without the formation of a green.

Contribution from the Department of Chemistry,
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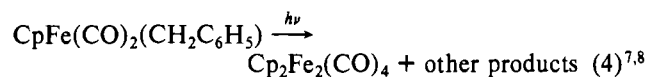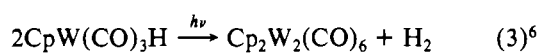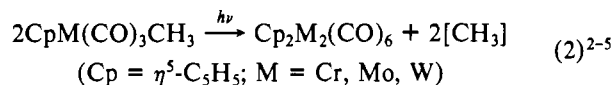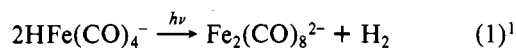# Photochemistry of (η^5-C₅H₅)W(CO)₃CH₃ in Solution. Mechanism of (η^5-C₅H₅)₂W₂(CO)₆ Formation

DAVID R. TYLER

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Irradiation (366 nm) of CpW(CO)₃CH₃ (Cp = η^5-C₅H₅) at room temperature in a variety of solvents produces Cp₂W₂(CO)₆ and methane. In CH₂Cl₂ and CHCl₃ solutions, CpW(CO)₃Cl and CpW(CO)₂Cl₃ are secondary and tertiary photoproducts, respectively. The disappearance quantum yield (366 nm) for CpW(CO)₃CH₃ in CH₂Cl₂ solution is 0.08; this value drops to 0.04 when excess CO is present. Irradiation of CpW(CO)₃CH₃ in the presence of PPh₃, AsPh₃, or CH₃CN gives the substituted products CpW(CO)₂(L)CH₃ (L = PPh₃, AsPh₃, CH₃CN). The quantum yield of disappearance for CpW(CO)₃CH₃ in these photosubstitution reactions is about 0.4. CpW(CO)₃CH₃ reacts photochemically with THF at −78 °C to give CpW(CO)₂(THF)CH₃. Solutions of this product are stable at −78 °C, but the complex decomposes to Cp₂W₂(CO)₆ and CpW(CO)₃CH₃ upon warming to room temperature. Irradiation (366 nm) of CpW(CO)₂(PPh₃)(COCH₃) at room temperature in CH₂Cl₂ or THF solution produces CpW(CO)₃CH₃ (and possibly CpW(CO)₂(PPh₃)CH₃). The disappearance quantum yield of CpW(CO)₂(PPh₃)(COCH₃) in this reaction is 0.10. The primary photoprocess of the CpW(CO)₃CH₃ complex is proposed to be be W–CO bond dissociation, and the following pathway is suggested for the formation of Cp₂W₂(CO)₆: CpW(CO)₃CH₃ $\xrightarrow{h\nu}$ CpW(CO)₂CH₃ + CO; CpW(CO)₂CH₃ + CpW(CO)₃CH₃ → Cp₂W₂(CO)₅ + 2CH₃; Cp₂W₂(CO)₅ + CO → Cp₂W₂(CO)₆. Consistent with this pathway is the observation that the quantum yield of the coupling reaction (0.08) is independent of the light intensity ((2.5–22) × 10⁻⁸ einstein/min). The source of the extra hydrogen for the methyl radical to form methane is proposed to be the solvent because, in benzene-d_6 and chloroform-d, CH₃D is formed.

Introduction

Irradiation of mononuclear metal carbonyl alkyl and hydride complexes often results in cleavage of the metal–alkyl or metal–hydrogen bond and formation of a metal–metal bonded dimer. Equations 1–4 illustrate several reactions of this type.

$$2HFe(CO)_4^- \xrightarrow{h\nu} Fe_2(CO)_8^{2-} + H_2 \qquad (1)^1$$

$$2CpM(CO)_3CH_3 \xrightarrow{h\nu} Cp_2M_2(CO)_6 + 2[CH_3]$$
$$(Cp = \eta^5\text{-}C_5H_5; M = Cr, Mo, W) \qquad (2)^{2-5}$$

$$2CpW(CO)_3H \xrightarrow{h\nu} Cp_2W_2(CO)_6 + H_2 \qquad (3)^6$$

$$CpFe(CO)_2(CH_2C_6H_5) \xrightarrow{h\nu}$$
$$Cp_2Fe_2(CO)_4 + \text{other products} \qquad (4)^{7,8}$$

In general, the mechanisms of these photochemically induced coupling reactions are poorly understood; some mechanistic information is available, however, on the reaction in eq 2.

In the earliest mechanistic study of reaction 2, Rausch and co-workers showed that methane was the major gaseous product formed in the photolysis of CpMo(CO)₃CH₃.[2] By

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