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A Kinetic Study of the Reduction of Bromate Ion by Neptunium(V) in Perchlorate Solution

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The empirical form of the rate law for the reaction 4Np(V) + Br(V) = 4Np(VI) + Br(I) at 25° in perchloric acid–lithium perchlorate solutions is $-d[\mathrm{Br(V)}]/dt = k_0[\mathrm{Br(V)}]^2[\mathrm{H^+}]^{1.51}$. This expression adequately correlates the kinetic data from 10 to 90% reaction over a large range of initial reactant concentrations. At least one induction period is observed. A complex reaction scheme is proposed in which the rate parameter is identified as $[k_a^2[\mathrm{H^+}]^2/4k_{c_0}]/[1 + (k_{c_1}/k_{c_0})[\mathrm{H^+}]]$, where k_a is the rate constant for the reaction between bromate ion and a bromous acid intermediate, and k_{c_0} and k_{c_1} are rate constants of parallel paths for the disproportionation of the same intermediate. Comparisons with other systems in which bromate ion is reduced by weak one-electron reductants are made.

Introduction

The oxidation of neptunium ions by bromate in acid solution is one step in a commonly used purification cycle for neptunium.[1,2] A preliminary study revealed a complicated reaction between Np(IV) and Br(V), with Np(V) apparently present as a reactive intermediate.[1] Our interest in the present system stems from the fact that Np(V) is a weak (standard oxidation potential of the Np(V)–Np(VI) couple = −1.15 V[3]) one-electron reducing agent. Several such species have been reported to exhibit an induction period in their oxidation by bromate, followed by a reaction rate that is second order in bromate and independent of the concentration and identity of the reducing agent.[4] This communication presents the results obtained in a kinetic study of the Np(V)–Br(V) reaction in acid perchlorate solution.

Experimental Section

Reagents. Np(V) stock solutions were prepared and assayed as previously described.[2] These solutions were used within a 24-hr period to minimize potential complications from peroxide production due to the α radiolysis of the water. However, stock solutions that had aged for *ca.* 50 hr gave kinetic results identical with those obtained immediately after preparation. Reagent grade sodium bromate was recrystallized either two or five times; both sources yielded identical results, as did a 2 year old stock solution. The preparation and standardization of hypobromous acid and lithium perchlorate have been described elsewhere.[5] Triply distilled water, once each from acid chromium trioxide and permanganate, was used. No detectable differences were observed when an independent source of triply distilled water, kindly furnished by Dr. J. C. Sullivan of Argonne National Laboratory, was used. G. F. Smith and Mallinckrodt reagent grade perchloric acids gave identical results. The special concern about the purity of the reagents used is due to the unusual kinetic results obtained for this system (*vide infra*).

Procedures. A Zeiss PMQ-H spectrophotometer equipped with a thermostated (± 0.1°), rapid-mixing (mixing time < 1 sec) sample compartment was used to monitor most of the experiments. Production of Np(VI) was monitored in the 2800–3950 Å region, and disappearance of Np(V) was measured at 6200 Å or occasionally at 9805 Å using a Cary Model 14MR recording spectrophotometer. Appropriate small corrections were applied for the absorbance changes due to production of hypobromous acid and consumption of Np(V). The molar absorptivity of Np(VI) was moderately sensitive to the solution composition and temperature.

Results

Stoichiometry. The following evidence is consistent with the stoichiometry

$$4\mathrm{NpO_2}^+ + \mathrm{BrO_3}^- + 5\mathrm{H}^+ = 4\mathrm{NpO_2}^{2+} + \mathrm{HOBr} + 2\mathrm{H_2O} \qquad (1)$$

Direct experiments showed that the rate of oxidation of Np(V) by HOBr is negligible under the conditions used in all the kinetic studies. Infinite-absorbance values in experiments monitored at 3950 Å (an absorption maximum for $\mathrm{Br_2}$[6]) rule out $\mathrm{Br_2}$ as the reduction product. $\mathrm{Br^-}$ cannot be a stable product due to its rapid oxidation by $\mathrm{BrO_3}^-$ in acid solution.[7] Indeed, it will be argued later that $\mathrm{Br^-}$ is never formed during the Br(V)–Np(V) reaction.

Kinetic Studies. Our limited supply of neptunium and the form of the rate law dictated that at least a small stoichiometric excess of $\mathrm{BrO_3}^-$ be employed. There is an induction period after initiation of the reaction during which no detectable consumption of reactants occurs. This period is poorly reproducible (±60% in the worst cases, usually ±20%) but does appear to be independent of the order of mixing and whether or not continuous stirring is applied. The duration decreased as $[\mathrm{BrO_3}^-]$, $[\mathrm{H^+}]$, and temperature increased.[8] The initial presence of the product HOBr (in amounts comparable to that produced during the reaction) nearly eliminated the induction period, but the initial presence of $\mathrm{NpO_2}^{2+}$ was without effect. After this period, the rate of reaction increased continuously until *ca.* 10% reaction. From this stage to from 2 to 4 half-lives the kinetic data were accurately correlated by the integrated form of the empirical rate expression

$$-d[\mathrm{BrO_3}^-]/dt = k[\mathrm{BrO_3}^-]^2 \qquad (2)$$

Values of the rate parameter k were determined from a least-squares analysis of 18–36 kinetic points for each experiment. The standard deviation in k was ≤0.9% (the

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[8] The following data give an indication of the length of the induction period. At 10.0° and 2.00 M $\mathrm{HClO_4}$, with $[\mathrm{Br(V)}]_0 = 1.08 \times 10^{-2}$ M and $[\mathrm{Np(V)}]_0 = 1.32 \times 10^{-3}$ M, the induction period was 23 ± 3 sec. At 25.0° and 2.00 M $\mathrm{HClO_4}$, with $[\mathrm{Br(V)}]_0 = 4.30 \times 10^{-3}$ M and $[\mathrm{Np(V)}]_0 = 1.32 \times 10^{-3}$ M, the duration was 7 ± 1 sec. Our interpretation (*vide infra*) requires the induction period to be dependent not only on the initial concentrations of $\mathrm{BrO_3}^-$, $\mathrm{NpO_2}^+$, and $\mathrm{H^+}$ but also on the presence of a trace impurity. The latter factor has frustrated our attempts to design experiments that will provide a quantitative description of the induction period.

Table I. Effect of Reactant Concentrations on k^a

$10^3[\text{Np(V)}]_0$, M	$10^3[\text{Br(V)}]_0$, M	k, M^{-1} sec^{-1}	$10^3[\text{Np(V)}]_0$, M	$10^3[\text{Br(V)}]_0$, M	k, M^{-1} sec^{-1}
16.2	27.0	0.152 ± 0.001	1.33	8.49	0.185 ± 0.002^b
16.2	16.4	0.158 ± 0.003	0.57	4.36	0.199 ± 0.004
16.2	11.0	0.173 ± 0.006	1.35	4.30	0.209 ± 0.006
1.35	8.60	0.187 ± 0.003	2.10	3.23	0.174 ± 0.001
4.16	8.53	0.175 ± 0.002	1.35	2.15	0.180 ± 0.005
					⟨k⟩ 0.179 ± 0.013

^{a} At 25.0°, I = 2.0 M, and $[\text{HClO}_4]$ = 1.99 M. Uncertainties are average deviations from replicate experiments. ^{b} Allyl alcohol added. $[\text{CH}_2{=}\text{CHCH}_2\text{OH}]_0 = 3.18 \times 10^{-4}$ M.

Table II. $[\text{H}^+]$ and Temperature Dependencies of k^a

	10^2k, M^{-1} sec^{-1}			
$[\text{H}^+]$, M	32.0°	25.0°	17.0°	10.0°
1.99	30.4 ± 0.2	17.9 ± 1.3^b	7.28 ± 0.07	3.45 ± 0.06
1.50	21.6 ± 0.1	11.7 ± 0.1	4.69 ± 0.02	2.26 ± 0.04
1.01	11.8 ± 0.4	6.32 ± 0.02	2.62 ± 0.02	1.22 ± 0.03
0.760	7.74 ± 0.06	4.12 ± 0.06	1.75 ± 0.01	0.777 ± 0.013
0.520	4.56 ± 0.01	2.43 ± 0.03	0.998 ± 0.002	0.452 ± 0.002
0.370	2.75 ± 0.07	1.42 ± 0.01	0.597 ± 0.002	0.264 ± 0.003
0.225	1.25 ± 0.02	0.632 ± 0.005	0.275 ± 0.001	0.118 ± 0.001
0.151	0.632 ± 0.004			

^{a} I = 2.0 M (maintained with LiClO_4). Uncertainties are average deviations from replicate experiments. $[\text{Np(V)}]_0 = (1.20\text{–}1.40) \times 10^{-3}$ M $[\text{Br(V)}]_0 = 5.40 \times 10^{-3}\text{–}6.35 \times 10^{-2}$ M. ^{b} Average value from Table I.

integration constant was left as a second parameter in the treatment to allow for error in the assignment of the conclusion of the induction period). The results presented in Table I indicate that the rate law 2 is valid over an extensive range of initial reactant concentrations and their ratio. Experiments conducted in the presence of allyl alcohol (which rapidly scavenges HOBr)[5,7b,9] show that the HOBr product does not affect the kinetic results. Essentially identical values of k were obtained by monitoring either the appearance of Np(VI) or the disappearance of Np(V). The following result indicates that the Np(VI) product does not influence the reaction rate. At 25.0° and an ionic strength of 2.0 M, with initial concentrations of $[\text{H}^+]$ = 1.24 M, [Np(V)] = 3.97×10^{-4} M, [Br(V)] = 2.81×10^{-3} M, and [Np(VI)] = 5.58×10^{-3} M, the rate parameter k was 0.0890 M^{-1} sec^{-1}. Under the same conditions, but without the addition of Np(VI), k was 0.0869 M^{-1} sec^{-1}. Finally, the reaction rate was not affected by stirring.

Table II contains a summary of the variation in k as a function of hydrogen ion concentration and temperature. An empirical formulation that summarizes the variation of k with change in hydrogen ion concentration is

$$k = k_0[\text{H}^+]^n \tag{3}$$

Values determined for n from a least-squares adjustment of the data are 1.50 ± 0.02, 1.51 ± 0.01, 1.49 ± 0.01, and 1.54 ± 0.01 at 32.0, 25.0, 17.0, and 10.0°, respectively. The usual power series development

$$k = a + b[\text{H}^+] + c[\text{H}^+]^2 \tag{4}$$

does not correlate the data very well, especially at the lower $[\text{H}^+]$ used, and yields statistically valid but negative values of a. Not surprisingly, the expression

$$k = a[\text{H}^+] + b[\text{H}^+]^2 \tag{5}$$

correlates the data quite poorly. However, the two-parameter expression

$$k = \alpha[\text{H}^+]^2/(1 + \beta[\text{H}^+]) \tag{6}$$

fits the data much better. The results of the least-squares adjustment of the data in terms of eq 6 are for α $(2.72 \pm 0.17) \times 10^{-1}$, $(1.20 \pm 0.05) \times 10^{-1}$, $(4.75 \pm 0.32) \times 10^{-2}$, and $(2.10 \pm 0.12) \times 10^{-2}$, and for β 1.26 ± 0.12, $(8.65 \pm 0.60) \times 10^{-1}$, $(8.11 \pm 0.96) \times 10^{-1}$, and $(7.12 \pm 0.74) \times 10^{-1}$ at 32.0, 25.0, 17.0, and 10.0°, respectively. The apparent activation energy calculated from the temperature variation of the parameter α is 20.0 ± 0.5 kcal/mol. The β parameter exhibits only a small variation with temperature.

Discussion

We are unable to propose a simple mechanism that is consistent with the data presented. It is extremely unlikely that a rate-determining, irreversible step involving two bromate ions and one or two hydrogen ions is operative. Further, if such a path were reversible, then some dependence on the reductant concentration would be necessary. Any scheme that invokes disproportionation of Np(V) to produce a more reactive Np(IV) intermediate can be rejected immediately since direct experiments indicate that the oxidation of Np(IV) by Br(V) is very slow under the conditions employed in this study.

A complex reaction scheme has been proposed for the reduction of bromate ion by weak one-electron reducing agents in acid solution,[10] *i.e.*

$$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightleftarrows 2\text{BrO}_2 + \text{H}_2\text{O} \tag{a}$$

$$\text{BrO}_2 + \text{R} + \text{H}^+ \rightleftarrows \text{HBrO}_2 + \text{Ox} \tag{b}$$

$$2\text{HBrO}_2 \rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+ \tag{c}$$

R is the reducing agent and Ox is its oxidized form; the charges of these species have been omitted. Some salient features of this scheme are as follows. (1) The direct reaction of R and BrO_3^- is very slow and does not contribute to the reaction rate. (2) Autocatalysis is accomplished by steps a and b. (3) The autocatalytic production of bromous acid is limited by the disproportionation reaction c, which is also responsible for the production of the hypobromous acid product. (4) Bromine dioxide is the species that oxidizes R.

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(9) R. C. Thompson, *Inorg. Chem.*, **10**, 1892 (1971).

(10) R. M. Noyes, R. J. Field, and R. C. Thompson, *J. Amer. Chem. Soc.*, **93**, 7315 (1971).

Under the restraints that the reverse of steps a and b are negligible and that the steady-state approximation for the BrO_2 and $HBrO_2$ intermediates is valid, the kinetic expression 7 obtains.

$$-d[BrO_3^-]/dt = [k_a^2/4k_c][BrO_3^-]^2[H^+]^2 \qquad (7)$$

A direct implication is that at a given temperature and hydrogen ion concentration, all reducing agents subject to the considerable restraints outlined above should yield identical second-order rate parameters. This feature has in fact been observed with Np(V) and large excesses of Ce(III) or Mn(II) in 3 *M* sulfuric acid.[4] Unfortunately, this result represents the major quantitative test of scheme (a)-(c). A large amount of supporting evidence has been cited, but it is mostly qualitative.[10] We have expended considerable effort in attempting to determine the rate expression for the Ce(III)-Br(V) system with Br(V) in excess.[11] Under these conditions the oxidation of Br(IV) by Ce(IV) and the reverse of steps a and b may well become important. The kinetic predictions of the scheme then become complicated but solvable. To date we have been unsuccessful. The major problem seems to be the attainment of the steady state.[12] Consistent with this conclusion is the observation that the reaction rate increases until *ca.* 30-35% reaction.

The Np(V)-Br(V) system is ideal in some respects. The reaction can be studied in perchloric acid solution, a more favorable medium than sulfuric acid for investigating the hydrogen ion dependence. Also, the data in Table I support the earlier conclusion that the rate expression 2 is adequate over a wide range of reactant concentrations.[4] However, the "simplicity" of the system prevents much additional testing of scheme (a)-(c).

The initial induction period has been attributed to scavenging of the bromous acid intermediate by trace amounts of bromide ion inadvertently present.[10,13] Considerable data amply support a very rapid reaction between bromous acid and bromide ion to produce hypobromous acid. The observation that hypobromous acid markedly reduces the duration of the induction period in the present system is consistent with this suggestion owing to the rapid and favorable equilibrium[14]

$$H^+ + Br^- + HOBr \rightleftarrows Br_2 + H_2O \qquad (8)$$

The source of the bromous acid may be a direct, albeit slow, reaction of Np(V) and Br(V). Whatever the origin, the induction period is not unique to the Np(V), Ce(III), and Mn(II) systems. It is also observed with the reductants chlorine dioxide, nitroferroin, and tris(2,2′-bipyridyl)ruthenium(II).[15] All six of these species are probably one-electron reducing agents with standard oxidation potentials $\leqslant -1.15$ V.[3,16] It is interesting that V(IV) (standard oxidation potential of the V(IV)-V(V) couple = −1.0 V) reacts directly with Br(V) and exhibits no induction period.[9]

The kinetic behavior after the initial induction period until *ca.* 10% reaction may amount to another induction period during which attainment of the steady state is achieved. As mentioned earlier, this period is considerably lengthened in the Ce(III)-Br(V) system when excess Br(V) is present.

The failure of eq 4 and 5 adequately to correlate the acid dependence is suggestive of a mechanism more complicated than parallel paths involving different numbers of hydrogen ions. Our interpretation requires that the second-order rate parameter k equals $(k_a^2/4k_c)f(H^+)$. One reasonable model would predict a first-order hydrogen ion dependence for reaction a. Hydrogen ion dependencies of 1 have been reported for the reduction of bromate ion by hydrazoic acid[5] and hydrogen peroxide[17] and of 2 for the reduction by bromide ion[7] and the oxygen-exchange rate of bromate ion.[18] Turney has discussed the possible role of BrO_2^+ in this context.[19] In the present system, a first-order hydrogen ion dependence in step a accounts for the $[H^+]^2$ term in the numerator of eq 6. If the disproportionation reaction c exhibits zero- and first-order hydrogen ion paths over the acid range utilized in this work, then the interpretation is harmonious with eq 6. Data are available on the disproportionation of bromous acid, but at much lower acidities. In the pH range 6.3-8.6, Massagli, Indelli, and Pergola[20] reported a rate law equivalent to $k'[HBrO_2]^2$ for the reaction

$$2Br(III) \rightarrow Br(V) + Br(I) \qquad (9)$$

However, they also suggested complicating reactions arising from the reaction of hypobromous acid and bromous acid at lower pH values down to 3.6. This latter reaction is also possible in our system, but the observation that scavenging hypobromous acid yields kinetic data identical with those obtained when this product is allowed to accumulate renders its importance unlikely, as does the lack of appreciable Br_2 product. We are still left with the problem that there is no precedent for the first-order hydrogen ion dependent term our model requires. Experimentally, a direct test of this prediction for $[H^+] = 0.10\text{-}2.0\,M$ would be extremely difficult even with stopped-flow techniques.[20]

The α parameter of eq 6 is identified as $k_a^2/4k_{c0}$, where k_{c0} is the rate constant for the hydrogen ion independent path of step c, by this analysis. Consequently, the apparent activation energy of α is $2E_a - E_{c0}$. Similarly, the β parameter is identified as k_{c1}/k_{c0}, where k_{c1} is the rate constant associated with the hydrogen ion dependent path for the disproportionation of bromous acid. The lack of a significant temperature dependence of β would be expected if the activation energies for the parallel paths (E_{c0} and E_{c1}) are similar, since the apparent activation energy would equal $E_{c1} - E_{c0}$.

The ionic strength dependence of the rate parameter k becomes marked above $I = 1.0\,M$. The major portion of this effect probably arises in step a. (See Table III.)

It should be noted that steps a, b, and c of the reaction scheme all involve bromous acid, but the direct reaction of this reactive intermediate and weak one-electron reducing agents is apparently unimportant. Even in the V(IV)-Br(V) system, where a direct reaction between the reactants is

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(11) This reaction was studied in sulfuric acid; it does not occur in perchloric acid. Some features of the kinetic behavior have been reported: G. J. Kasperek and T. C. Bruice, *Inorg. Chem.*, 10, 382 (1971); V. A. Vavilin and A. M. Zhabotinskii, *Kinet. Katal.*, 10, 83 (1969).

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Table III. Effect of Ionic Strength on k^a

I, M	10^3k, M^{-1} sec^{-1}	I, M	10^3k, M^{-1} sec^{-1}
0.22	4.79 ± 0.03	2.02	6.11 ± 0.05
0.47	4.08 ± 0.04	2.52	8.17 ± 0.06
1.02	4.28 ± 0.01	3.23	12.6 ± 0.2

^{a} At 25.0°, $[HClO_4] = 0.220\ M$, $[Np(V)]_0 = 1.40 \times 10^{-3}\ M$, and $[Br(V)]_0 = 2.15 \times 10^{-2}\ M$. Ionic strength maintained with $LiClO_4$. Uncertainties are average deviations from replicate experiments.

observed, competition between bromous acid disproportionation and its reduction by V(IV) has been suggested.[9] With the potentially multiequivalent reducing agents HN_3,[5] H_2O_2,[17] and Br^-,[7] however, the sole fate of the bromous acid appears to be reduction to hypobromous acid.

Clearly, the demonstration of the validity of the full reaction scheme (a)-(c) proposed for these intriguing systems will require considerable additional investigation. The present study, because of its apparent simplicity, will hopefully provide a foundation on which further results can be added.

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Electrochemical Behavior of Copper, Nickel, Cobalt, and Metal-Free Hemiporphyrazines in a 50% v/v Dimethyl Sulfoxide-Benzene Mixture

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The electrochemical behavior of the copper(II), nickel(II), and cobalt(II) complexes of hemiporphyrazine (hpM) and of metal-free hemiporphyrazine (hpH_2) has been examined by voltammetry at the dme and rpe, by cyclic voltammetry, and by coulometry. For hpCo and hpNi, these studies established that the polarographic reduction steps of these two hemiporphyrazines involve 1:1:2:1 electrons and the oxidation step involves one electron. In the case of hpCu and hpH_2, the reduction steps involve 1:1:3 and 1:1:2:1 electrons, respectively. No oxidation step was observed for the latter two compounds. The electrochemical studies supported by polarography in the presence of the protic source benzoic acid indicate the hemiporphyrazines hpNi, hpCo, and hpH_2 undergo reductions involving only molecular orbitals of primarily ligand character. Importantly, in the case of hpCu, the first reduction step can be designated as involving a molecular orbital of primarily metal character with the remaining steps involving orbitals of primarily ligand character.

Introduction

Phthalocyanine with four nitrogens bridging four isoindole rings is an attractive and easily obtainable model compound for the porphyrin skeleton. Complexes of phthalocyanine and phthalocyanine itself, therefore, have received a great deal of attention. Of special interest is the recent report of the preparation of a compound in which a trans pair of isoindoles in the phthalocyanine molecule is replaced by two pyridines.[1-5] The aromaticity of the restricted coordination environment of the metal complexes of this macrocycle, hemiporphyrazine,[5] has been shown to be considerably less than that of the complexes of phthalocyanine.[6,7] In view of the interesting electrochemical data in the literature on metallophthalocyanines and metalloporphyrins[8] and the lack of any such data on metallocomplexes of this less aromatic macrocycle, we have examined the electrochemical behavior of the copper(II), cobalt(II), and nickel(II) complexes of hemiporphyrazine (Figure 1) and of the metal-free species in 50:50 (by volume) dimethyl sulfoxide-benzene.

Experimental Section

Materials. Dimethyl sulfoxide (DMSO) from Crown Zellerbach was distilled two times from calcium hydride under reduced pressure (*ca.* 1 mm, 35°). The middle 80% of the distillate was collected each time. The final product was stored under dry nitrogen, with no noticeable change in composition over a period of several months. Reagent grade benzene was refluxed over concentrated sulfuric acid for 3-4 hr, decanted, and distilled. The initial and final 10% portions of the distillate were discarded.

The purified DMSO and benzene were examined by gas chromatography with a Chromosorb 102 (60-80 mesh) column. The water content of the purified DMSO was found to be $10^{-2}\ M$. The detection limit was $10^{-3}\ M$. The peak heights of dimethyl sulfide in the gas chromatograms were usually about that of water. Because of the possibility of dimethyl sulfide resulting from decomposition of DMSO at the operating temperatures of the gas chromatograph, no attempt was made to determine the quantity of dimethyl sulfide. Instead, small amounts of dimethyl sulfide were added to the solutions used in the voltammetric studies, and no change in the electrochemical results was noted. Purified benzene contained no detectable impurities.

Tetraethylammonium perchlorate (Et_4NClO_4), Eastman Organic Chemicals, was recrystallized one or two times from water. The purified salt was dried *in vacuo* at *ca.* 70° and stored over Drierite. Maleimide from Aldrich Chemical Co. was sublimed before use. Reagent grade benzoic acid (Merck) was used without further purification. Solid tetramethylammonium hydroxide was obtained by heating a 10% solution of the hydroxide from Eastman Organic Chemicals to dryness *in vacuo* with an infrared lamp. The white, hygroscopic crystals were stored over Drierite.

Preparation of Compounds. Metal-Free Hemiporphyrazine, hpH_2. The method reported by Esposito, Sutton, and Kenney was followed.[6]

When 0.2 mol of phthalonitrile and 0.2 mol of 2,6-diaminopyridine were combined, the yield of purified product was 40%. The dried product melted at 340-342° (lit.[1] mp 344°). *Anal.* Calcd for hpH_2: C, 70.9; H, 3.67; N, 25.4. Found: C, 71.1; H, 3.69; N, 25.6.

Cobalt, Nickel, and Copper Hemiporphyrazines, hpCo, hpNi, and hpCu. Procedures for the preparation of hpCu,[1] hpNi,[1] and hpCo[5] have been described previously. In this study, hpCo was

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