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Contribution from the Department of Chemistry,
University of Victoria, Victoria, B.C., Canada V8W 2Y2

Kinetics and Mechanisms of the Reactions of a Nickel(IV) Complex with Iron(II), Vanadium(IV), and Nickel(II) Cyclam Ions in Aqueous Perchlorate Media

D. H. MACARTNEY[†] and A. MCAULEY*

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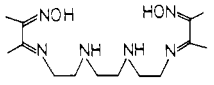
The kinetics of the reduction of a nickel(IV) oxime complex, NiL^{2+}, by Fe^{2+}, VO^{2+}, and $Ni(cyclam)^{2+}$ have been investigated in aqueous perchlorate media. At 25 °C in 1.00 M $HClO_4$ the following second-order rate constants were found: Fe^{2+}, $k = 142\ M^{-1}\ s^{-1}$; VO^{2+}, $k = 0.933\ M^{-1}\ s^{-1}$; $Ni(cyclam)^{2+}$, $k = 11.4\ M^{-1}\ s^{-1}$. Inverse hydrogen ion concentration rate dependences in the Fe^{2+} and VO^{2+} reactions and a $[SO_4^{2-}]$ dependence in the Fe^{2+} oxidation were also observed. The application of the Marcus theory relationship to the experimental parameters leads to a self-exchange activation energy of 8.5 kcal mol^{-1} ($6 \times 10^4\ M^{-1}\ s^{-1}$) for the $Ni^{IV}L^{2+}/Ni^{III}L^{+}$ reaction. The electron-exchange rates of Ni(III)/Ni(IV) and Co(II)/Co(III) reactions are compared and discussed in terms of the spin configurations and metal–nitrogen bond lengths in the reduced and oxidized species.

Introduction

Metal complexes containing nickel in the trivalent and tetravalent states have recently been the subject of considerable interest and study. Significant progress has been made in the understanding of nickel(III) species,[1,2] with numerous investigations on macrocyclic complexes. There are fewer reported nickel(IV) complexes.[2] Stable species containing dioxime ligands, however, have been prepared and studied.[3-9]

The hexadentate ligand 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime (**1**) (H_2L) forms pseudooctahedral NiN_6 complexes with nickel(II), -(III), and -(IV). The nickel(IV) complex, NiL^{2+} (**2**), forms with the loss of a proton from each oxygen.[3] The negative charge on the oximate (=N—O⁻) group stabilizes the higher oxidation level by means of partial neutralization of the metal charge through inductive transmission and σ-donation.[3] It has been demonstrated[4] that one oxime group is required for each level that the oxidation state of nickel is raised above +2.



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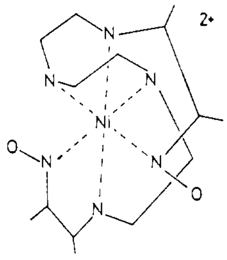

(2)

In aqueous solution NiL^{2+} behaves as a moderately strong oxidizing agent. Electrochemical studies[7] on NiL^{2+} complexes reveal pH-dependent redox equilibria.

Below pH 5, a single two-electron process is observed:

$$NiL^{2+} + 2e^- + 2H^+ \rightleftharpoons Ni(H_2L)^{2+} \qquad (1)$$

with $E°(1) = 0.94$ V (vs. NHE). Above pH 5, the couple is replaced by two separate one-electron reductions. The Ni(IV)/Ni(III) step

$$NiL^{2+} + e^- \rightleftharpoons NiL^+ \qquad (2)$$

is independent of $[H^+]$, whereas the reduction of nickel(III)

$$NiL^+ + e^- + 2H^+ \rightleftharpoons Ni(H_2L)^{2+} \qquad (3)$$

$$NiL^+ + e^- + H^+ \rightleftharpoons Ni(HL)^+ \qquad (4)$$

$$NiL^+ + e^- \rightleftharpoons NiL \qquad (5)$$

is pH dependent, arising from the proton equilibria ($pK_1 = 5.90$, $pK_2 = 7.80$).[3] The reduction potentials $E°(2) = 0.66$ V, $E°(3) = 1.25$ V, $E°(4) = 0.89$ V, and $E°(5) = 0.39$ V were obtained for the one-electron processes.

In acidic aqueous solution NiL^{2+} has been observed to oxidize rapidly a number of reducing agents including Fe^{2+}, $Fe(CN)_6^{4-}$, and $S_2O_3^{2-}$. The only previous kinetic study of the reduction of NiL^{2+} is the report by Lappin[8] of the oxidation of ascorbic acid. Two reaction pathways were observed, corresponding to NiL^{2+} and an "outside protonated" $Ni(HL)^{3+}$ species, with the latter more reactive.

In order to obtain further information on the redox chemistry of this nickel(IV) complex, a study was undertaken of the kinetics and mechanisms of the reduction of NiL^{2+} by a number of metal ion complexes. The reductants employed were the Fe^{2+} and VO^{2+} aquo ions and $Ni(cyclam)^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).

Kinetic measurements were made in 1.00 M $HClO_4$ at several temperatures in order to derive NiL^{2+}/NiL^+ electron-exchange parameters with use of the Marcus theory[10] cross correlations. In addition, rate constants were measured at lower $[H^+]$ in an attempt to determine whether pH rate dependences existed and which reactant species were responsible.

Experimental Section

Reagents. The nickel(II) oxime, $Ni(H_2L)(ClO_4)_2$, was prepared by the addition of the ligand H_2L (H_2L = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) (**1**) to a methanol solution of nickel(II) perchlorate, with subsequent recrystallization from water.[3] Analysis of the product, performed by the Canadian Microanalytical Service, was satisfactory. Anal. Calcd: C, 29.49;

[†] Present address: Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.

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H, 4.91; N, 14.70. Found: C, 29.71; H, 5.02; N, 14.75.

The nickel(II) oxime was oxidized to the nickel(IV) complex, $NiL(ClO_4)_2$, by using concentrated nitric acid.[3] Dark violet crystals were filtered off and washed with ethanol and ether. Anal. Calcd: C, 29.60; H, 4.62; N, 14.80. Found: C, 29.25; H, 4.67; N, 15.04. Solutions of the nickel(IV) species were standardized spectrophotometrically at 500 nm (ϵ = 5960 M^{-1} cm^{-1}).[3]

Iron(II) perchlorate was prepared by the oxidation of powdered iron metal (Fisher) in perchloric acid. The iron(II) concentration was determined from titrations against standard $KMnO_4$. The acidity of the stock solution was measured by titration against NaOH with methyl orange as indicator. Stock solutions of vanadium(IV) perchlorate were prepared by the addition of a stoichiometric amount of barium perchlorate to a solution of vanadyl sulfate (Fisher) in perchloric acid, followed by the removal of the precipitated barium sulfate by decantation and filtration. The solutions were analyzed for VO^{2+} by titration against ammonium ceric nitrate in acetic acid using a ferroin indicator.[11]

Nickel(II) cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) was prepared by the addition of cyclam (Strem) to nickel perchlorate in methanol. Anal. Calcd for $Ni(cyclam)(ClO_4)_2$: C, 26.23; H, 5.28; N, 12.24. Found: C, 26.23; H, 5.53; N, 12.13.

The hydrogen ion concentration of the reaction mixtures was controlled with use of acetate buffer or appropriate amounts of $HClO_4$, while the ionic strength was maintained with $NaClO_4$.

Kinetic Studies. The kinetic measurements were made with a stopped-flow apparatus described previously.[12] Thermostating was maintained to within ±0.05 °C over the temperature range (11.6–34.6 °C) employed. The reactions were followed by monitoring the disappearance of the nickel(IV) species at 500 nm. All measurements were made under pseudo-first-order conditions of excess reductant concentrations. Plots of ln $(A_t - A_\infty)$ against time, derived from absorbance data collected by a PCM-12 minicomputer, were linear for 3 half-lives or more.

Spectroscopic Studies. UV-visible spectra were recorded on a Beckman DU-8 spectrophotometer. Electron spin resonance spectra were measured at 77 K with a Varian E6 spectrometer, with diphenylpicrylhydrazyl (DPPH) (g = 2.0037) as an internal reference standard.

Results

The stoichiometries of the overall reactions of $Ni^{IV}L^{2+}$ with the reductants used in this study were determined by spectrophotometric titrations monitored at 500 nm. The numbers of moles oxidized per mole of $Ni^{IV}L^{2+}$ reduced were as follows: Fe^{2+}, 2.06 ± 0.08; VO^{2+}, 1.97 ± 0.05; $Ni(cyclam)^{2+}$, 1.98 ± 0.03. This is consistent with the overall reaction for the oxidation of Fe^{2+}, for example

$$Ni^{IV}L^{2+} + 2Fe(H_2O)_6^{2+} + 2H^+ \rightarrow 2Fe(H_2O)_6^{3+} + Ni^{II}(H_2L)^{2+} \quad (6)$$

A similar result has been reported previously for the reduction of NiL^{2+} and other Ni(IV) oxime complexes by the iron(II) ion.[3]

A first-order dependence of the observed rate constant on excess reductant concentration was found for each of the reducing agents:

$$-d[Ni(IV)]/dt = k_0[Ni(IV)][reductant] \quad (7)$$

With solutions of (2–5) × 10^{-5} M Ni(IV), at pH 4.50, k_0 = 3408 ± 28 M^{-1} s^{-1} over the concentration range [Fe(II)] = (1.90–9.50) × 10^{-4} M; at $[H^+]$ = 1.00 M, for the vanadium(IV) reaction ([V(IV)] = (3.5–63) × 10^{-4} M) k_0 = 0.95 ± 0.02 M^{-1} s^{-1}, for the nickel(II) cyclam reduction ($[Ni^{II}L]$ = (2.3–18.3) × 10^{-4} M), k_0 = 11.3 ± 0.2 M^{-1} s^{-1}.

The rate constants were determined for each of the reductants in 1.00 M $HClO_4$ at several temperatures. These values, together with the corresponding activation parameters, are listed in Table I. The parameters obtained under these conditions were used in the formulation of a Marcus theory[10] correlation. In addition, kinetic measurements were made at lower acidities at 25 °C to investigate possible hydrogen ion rate dependences.

Table I. Rate and Activation Parameters for the Reduction of $Ni^{IV}L^{2+}$ by Various Reductants in 1.00 M $HClO_4$

reductant	T^a	k^b	$\Delta H^{\ddagger\, c}$	$\Delta S^{\ddagger\, d}$
Fe^{2+}	11.6	94	4.3 ± 0.3	−35 ± 4
	16.2	114		
	19.9	125		
	25.0	142		
	29.4	155		
	34.6	186		
VO^{2+}	12.1	0.468	8.7 ± 0.3	−30 ± 4
	16.2	0.585		
	20.7	0.702		
	25.0	0.933		
	29.9	1.22		
	34.4	1.52		
$Ni(cyclam)^{2+}$	11.8	7.26	5.4 ± 0.3	−35 ± 4
	16.2	8.43		
	20.3	9.60		
	25.0	11.4		
	29.6	13.7		

[a] °C. [b] M^{-1} s^{-1}. [c] kcal mol^{-1}. [d] cal deg^{-1} mol^{-1}.

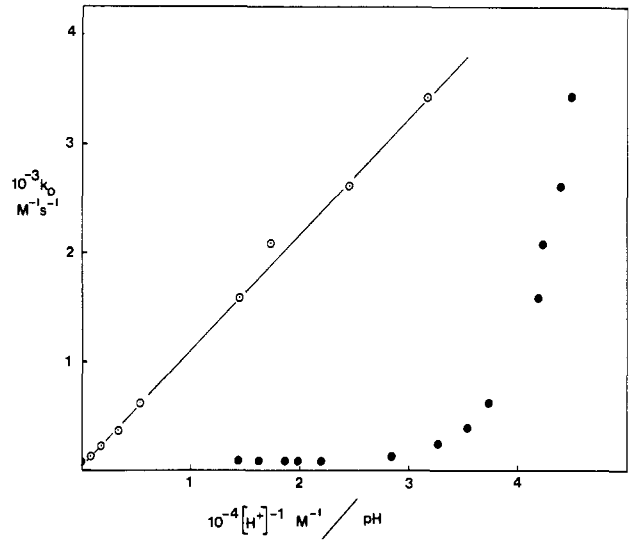

Figure 1. Plot of k_0 against $[H^+]^{-1}$ (⊙) and pH (●) for the reduction of NiL^{2+} by Fe^{2+} at 25 °C (I = 0.1 M ($NaClO_4$)).

Reduction by Fe^{2+}. In the acidity range $[H^+]$ = 0.20–1.00 M at an ionic strength of 1.00 M ($NaClO_4$) no hydrogen ion dependence of the rate constant was observed. Above pH 2, however, the rate constant k_0 increased with increasing pH (Figure 1). The oxime protons on NiL^{2+} have a pK_a < 1[3] so that the acid dependence is likely related to the hydrolysis of the iron(II) ion (pK_h = 8.1).[13] The values measured between pH 2 and 5 (Table II) are consistent with a mechanism of the form

$$Fe(H_2O)_6^{2+} \overset{K_h}{\rightleftharpoons} Fe(H_2O)_5OH^+ + H^+ \quad (8)$$

$$Fe^{2+} + NiL^{2+} \xrightarrow{k_9} Fe^{3+} + NiL^+ \quad (9)$$

$$FeOH^+ + NiL^{2+} \xrightarrow{k_{10}} FeOH^{2+} + NiL^+ \quad (10)$$

leading to the expression

$$k_0 = k_9 + k_{10}K_h/[H^+] \quad (11)$$

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Table II. Hydrogen Ion Dependence of the Rate Constants for the Reduction of $\mathrm{Ni^{IV}L^{2+}}$ by $\mathrm{Fe^{2+}}$, $\mathrm{VO^{2+}}$, and $\mathrm{Ni(cyclam)^{2+}}$ at 25 °C

pH	$\mathrm{Fe^{2+}}$ k, $\mathrm{M^{-1}\ s^{-1}}$ [a]	pH	$\mathrm{Fe^{2+}}$ k, $\mathrm{M^{-1}\ s^{-1}}$ [a]
1.45	77	3.72	625
1.64	76	4.16	1580
1.87	76	4.24	2090
1.99	81	4.39	2610
2.20	82	4.50	3420
2.85	120	4.90	5300
3.27	238	5.00	5700
3.54	385	5.10	8800

$[\mathrm{H^+}]$	$\mathrm{VO^{2+}}$ k, $\mathrm{M^{-1}\ s^{-1}}$ [b]	$\mathrm{Ni(cyclam)^{2+}}$ k, $\mathrm{M^{-1}\ s^{-1}}$ [b]
1.00	0.933	11.4
0.80	0.991	11.3
0.60	1.17	11.6
0.40	1.46	11.1
0.20	2.33	11.4

[a] $I = 0.10$ M ($\mathrm{NaClO_4}$). [b] $I = 1.00$ M ($\mathrm{NaClO_4}$).

with $k_9 = 76 \pm 3\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{10}K_h = 0.11 \pm 0.005\ \mathrm{s^{-1}}$ (Figure 1).

While the reaction rate for (9) can be assigned to the iron(II) aquo reduction, the net activation process for (10) is similar to that observed by Daugherty and Newton[14] in the V(III)/V(V) reaction in which a pathway with an $[\mathrm{H^+}]^{-1}$ term predominates. Following the production of Ni(III) and Fe(III) in the rate-determining step, the Ni(III) is rapidly reduced by $\mathrm{Fe^{2+}}$. In some initial kinetic runs, iron(II) ammonium sulfate was used as the source of Fe(II). An apparent second-order dependence in [iron(II)], not observed when iron(II) perchlorate was employed, was found and may be attributed to a first-order term in $[\mathrm{SO_4^{2-}}]$ over the range $(1-15) \times 10^{-3}$ M $\mathrm{SO_4^{2-}}$. The increase in the observed rate constant in the presence of sulfate ions may be accommodated by the formation of a reactive $\mathrm{FeSO_4}$ species ($K_m \sim 10\ \mathrm{M^{-1}}$ at 25 °C):[15]

$$\mathrm{FeSO_4 + Ni^{IV}L^{2+} \xrightarrow{k_{12}} Fe(III) + Ni^{III}L} \qquad (12)$$

$$K_m = [\mathrm{FeSO_4}]/([\mathrm{Fe^{2+}}][\mathrm{SO_4^{2-}}])$$

Analysis of the rate dependence on $[\mathrm{SO_4^{2-}}]$ at pH 1.32 and 3.06 leads to a value of $(2.0 \pm 0.1) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ for k_{12}. Kinetic results presented in Tables I and II were obtained with sulfate-free perchlorate solutions.

Reaction of $\mathrm{VO^{2+}}$. The oxidation of the $\mathrm{VO^{2+}}$ ion by $\mathrm{NiL^{2+}}$ produced a vanadium(V) species (probably $\mathrm{VO_2^+}$ in the acidic solutions (pH <2) and concentrations ($<10^{-3}$ M) used),[16] characterized by formation of a red V(V) peroxo complex upon addition of hydrogen peroxide to the product solution.[17] The second-order rate constants observed increased with increasing pH, in a manner similar to that described in the iron(II) system (Table II).

The rate law includes both an acid-independent and an inverse-acid term, implying the operation of two reaction paths, the second involving one proton less than the first

$$\mathrm{VO^{2+} + NiL^{2+} + H_2O \xrightarrow{k_{13}} VO_2^+ + NiL^+ + 2H^+} \qquad (13)$$

$$\mathrm{VO^{2+} + NiL^{2+} + H_2O \xrightarrow{k_{14}} [VO(OH){\cdot}NiL]^{3+} + H^+} \qquad (14)$$

where the activation process in (14) is in the form proposed previously.[14] The second-order rate constant is thus of the form

$$k_0 = k_{13} + k_{14}/[\mathrm{H^+}] \qquad (15)$$

Plots of k_0 against $[\mathrm{H^+}]^{-1}$ showed good linearity with $k_{13} = 0.57 \pm 0.05\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{14} = 0.35 \pm 0.02\ \mathrm{s^{-1}}$, respectively. Similar hydrogen ion dependences involving vanadium(IV) with outer-sphere oxidants have been reported previously by Birk.[18,19] The oxidation of $\mathrm{VO^{2+}}$ by $\mathrm{IrCl_6^{2-}}$ and $\mathrm{Fe(bpy)_3^{3+}}$ has been studied (1.0 M $\mathrm{HClO_4}$), and the following specific rate constants have been found at 25 °C: $\mathrm{IrCl_6^{2-}}$, $k_{13} = 2.7 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{14} = 9.7 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$; $\mathrm{Fe(bpy)_3^{3+}}$, $k_{13} = 7.15 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{14} = 5.4 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$. The ratio of the rate constants for the $\mathrm{VOOH^+}$ and $\mathrm{VO^{2+}}$ reaction pathways, k_{13}/k_{14}, is approximately unity for these two oxidants and for $\mathrm{NiL^{2+}}$, suggesting a common mechanism for each.

Reduction by $\mathrm{Ni(cyclam)^{2+}}$. The oxidation of $\mathrm{Ni(cyclam)^{2+}}$ by $\mathrm{NiL^{2+}}$ in aqueous acidic media produced a species identified, by UV-visible and ESR spectroscopy, as $\mathrm{Ni^{III}(cyclam)^{3+}}$. The spectra were recorded in the presence of excess sulfate[4] ions, which stabilize the Ni(III) species through the formation of $\mathrm{Ni(cyclam)(SO_4)_2^-}$ complexes.[20] The UV-visible spectrum exhibited absorption peaks at 302 nm ($\epsilon = 10\,900\ \mathrm{M^{-1}\ cm^{-1}}$) and 380 nm (shoulder), in agreement with values reported for $\mathrm{Ni(cyclam)^{3+}}$ produced electrochemically.[1,20] An ESR spectrum of the same solution, frozen at 77 K, displayed signals at $g_\perp = 2.219 \pm 0.001$ and $g_\parallel = 2.025 \pm 0.001$, with DPPH ($g = 2.0037$) as an internal reference standard. These values are consistent with those for $\mathrm{Ni(cyclam)^{3+}}$ ($g_\perp = 2.212$ and $g_\parallel = 2.026$),[1,20] a $\mathrm{d^7}$ complex with a tetragonal geometry. A solution of the reactants, quenched at 77 K after partial reaction, exhibited only the peaks observed above, with no evidence of a $\mathrm{Ni^{III}L^+}$ species, for which signals at $g_\perp = 2.11$ and $g_\parallel = 2.04$ have been reported.[7]

The second-order rate constants k_0 were measured over the $[\mathrm{H^+}]$ range 0.20–1.00 M, with no hydrogen ion dependence observed (Table II). At higher pHs, however, the overall equilibrium constant appeared to decrease up to pH ~3. Such an effect may be due to changes in the redox potential of the Ni(III)/Ni(II) couple with increasing pH. Unfortunately the rate of decomposition at higher pH both of $\mathrm{NiL^{2+}}$ and of the nickel(III) cyclam formed interferes with the redox process, preventing accurate acquisition of rate and equilibrium measurements.

Discussion

The results of the kinetic study of the reduction of $\mathrm{NiL^{2+}}$ by $\mathrm{Fe^{2+}}$, $\mathrm{VO^{2+}}$, and $\mathrm{Ni(cyclam)^{2+}}$ are consistent with the general mechanism shown in (16) and (17).

$$\mathrm{NiL^{2+} + M^{n+} \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} NiL^+ + M^{(n+1)+}} \qquad (16)$$

$$\mathrm{NiL^+ + M^{n+} + 2H^+ \xrightarrow{k_{17}} Ni(H_2L)^{2+} + M^{(n+1)+}} \qquad (17)$$

The one-electron reductions of the nickel(IV) complex ($E° = 0.65$ V) by the majority of the reductant species ($\mathrm{M^{n+}}$) in this study have $\Delta E° < 0$. These reductions (k_{16}) may be observed because (a) the subsequent reduction of the nickel(III) intermediate ($E° = 1.25$ V)[7] is a favorable process and is observed to be very fast and (b) pseudo-first-order conditions of excess $[\mathrm{M^{n+}}]$ were employed, such that $k_{17}[\mathrm{M^{n+}}] >> k_{-16}[\mathrm{M^{(n+1)+}}]$.

The rate of ligand exchange on $\mathrm{NiL^{2+}}$ is expected to be very slow as found with other octahedral low-spin $\mathrm{d^6}$ complexes.[21]

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Table III. Thermodynamic Parameters for the Reaction of NiL^{2+} with Several Reductants

reductant	$E°$ [f]	$\Delta G_{12}°$ [a]	ΔG_{12}^* [a]	λ_{12} [a,b]	Q_{12} [a,c]
$FeSO_4$	0.68	+0.60	9.5	39	−0.25
Fe^{2+}	0.78[28]	+2.47	11.9	43	+1.11
ascorbate anion[d]	0.68[31]	+0.91	9.8	39	+0.05
$Ni(cyclam)^{2+}$	0.96[1]	+6.80	13.1	37	+3.54
VO^{2+}	1.03[23]	+8.28	15.0	43	+3.85
hydroquinone[e]	1.08[30]	+9.69	11.9	26	+4.50
catechol[e]	1.17[30]	+11.8	13.4	26	+5.56

[a] kcal mol^{-1}. [b] Using $\Delta G_{11}^*(NiL^{2+}/NiL^+) = 8.5$ kcal mol^{-1}. [c] $Q_{12} = \Delta G_{12}^* - \lambda_{12}/4 - (\Delta G_{12}°)^2/4\lambda_{12}$. [d] Reference 8. [e] Reference 27. [f] V.

Optically active solutions of NiL^{2+} displayed no racemization after several days,[9] suggesting that this complex should behave as an outer-sphere oxidant. The possibility does exist for an inner-sphere complex being formed with Fe^{2+} and VO^{2+}, with bridging through the oxime oxygens on NiL^{2+}, since the redox constants (Table I) are lower than the water-exchange rate constants of $Fe(OH_2)_6^{2+}$ ($k_{ex} = 3 \times 10^6$ s^{-1})[22] and VO^{2+} ($k_{ex} > 500$ s^{-1}).[23] Rosseinsky[23] has reviewed the relative reactivities of V(IV) and Fe(II) as reductants and has described for outer-sphere processes a relationship of the type

$$\log k_{Fe^{2+}} = 0.98 \log k_{VO^{2+}} + 2.03 \qquad (18)$$

The data from the present studies fall on this line, consistent with an outer-sphere process for these reactions. A similar mechanism has been postulated by Lappin[8] for the oxidation of ascorbic acid by NiL^{2+}. Additional evidence in support of this mechanism is found in the behavior of NiL^{2+} with respect to Marcus's linear free energy relationship.

The Marcus theory[10] for outer-sphere electron-transfer reactions establishes a relationship (eq 19) between the free energy of reaction ($\Delta G_{12}°$) and the free energies of activation for the cross reaction (ΔG_{12}^*) and the reductant and oxidant self-exchange reactions (ΔG_{11}^* and ΔG_{22}^*):

$$\Delta G_{12}^* = \frac{\lambda_{12}}{4} + \frac{\Delta G_{12}°}{2} + \frac{(\Delta G_{12}°)^2}{4\lambda_{12}} \qquad (19)$$

where $\lambda_{12} = 2(\Delta G_{11}^* + \Delta G_{22}^*)$.

Each of the free energy parameters is accompanied by a work term (w) for the energy required to bring the reactants together. An expression for w is derived from the Debye–Hückel theory.[24] The Marcus free energy expression may thus be written as (20).[24]

$$\Delta G_{12}^* - w_{12} = \frac{\Delta G_{11}^* - w_{11} + \Delta G_{22}^* - w_{22}}{2} + \frac{\Delta G_{12}° + w_p - w_{12}}{2} + \frac{(\Delta G_{12}° + w_p - w_{12})^2}{8(\Delta G_{11}^* - w_{11} + \Delta G_{22}^* - w_{22})} \qquad (20)$$

The work terms for similarly charged reactants partially cancel each other and are, at an ionic strength (I) of 1.00 M, usually small. In order, however, to correlate the results of this study with reactions involving reductants of different size and charge, the work terms, which make small (<0.5 kcal mol^{-1}) but important contributions to the free energy parameters, are included in ΔG^* and $\Delta G°$.

Table III contains the free energy parameters used in the Marcus correlation in Figure 2. Included in this table are data for the reduction of NiL^{2+} by hydroquinone and catechol[26] (in 1.00 M $HClO_4$) and the ascorbate anion.[8]

The free energies of activation for the self-exchange and cross reactions were calculated from the experimental activation parameters ($\Delta G^* = \Delta G^\ddagger + RT \ln (hZ/kT)$) or from rate constants by means of the relationship

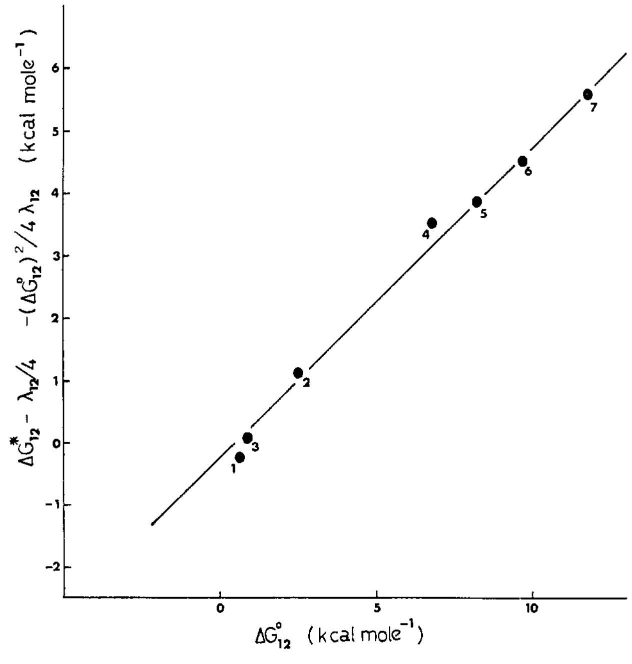

Figure 2. Marcus theory correlation of $\Delta G_{12}^* - \lambda_{12}/4 - (\Delta G_{12}°)^2/4\lambda_{12}$ with $\Delta G_{12}°$ for the reduction of NiL^{2+} by (1) $FeSO_4$, (2) Fe^{2+}, (3) ascorbate anion, (4) $Ni(cyclam)^{2+}$, (5) VO^{2+}, (6) hydroquinone, and (7) catechol.

$$k = Ze^{-(\Delta G^*/RT)} \qquad (21)$$

where Z is the collision frequency and usually taken as 10^{11} M^{-1} s^{-1}.

The self-exchange rate constant of ~10^{-1} s^{-1} for $Fe^{2+/3+}$ at $I = 1.0$ M was calculated from the value measured experimentally[27] at $I = 0.50$ M (4.0 M^{-1} s^{-1}). For the $FeSO_4^{0/+}$ couple a value of ~700 M^{-1} s^{-1} was reported from a study of the Fe^{2+}/Fe^{3+} reaction in sulfate media.[28]

The rate constant for the VO^{2+}/VO_2^+ exchange reaction has been inferred[23] as being very similar to that of Fe^{2+}/Fe^{3+}, upon comparisons of the rates of oxidation of VO^{2+} and Fe^{2+} by a set of common oxidants. For $Ni(cyclam)^{2+/3+}$ a value of ~1×10^3 M^{-1} s^{-1} measured in ESR experiments[29] with spin-labeled $^{61}Ni(cyclam)^{2+}$. Self-exchange rate constants of $(0.2–1.0) \times 10^8$ M^{-1} s^{-1} have been estimated[30] for hydroquinone and catechol from rate measurements between the quinones and their radical ions. Creutz[31] has recently evaluated the $HA\cdot/HA^-$ rate constant to be 10^2–10^4 M^{-1} s^{-1} on the basis of a reduction potential of 0.68 V.

The Marcus relationship in eq 19 may be rearranged, and a plot of $\Delta G_{12}^* - \lambda_{12}/4 - (\Delta G_{12}°)^2/4\lambda_{12}$ against $\Delta G_{12}°$ constructed by using the data in Table III is shown in Figure 2. With use of $E° = 0.65$ V (eq 2) and $\Delta G_{22}^* = 8.5$ kcal mol^{-1} for the NiL^{2+}/NiL^+ self-exchange reaction, a slope of 0.51 ± 0.05 and an intercept of −0.028 ± 0.50 were obtained. This free energy of activation corresponds (eq 21) to a rate constant of 6×10^4 M^{-1} s^{-1}, in reasonable agreement with Lappin's estimate of 10^3–10^4 M^{-1} s^{-1} derived from kinetic data for the reaction of NiL^{2+} with the ascorbate anion.[8]

The NiL^{2+}/NiL^+ reaction involves the exchange of an electron between octahedral, low-spin d^6 and d^7 complexes.

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This system may be compared with Co^{III}(d^6)/Co^{II}(d^7) reactions such as those involving Co(en)$_3^{2+/3+}$, Co(phen)$_3^{2+/3+}$, and Co(sep)$^{2+/3+}$ (en = ethylenediamine, phen = phenanthroline, sep = sepulchrate). The cobalt self-exchange rate constants are much lower than k_{11} for NiL^{2+}/NiL^{+}: for Co(en)$_3^{2+/3+}$, $k = 3 \times 10^{-5}$ M^{-1} s^{-1};[32] for Co(sep)$^{2+/3+}$, $k = 5.1$ M^{-1} s^{-1};[33] and for Co(phen)$_3^{2+/3+}$, $k = 45$ M^{-1} s^{-1}.[34] The slowness of the cobalt-exchange reactions may be accounted for in part by a consideration of the energy required for reorganization of the spin configurations.[21,35]

An important contribution to the self-exchange reorganizational energy is made by the changes in metal-ligand lengths of the ground-state reactants in forming the Franck-Condon activated complex.[36] The differences in metal-nitrogen bond lengths between the reduced and oxidized forms of the nickel and cobalt complexes may be correlated with the electron-exchange parameters.

The crystal structure of a NiL^{2+} complex has not been published, but information on Ni^{IV}-N bond lengths is available from the reported structure of a similar compound, bis[2-((2-aminoethyl)imino)-3-butanone oximato]nickel(IV) diperchlorate.[6] The average Ni^{IV}-N bond length is 1.948 Å, which is 0.14 Å shorter than the average Ni^{II}-N distance in a similar Ni(II) complex, bis[2,2′-iminobis(acetamidoxime)]nickel(II) chloride dihydrate.[37] Interpolation of these distances to an octahedral Ni^{III}N$_6$ species, for which crystallographic data are not yet available, yields a difference of ~0.07 Å between the Ni-N bond lengths between NiL^{2+} and NiL^{+}. A similarity in Ni-N bond length changes in the Ni(IV)/Ni(III) and Ni(III)/Ni(II) oxime complexes is suggested by the similar self-exchange rates determined for these systems.[38] For Co(en)$_3^{2+/3+}$ and Co(sep)$^{2+/3+}$, the Co(II)/Co(III) metal-nitrogen bond length differences are 0.21[39,40] and 0.19 Å,[33] respectively, substantially larger than for NiL$^{2+/+}$, and probably are the source of a sizable barrier to electron exchange.

Further kinetic studies currently in progress of differing nickel(IV) and -(III) complexes reacting with one- and two-electron reductants may prove useful in identifying other contributions to the self-exchange rates for these systems.

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Registry No. 2, 55188-33-5; Fe, 7439-89-6; V, 7440-62-2; Ni, 7440-02-0; Ni(cyclam)(ClO$_4$)$_2$, 15220-72-1.

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Contribution from the Department of Chemistry,
The University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Hexacoordinate Phosphorus. 2. Formation and Dynamic Exchange Processes in Methyltris(trifluoromethyl)(dimethylcarbamato-*O*,*O*′)phosphorus(V)

RONALD G. CAVELL* and LARRY VANDE GRIEND

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The reaction of CO$_2$ with CH$_3$(CF$_3$)$_3$PN(CH$_3$)$_2$ yields the neutral six-coordinate phosphorus carbamate CH$_3$(CF$_3$)$_3$PO$_2$CN(CH$_3$)$_2$. Carbon-13 CO$_2$ exchange and HN(CD$_3$)$_2$ exchange in this compound have been studied in the absence and presence of the amine trap (CH$_3$)$_3$SiCl. The results indicate that the mechanism for formation of the carbamate as well as for carbon dioxide exchange is catalyzed by the presence of fortuitous free amine. Dynamic ^{19}F and ^{31}P NMR methods demonstrate the equivalency of the CF$_3$ groups at room temperature while at lower temperatures the solution structure corresponds to that determined in the solid state by X-ray methods. The barrier to the rearrangement process, which equilibrates the CF$_3$ groups, is independent of solvent or concentration and has been determined by line shape analysis of the ^{31}P{^{1}H} temperature-dependent spectra to be 13.5 ± 0.7 kcal. Evidence is also presented showing formation of an adduct between Me$_3$N and CH$_3$(CF$_3$)$_3$PO$_2$CN(CH$_3$)$_2$ in solution.

Introduction

In part 1,[1] the synthesis and the crystal and molecular structure of the hexacoordinate (carbamato)phosphorus(V) complex CH$_3$(CF$_3$)$_3$PO$_2$CN(CH$_3$)$_2$ was reported. This carbamate differs from the mono- and dithio analogues reported in the same paper in that the carbamate is fluxional in solution at ordinary temperatures whereas the sulfur-containing compounds are static. According to the crystal structure,[1] the carbamate is clearly six-coordinate in the solid state. The rather unusual fluxional behavior of this compound and the fact that these six-coordinate compounds can be formed by an "insertion" reaction involving the P-N bond of the phosphorane prompted us to investigate the fluxional process in more depth and to evaluate the pathway for the formation of these molecules with the aid of isotopically labeled reagents. Of particular interest in this latter context are the divergent views expressed about the mode of CO$_2$ insertion in silicon-,[2] transition-metal-,[3] and tin-based[4] systems. Furthermore, it was of interest to ascertain whether this high-valent phosphorus compound resembled analogous transition-metal systems wherein similar reactions have been observed.

Experimental Section

General Procedures. Both the ^{13}CO$_2$ (90.5 atom % ^{13}C) and HN(CD$_3$)$_2$ (99 atom % D) were obtained from Merck Sharp & Dohme. The solvent, CD$_3$CN, used in all the exchange experiments was dried

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