Polyhedron Vol. 4, No. 6, pp. 993–997, 1985
Printed in Great Britain

0277–5387/85 \$3.00 + .00

THE TRIS(PICOLINATE)VANADATE(II) ION: REDOX PROPERTIES AND ELECTRON TRANSFER KINETICS WITH COBALT(III) AMINES

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(*Received* 2 *July* 1984; *accepted after revision* 6 *October* 1984)

Abstract—Vanadium(II) ions form with the pyridine-2-carboxylate ligand a deep blue, tris-substituted complex absorbing at 660 nm ($\varepsilon = 7.2 \times 10^3\ M^{-1}\ cm^{-1}$) with a shoulder at 450 nm. Reversible spectroelectrochemistry and cyclic voltammetry were observed for this complex, with $E_{1/2} = -0.448$ V vs NHE, and $\Delta S^{\circ}_{rc} = -6\ cal \cdot mol^{-1} \cdot deg^{-1}$. Electron transfer kinetics with $[Co(en)_3]^{3+}$ led to $k_{12} = 3100\ M^{-1}\ s^{-1}$, $\Delta H^{+} = 12.4\ kcal \cdot mol^{-1}$ and $\Delta S^{+} = -0.9\ cal \cdot mol^{-1} \cdot deg^{-1}$ ($I = 0.10$ M). For the related $[Co(NH_3)_6]^{3+}$ complex, $k_{13} = 1.9 \times 10^4\ M^{-1}\ s^{-1}$. The self-exchange rate constant and activation parameters were analysed in terms of relative Marcus theory.

This work deals with the properties and reactivity of the tris(picolinate)vanadate(II) ion.[1] Vanadium(II) complexes are extraordinary in terms of redox reactivity, particularly with respect to oxygen, water and dinitrogen. Because of this, however, only a few complexes have been investigated in aqueous solution.

The $[V(pic)_3]^-$ complex is not an exception in terms of reactivity; however, its unusual deep blue color, in addition to a long life-time in aqueous solution, stimulate spectroscopic and electrochemical studies which are particularly important in vanadium(II) chemistry. The π-conducting picolinate ligand is expected to improve the electron transfer characteristics of the vanadium(II) complex, e.g. increasing the adiabaticity making it useful as a strongly reducing probe in studies of redox reactivity of inorganic and biological complexes.[2,3] To evaluate this point, we have studied the kinetics of the $[Co(en)_3]^{3+}[V(pic)_3]^-$ and $[Co(NH_3)_6]^{3+}$ $[V(pic)_3]^-$ electron transfer reactions, including a relative Marcus theory evaluation of the self-exchange rate constants and the corresponding activation parameters.

EXPERIMENTAL

Aqueous vanadium(II) ions were generated from vanadium(III) trichloride (Alfa) or vanadyl trifluoroacetate solutions, in the presence of zinc amalgam, under argon atmosphere. Lithium picolinate was prepared by reacting picolinic acid (Aldrich) and lithium hydroxide (Fisher), and recrystallized several times from aqueous solution, after a treatment with activated charcoal to remove eventual oxidizing impurities. The tris(picolinate)vanadate(II) complex was always freshly prepared by reacting aqueous vanadium(II) ions with an excess of the picolinate ligand, under argon atmosphere. The ionic strength was adjusted with lithium trifluoroacetate, because vanadium(II) ions are not stable in perchlorate solutions. The complexes $[Co(NH_3)_6](ClO_4)_3$, $[Co(en)_3]I_3$ and $[Co(en)_3]Cl_3$ were prepared as described in the literature.[4,5]

All the measurements in this work were carried out under argon atmosphere. Cyclic voltammetry was performed with a Princeton Applied Research Corporation instrument, consisting of a 173 potentiostat and a 175 Universal programmer. A gold disk electrode was employed for the measurements, with Ag/AgCl (1 M KCl) as the reference electrode, using the conventional Luggin capillary arrangement to minimize the ohmic drop. A platinum wire was used as the auxiliary electrode. Temperature dependence studies were performed using a non-isothermic arrangement, as described in the literature.[6]

The electronic spectra of the complexes in the visible and near-UV region were recorded on a Cary 17 spectrophotometer, fitted with thermostatted cell

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compartments. Spectroelectrochemical measurements were performed with a PAR 173 potentiostat, in parallel with the Cary 17 spectrophotometer. A three electrode system was designed for a rectangular quartz cell of 0.3 mm internal optical pathlength. A gold minigrid was used as transparent working electrode, in the presence of a small Ag/AgCl reference electrode and of a platinum auxiliary electrode.

The stopped-flow kinetics were carried out with a Durrum D-150 instrument, equipped with a Kel-F flow system. The kinetics were studied under pseudo-first order conditions, by following the decay of the absorption band of the $[V(pic)_3]^-$ complex at 660 nm, in the presence of an excess of the oxidizing agent.

RESULTS AND DISCUSSION

Vanadium(II) ions react with picolinate ligands producing violet–blue complexes in aqueous solution. A small excess of the free ligand, e.g. 10^{-3} M, is enough to convert the intermediate successive complexes to the tris(picolinate)vanadate(II) ion, which has a stability constant of 7.6×10^{13} M^{-3}, at 25°C, and $I = 0.6$ M (lithium trifluoroacetate).[1]

The deep blue color of $[V(pic)_3]^-$ fades within a few hours in deaerated solutions, even under continuous flow of argon. For this reason, the spectra of the tris-picolinate ion were obtained spectroelectrochemically, as shown in Fig. 1, with a gold minigrid electrode kept at −800 mV vs Ag/AgCl (1 M KCl). A strong absorption band is observed at 660 nm, with a shoulder around 450 nm. The extinction coefficients are 7.2×10^3 and 4×10^3 $M^{-1}\,cm^{-1}$, respectively. We assigned these bands to charge transfer transitions from the metal d_π orbitals to the ligand p_π orbitals, in comparison to the spectra of the iron(II) picolinates and related complexes.[7]

Spectroelectrochemistry of $[V(pic)_3]^-$ is Nernstian up to −0.600 V, corresponding to a reversible monoelectronic oxidation process, with $E^{\circ} \cong -0.68$ V vs Ag/AgCl (1 M KCl), at 28°C, in the presence of 0.100 *M* lithium picolinate and 0.400 *M* lithium trifluoroacetate. Oxidation proceeds irreversibly above −0.500 V, generating vanadium(IV) complexes.

Cyclic voltammograms of the tris-substituted complex, in the presence of 0.35 M lithium picolinate and 0.60 *M* lithium trifluoroacetate were reversible, with a linear behaviour of the peak currents vs the concentration of the vanadium complex, and the square root of the scan rates. The peak separation is close to 60 mV, with $E_{1/2} = -0.670$ V vs Ag/AgCl (1 M KCl) or −0.448 V vs NHE, and a diffusion coefficient of 4.8×10^{-6} $cm^2\,s^{-1}$, at 25°C. The half-wave potentials measured at 5, 15, 35 and 45°C were −0.664, −0.667, −0.672 and −0.675 V, respectively. From these values we have calculated the redox couple entropy, $\Delta S^{\circ}_{rc} = -6$ $cal \cdot mol^{-1} \cdot deg^{-1}$.

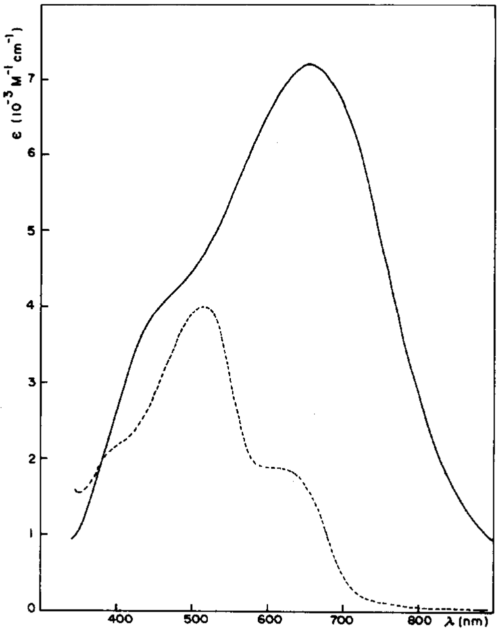

Fig. 1. Electronic spectra of $V(pic)_3^-$ (——) and $V(pic)_3$ (– – –) obtained spectroelectrochemically at −800 and −500 mV vs NHE, respectively, in the presence of 0.10 M lithium picolinate and 0.40 M lithium trifluoroacetate.

The equilibrium constant of the tris(picolinate)vanadium(III) complex, based on equation (1) is 2.1×10^{15} M^{-3}, with $E^{\circ}_{V(H_2O)_6^{3+/2+}} = -0.253$ V.

$$\Delta E^{\circ}_{V(pic)_3^{0/-1}} = \Delta E^{\circ}_{V(H_2O)_6^{3+/2-}} + \frac{RT}{nF}\ln\frac{\beta_{II}}{\beta_{III}}. \quad (1)$$

The electron transfer reaction of $[V(pic)_3]^-$ and $[Co(en)_3]^{3+}$ proceeds according to a first order kinetics for at least three half-lives, in the presence of an excess of the cobalt(III) complex.

$$[V(pic)_3]^- + [Co(en)_3]^{3+} \xrightarrow{k_{12}} V(pic)_3 + [Co(en)_3]^{2+}$$

$$-\frac{d[V(pic)_3^-]}{dt} = k_{12}[V(pic)_3^-][Co(en)_3^{3+}]. \quad (2)$$

The experimental rate law is consistent with an outer sphere mechanism, where $k_{12} = 3100$ $M^{-1}\,s^{-1}$, at 25°C, and $I = 0.100$ *M* (KCl, or lithium trifluoroacetate). No evidence for rate saturation has been detected under the conditions employed for the experiments. The kinetics data at several temperatures are shown in Table 1.

Table 1. Kinetic results for the $V(pic)_3^-$–$Co(en)_3^{3+}$ and $V(pic)_3^-$–$Co(NH_3)_6^{3+}$ reactions

T (°C)	I (M)	[Co(III)] (M)	k_{obs}* (s^{-1})	k_{ij} ($M^{-1}\,s^{-1}$)
16.8	0.10†	5.90×10^{-3}‡	9.4	1.59×10^{3}
20.2	0.10†	5.90×10^{-3}‡	12.6	2.13×10^{3}
25.0	0.10†	2.04×10^{-3}‡	6.0	2.95×10^{3}
25.0	0.10†	2.37×10^{-3}‡	7.5	3.16×10^{3}
25.0	0.10§	5.00×10^{-3}‖	16.5	3.3×10^{3}
25.0	0.10†	5.90×10^{-3}‡	18.5	3.13×10^{3}
25.0	1.00†	5.90×10^{-3}‡	15.1	2.6×10^{3}
25.0	0.10†	9.30×10^{-3}‡	28.9	3.10×10^{3}
25.0	0.10§	1.00×10^{-2}‖	30.0	3.00×10^{3}
25.0	0.10§	1.75×10^{-2}‖	53	3.2×10^{3}
25.0	0.10§	2.50×10^{-2}‖	79	3.16×10^{3}
30.0	0.10†	5.90×10^{-3}‡	27.4	4.7×10^{3}
35.0	0.10†	5.90×10^{-3}‡	37.5	6.3×10^{3}
25.0	0.090§	1.00×10^{-3}¶	22.0	2.2×10^{4}
25.0	0.090§	2.00×10^{-3}¶	38	1.90×10^{4}
25.0	0.090§	5.00×10^{-3}¶	91	1.82×10^{4}

* $[V(pic)_3^-] = 3\times10^{-5}$ M, in the presence of 0.04 M lithium picolinate, pH 6.

† Ionic strength adjusted with KCl.

‡ $[Co(en)_3]Cl_3$.

§ Ionic strength adjusted with lithium trifluoroacetate.

‖ $[Co(en)_3]I_3$.

¶ $[Co(NH_3)_6](ClO_4)_3$.

To evaluate the self-exchange rate constants for the $[V(pic)_3]^-$ complex, we have employed the Marcus theory with the Wherland–Gray[8] formalism for the work terms, W_{ii} and W_{ij}. The reorganization free energies, ΔG_{ii}^{**} are given by the equation,

$$\Delta G_{11}^{**} = 2\Delta G_{12}^{**} - \Delta G_{22}^{**} - \Delta G_r^{\circ}(1-\alpha_{12}), \tag{3}$$

where

$$\alpha_{12} = \frac{\Delta G_r^{\circ}}{4(\Delta G_{11}^{**} + \Delta G_{22}^{**})} \tag{4}$$

and

$$\Delta G_{12}^{**} = \Delta G_{12}^{*} - W_{12} \tag{5}$$

$$\Delta G_{11}^{**} = \Delta G_{11}^{*} - W_{11} \tag{6}$$

$$\Delta G_{22}^{**} = \Delta G_{22}^{*} - W_{22} \tag{7}$$

$$\Delta G_r^{\circ} = \Delta G_{12}^{\circ} - W_{12} + W_{21}. \tag{8}$$

Analogously to Wherland and Gray,[9] we have used a pre-exponential factor of 6×10^{12} $M^{-1}\,s^{-1}$ (instead of 10^{11} $M^{-1}\,s^{-1}$) in the Marcus equation, as in the semiclassical formalism[10]

$$k = \kappa_{el}\Gamma_n V \nu_n \exp-(\Delta G^*/RT), \tag{9}$$

where the product of the electronic and nuclear tunneling factors, $\kappa_{el}\Gamma_n$, is close to unity; $V = 4\pi N r^3/300$; ν_n is the nuclear vibration frequency, and $V\cdot\nu_n \cong kT/h$.

The self-exchange rate constant, k_{22}, for the $[Co(en)_3]^{3+}$ complex has been measured by Lewis *et al.*[11] and by Dwyer and Sargeson[12] as 5.2×10^{-5} $M^{-1}\,s^{-1}$ and 7.7×10^{-5} $M^{-1}\,s^{-1}$ (25°C, $I = 1$ M), respectively. The extrapolated value at $I = 0.1$ M is 2.75×10^{-5} $M^{-1}\,s^{-1}$. The input and output parameters are given in Table 2.

The calculated self-exchange rate constant for the $[V(pic)_3]^{0/-}$ couple, based on the $[Co(en)_3]^{3+}$–$[V(pic)_3]^-$ reaction is 9.7×10^{5} $M^{-1}\,s^{-1}$, at $I = 0.100$ M. This value is in good agreement with preliminary data based on $Co(sepulchrate)^{3+}$ and bis(histidinate)–cobalt(III) complexes.[1] In comparison to the self-exchange rate constant for the $[V(H_2O)_6]^{3+/2+}$ couple, ($k_{ii} = 1.0\times10^{-2}$ $M^{-1}\,s^{-1}$ at $I = 1.0$ M), one can see that electron-transfer in the picolinate complex is more effective by seven orders of magnitude. Part of this difference arises from the work term, which is null for $[V(pic)_3]^{0/-}$ and 0.79 kcal mol^{-1} for $[V(H_2O)_6]^{3+/2+}$. The major contribution, however, comes from the smaller reorganization barrier, ΔG_{ii}^{**}, of the $[V(pic)_3]^-$ complex.

The reorganization entropies, ΔS_{ii}^{**} and ΔS_{ij}^{**}, are given by

$$\Delta S_{12}^{**} = \left(\frac{\Delta S_{11}^{**}}{2} + \frac{\Delta S_{22}^{**}}{2}\right)(1-4\alpha_{12}^2) + \frac{\Delta S_r^{\circ}}{2}(1+2\alpha_{12}), \tag{10}$$

where

$$\Delta S_{11}^{**} = \Delta S_{11}^{*} + \frac{\partial W_{11}}{\partial T} \tag{11}$$

$$\Delta S_{22}^{**} = \Delta S_{22}^{*} + \frac{\partial W_{22}}{\partial T} \tag{12}$$

$$\Delta S_{12}^{**} = \Delta S_{12}^{*} + \frac{\partial W_{12}}{\partial T} \tag{13}$$

$$\Delta S_r^{\circ} = \Delta S_{12}^{\circ} + \frac{\partial W_{12}}{\partial T} - \frac{\partial W_{21}}{\partial T}. \tag{14}$$

The reaction entropy ΔS_{12}° can be obtained from the difference of the experimental redox couple entropies:

$$\Delta S_{12}^{\circ} = \Delta S^{\circ}_{rc[Co(en)_3^{3+/2+}]} - \Delta S^{\circ}_{rc[V(pic)_3^{0/-}]}. \tag{15}$$

Derivation of the work terms is given by[10]

$$\frac{\partial W}{\partial T} = -\frac{W}{2T(1+\beta r I^{1/2})}\left[2\left(\frac{\partial \ln D_s}{\partial \ln T}\right) + \beta r I^{1/2}\left(\frac{\partial \ln D_s}{\partial \ln T}\right) - \beta r I^{1/2}\right] \tag{16}$$

Table 2. Self-exchange rate constants and activation parameters for the $V(pic)_3^-$–$Co(en)_3^{3+}$ system at 25°C and $I = 0.10$ M

	V(II)/Co(III)	Co(III)/Co(II)	V(III)/V(II)
r (10^2 pm)	5.6/3.4	3.4/3.5	5.5/5.6
W_{ij}, W_{ii} ($kcal \cdot mol^{-1}$)	−0.604	1.892	0
$\frac{\partial W_{ij}}{\partial T}$, $\frac{\partial W_{ii}}{\partial T}$ ($cal \cdot mol^{-1} \cdot deg^{-1}$)	2.87* 2,59†	9.07* 8.20†	0 0
ΔE°, E_{rc}° (V vs NHE)	0.228	−0.220 −0.216‡	−0.448
k_{ij}, k_{ii} ($M^{-1}\, s^{-1}$)	3.1×10^3	2.7×10^{-5}	9.7×10^5
$\Delta G_{ij}^{\ddagger *}$, $\Delta G_{ii}^{\ddagger *}$ ($kcal \cdot mol^{-1}$)	13.28	21.76	9.28
ΔS_{12}°, ΔS_{rc}° ($cal \cdot mol^{-1} \cdot deg^{-1}$)	41	35 37‡	−6
$\Delta S_{ij}^{\ddagger *}$, $\Delta S_{ii}^{\ddagger *}$ ($cal \cdot mol^{-1} \cdot deg^{-1}$)	3.9* 3.7†	−22.6* −23.5†	−10.2* −9.7†
$\Delta S_{ij}^{\ddagger}$, $\Delta S_{ii}^{\ddagger}$ ($cal \cdot mol^{-1} \cdot deg^{-1}$)	−0.9	−33.7§	−12.1* −11.6†
$\Delta H_{ij}^{\ddagger *}$, $\Delta H_{ii}^{\ddagger *}$ ($kcal \cdot mol^{-1}$)	14.4* 14.4†	15.0* 14.7†	6.2* 6.4†
$\Delta H_{ij}^{\ddagger}$, $\Delta H_{ii}^{\ddagger}$ ($kcal \cdot mol^{-1}$)	12.4	13.6§	5.6* 5.8†

* Based on eqn (17).
† Eqn (16).
‡ Ref. 18.
§ Ref. 12.

or alternatively,[13] by

$$\frac{\partial W}{\partial T} = Z_1 Z_2 \left(0.868 I^{1/2} + \frac{19.5}{r} \right) \times \exp(-0.329 r I^{1/2}), \quad (17)$$

where D_s is the static dielectric constant, r is the metal–metal separation in the activated complex, and the other terms have the conventional meanings. For an adiabatic mechanism,[10]

$$\Delta S^{\ddagger} = \Delta S^{**} - \frac{\partial W}{\partial T} - R \quad (18)$$

and

$$\Delta H^{\ddagger} = \Delta H^{**} + W - T\frac{\partial W}{\partial T} - RT. \quad (19)$$

The calculated activation parameters for the $[Co(en)_3]^{3+/2+}$–$[V(pic)_3]^-$ reaction are presented in Table 2. As one can see in Table 2, the use of equations (16) and (17) leads to similar results for the $[V(pic)_3]^-$ complex.

In the present work we assumed an adiabatic mechanism for $[Co(en)_3]^{3+}$, based on recent theoretical calculations[14] and discussion.[15] As a matter of fact, the Franck–Condon or nuclear factors related to $\Delta G_{ii}^{\ddagger *}$ have been estimated as 10^{-4}, in comparison to 10^{-3}–10^{-2} for the electronic factor associated with non-adiabaticity.[14] On the other hand, it has been shown that the electronic factor spans the range $10^{-3} - 1$ for typical iron and ruthenium complexes.

The reaction of $[V(pic)_3]^-$ with $[Co(NH_3)_6]^{3+}$ follows a rate-law analogous to that for the $[Co(en)_3]^{3+}$ reaction, with $k_{13} = 1.9 \times 10^4\ M^{-1}\,s^{-1}$, as shown in Table 1. According to Marcus theory, the ratio k_{13}/k_{12} for electron transfer with hexaamine and ethylenediamine complexes should be relatively constant.[15] Typical values from the literature for V^{2+}, Cr^{2+}, $Cr(bipy)_3^{2+}$ and $Co(sepulchrate)^{2+}$ reactions with $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ complexes vary from 2.9 to 18.1. Our experimental value of k_{13}/k_{12} is 6.1.

Using the calculated self-exchange rate constant for $[V(pic)_3]^-$, we have estimated k_{33} for the $[Co(NH_3)_6]^{3+/2+}$ couple, assuming $r(Co^{II}) = 0.34$ nm, $r(Co^{III}) = 0.32$ nm and $E_{rc}^{\circ} = 0.057$ V,[16] or 0.018 V.[17] Our result for k_{33} was $2.5 \times 10^{-6}\ M^{-1}\,s^{-1}$, or $6.7 \times 10^{-7}\ M^{-1}\,s^{-1}$, respectively. This is in good agreement with the range of values recently proposed in the literature.[15,19]

Acknowledgements—We thank FAPESP and CNPq for support.

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