For example, we obtain

$$A = -2(2J(x\pm,x\pm) + 2J(x\pm,x\mp) + 4J(x\pm,x0) + J(x0,x0))/9 \qquad (A2.4)$$

If the kinetic approximation (eq 8) is valid, then

$$\begin{aligned} A &\simeq (2J'_\pi + J_\sigma)/9 \\ B &\simeq (J'_\pi + 2(J_\sigma J'_\pi)^{1/2})/9 \\ C &\simeq (-J'_\pi + J_\sigma)/9 \\ D &\simeq (J'_\pi - (J_\sigma J'_\pi)^{1/2})/9 \\ 3(K + L) &\simeq (J'_\pi + 2J_\sigma)/3 \\ 3(M + N) &\simeq (2J'_\pi + (J_\sigma J'_\pi)^{1/2})/3 \\ -3(K - L) &\simeq J'_\pi \\ -3(M - N) &\simeq (J_\sigma J'_\pi)^{1/2} \qquad (A2.5) \end{aligned}$$

where $J'_\pi = J_\pi/9 = 4h(x\pm,x\pm)^2/U$, and we have assumed that the transfer integrals $h(x\pm,x\pm) = h(x,x)$ and $h(x0,x0) = h(z,z)$ have the same sign.

Using eq A2.5 and A2.3, one can show that large J_σ causes extensive mixing between ${}^4A_2{}^2E_{u\pm}$ and ${}^4A_2{}^2T_{1a\pm}$ states. This is precisely what is observed in tris(μ-hydroxo)bis(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III) ion.[34,35]

In order to derive the eigenvalues it is necessary to include single-ion Coulombic and trigonal perturbations that remove the quasi-degeneracy of the ${}^2T_1$ and ${}^2E$ states and also produce zero-field splittings. The simplest procedure is to introduce an empirically derived energy separation $E({}^2T_1,{}^2E)$ and determine the zero field splittings with the effective Hamiltonians[36]

$$\mathbf{H}({}^2E) = -D({}^2E)S_zT_z$$

$$\mathbf{H}({}^2T_1) = -F({}^2T_1)(3T_z{}^2 - T(T+1)) + \lambda_0 S_zT_z + \lambda(S_xT_x + S_yT_y) \qquad (A2.6)$$

where $D({}^2E) = E(\mp{}^1/_2u\pm) - E(\pm{}^1/_2u\pm)$, and F, λ_0, and λ are the effective trigonal field and spin–orbit parameters for the ${}^2T_1$ multiplet. $D({}^2E)$ is mainly determined by the trigonal field parameter[37] v while $F({}^2T_1)$ is more sensitive[38] to v′. In fact we find[38] that $F({}^2T_1) \simeq -v'/10$. The parameters λ and λ_0 are complicated functions of v and v′. For large |v′| the zero-field splitting of the ${}^2T_1$ state is mainly determined by $F({}^2T_1)$, and as a first approximation λ and λ_0 may be neglected.

We now consider in more detail the single-ion perturbations in the tris(hydroxo) complex.[34] The structural data[39] for the iodide salt gives the bond lengths, r(Cr–O) = 1.97 Å, r(Cr–N) = 2.09 Å, and r(Cr–Cr) = 2.64 Å. The polar angle, with respect to the C_3 axis, for the bridging oxygen atoms is $\theta_b = 48.0°$, and for the terminal nitrogen atoms, $\theta_t = 50.5°$. Hence the Cr(III) ion has two strong "elongated" trigonal fields as well as an axial field generated by the second Cr(III) ion.

The observed zero-field splitting in the ground multiplet is nearly all due to single-ion anisotropy[34] and $D({}^4A_2) = (\pm{}^1/_2) - (\pm{}^3/_2) \simeq -1.8$ cm^{-1}. This value is similar to that for Cr^{3+}:$ZnAl_2O_4$ (spinel),[37] where $D({}^4A_2) = -1.86$ cm^{-1}. Macfarlane[37] has shown that for Cr(III) doped in oxide lattices, $D({}^4A_2)$ varies linearly with v′ and v′ ≃ −1700 cm^{-1} for $ZnAl_2O_4$. For the hydroxo dimer we expect[38] that $F({}^2T_1) \simeq +170$ cm^{-1}, so that $E({}^2T_{10}) - E({}^2T_{1\pm}) \simeq +510$ cm^{-1}, which agrees with the empirical value[35] of +450 cm^{-1}.

The bridging angles and bridging bond lengths in the hydroxo dimer are almost identical with those in the 1*nn* pair in ruby.[40] It is therefore not surprising to find that the ground exchange parameters are very similar for the two pairs.[34] However, the single-ion perturbations should be significantly different. For example in ruby the terminal oxygen atoms[40] have $\theta_t = 63.1°$ and r(Al–O) = 1.86 Å, and contribute a large "compressed" trigonal field. Calculations,[38] based on the linear ligator AOM[41] model and including the axial field of the second Cr(III) ion, suggest that v′ ≃ −1800 cm^{-1} and v ≃ −1000 cm^{-1} for the hydroxy dimer. For ruby, Macfarlane[37] gives $D({}^4A_2) = +0.38$ cm^{-1}, v′ = +680 cm^{-1} and v = +800 cm^{-1}.

Registry No. $Cs_3Mo_2Cl_9$, 29013-02-3.

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Isolation and Characterization of Novel Photoproduced $M(CO)_5(en)$ Complexes (M = Cr, Mo, W; en = Ethylenediamine)

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Novel monodentate $M(CO)_5(en)$ complexes, where M = Cr, Mo, W and en = ethylenediamine, are formed on UV photolysis of $M(CO)_6$ solutions containing en. These compounds have been isolated and characterized by infrared and electronic absorption spectroscopy and by elemental analyses. The $M(CO)_5(en)$ complexes undergo chelation via a first-order kinetic process to form $M(CO)_4(en)$ and CO products. Determined reaction rates of $M(CO)_5(en)$ are as follows: 3.0 × 10^{-4} s^{-1} (for M = Cr at 323 K), 3.5 × 10^{-4} s^{-1} (for M = Mo at 298 K), and 4.2 × 10^{-5} s^{-1} (for M = W at 323 K). The order Mo > Cr > W is consistent with that of the reactivity and calculated M–C force constants of $M(CO)_6$ complexes in solution. Light irradiation of $M(CO)_5(en)$ solutions that contain an excess concentration of PPh_3 result in substitution of the unique ligand and formation of $M(CO)_5(PPh_3)$ products.

Introduction

Ethylenediamine (en) is an important ligand and is known to undergo bidentate coordination with a wide range of transition-metal centers. Indeed, metal complexes containing the en ligand have been studied extensively and over 5700 papers on this subject have appeared in the literature since 1968.[1] Only a few of these studies have characterized reaction intermediates in which en is

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(1) Results obtained from a computer-generated search of *Chemical Abstracts*, using the CAS Online service.

coordinated in a monodentate fashion.[2-7] To date, however, there are no reports of a stable monodentate en complex, where the en ligand has both nitrogen atoms in the active (unprotonated) form.

Recently, we have been investigating the kinetics and mechanism of chelation reactions following the photogeneration of $M(CO)_5L$ complexes, where M = Cr, Mo, W and L = a series of bidentate ligands.[8] These $M(CO)_5L$ species proceed to form $M(CO)_4L$ and CO products via a thermal ring closure process. The coordination abilities of a number of dipyridylalkane ligands with metal carbonyl systems have also been studied.[9] During the course of this work we have found, unexpectedly, a stable pentacarbonyl complex with the en ligand coordinated in a monodentate manner. This paper reports the synthesis, characterization, and thermal and photochemical properties of these monodentate $M(CO)_5(en)$ (M = Cr, Mo, W) species.

Experimental Section

Materials. The parent metal hexacarbonyls were obtained from Strem Chemicals, Inc., and used without further purification. Ethylenediamine was obtained as reagent grade material from J. T. Baker Chemical Co. and distilled immediately prior to use. Spectroscopic grade chloroform and cyclohexane were purchased from Aldrich Chemical Co. Spectroscopic grade benzene and isooctane were obtained from J. T. Baker Chemical Co. Magnesium carbonate used in chromatographic purification was purchased from J. T. Baker Chemical Co. Nitrogen used for deoxygenating was obtained in a high research purity grade (>99.99%) and was further purified by passage through two 1 m × 2 cm tubes, the first containing dry $CaSO_4$ (W. A. Hammond Drierite Co.) and P_2O_5 (Fisher Scientific Co.) in alternating 20-cm lengths and the second containing a Cu catalyst (Chemical Dynamics Corp., BASF R3-11). The catalyst was activated prior to use by heating to 393 K while flushing with a steady stream of hydrogen. In this reduced form, the catalyst removes trace amounts of H_2O and O_2. Caution! The activated catalyst is pyrophoric.

Synthesis of $M(CO)_5(en)$ Complexes. Solid $M(CO)_5(en)$ complexes were prepared by UV irradiation with a 200-W medium-pressure Hg lamp of a continuously N_2-purged hexanes solution (300 mL) containing the parent hexacarbonyl (2.0 mmol) and an excess of ethylenediamine (6.0 mmol). Nitrogen purging was maintained throughout the course of the reaction to avoid oxidation of the complex, and the typical photolysis time was 30 min. Immediately following irradiation the solvent was removed by rotary evaporation. The product was then redissolved in isooctane and purified by column chromatography on magnesium carbonate to remove the unreacted starting materials. The product was eluted from the column with benzene, isolated by rotary evaporation, and further purified by sublimation at 303 K and 10^{-4} Torr. The complexes are stable in the solid form, although their long-term stabilities were enhanced by storing under N_2 at 278 K.

Elemental analysis of $W(CO)_5(en)$ was performed by MIC Anal of Tucson, Az. Anal. Calcd for $C_7H_8N_2O_5W$: C, 21.9; H, 2.10; N, 7.29. Found: C, 21.3; H, 2.16; N, 7.00.

Equipment and Procedures. Infrared spectra were recorded as chloroform solutions in a 1 mm path length NaCl cell on a Perkin-Elmer Model 283B spectrophotometer. Band maxima are considered accurate to ±2 cm^{-1}. Electronic absorption spectra were recorded on a Hewlett-Packard 8450A spectrophotometer, which utilizes a diode-array detection system. The absorption band maxima are considered accurate to ±2 nm in the visible region and ±1 nm in the ultraviolet region.

The 458-nm photolysis experiments were performed with a Lexel Corp. Model 95-4 4W argon ion laser. Typical laser power was 50 mW, measured by a Lexel Corp. Model 504 power meter. The sample solutions were doubly filtered through 0.22-μm Millipore filters and N_2-purged for at least 15 min prior to irradiation. During reaction the concentration of reactants and products was monitored by UV-visible absorption spectroscopy. Photochemical quantum yields (ϕ_{cr}) were obtained by monitoring the disappearance of the $M(CO)_5(en)$ complex in the 400-nm region; the values were corrected for a changing degree of light absorption and are considered accurate to ±10%.

Table I. Infrared C-O Stretching Frequencies for $M(CO)_5(en)$ Complexes[a]

	infrared bands, cm^{-1}			
complexes	A_1^1	B_1	E	A_1^2
$Cr(CO)_5(en)$	2068	1984	1935	1900[b]
$Mo(CO)_5(en)$	2078	1992	1946	1904[b]
$W(CO)_5(en)$	2074	1975	1927	1899[b]

[a] Recorded in chloroform at 293 K. [b] Observed as a shoulder.

Table II. Electronic Absorption Data and Assignments for $M(CO)_5(en)$ Complexes in Chloroform at 293 K

complex	band max, nm (ϵ, M^{-1} cm^{-1})
$Cr(CO)_5(en)$	415 [d → d] (3958)
$Mo(CO)_5(en)$	385 [d → d] (5094)
$W(CO)_5(en)$	406 [d → d] (4235), 438 [d → d] (859)[a]

[a] Spin-forbidden transition observed as a shoulder.

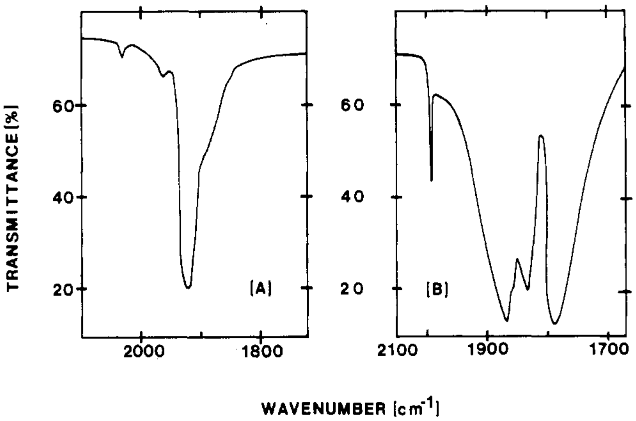

Figure 1. Infrared spectra of (A) $W(CO)_5(en)$ and (B) $W(CO)_4(en)$ complexes in chloroform at 293 K.

Thermal reactions were also monitored by UV-visible spectroscopy. All manipulations and measurements were carried out in the dark. The sample temperature was maintained in either the photolysis or thermal experiments at the stated values (to ±0.1 K) by means of a Fisher Scientific Model 900 circulating constant-temperature bath.

Results and Discussion

Infrared spectra have been recorded in the carbonyl stretching region for each of the $M(CO)_5(en)$ complexes, and the data are summarized in Table I. The spectrum obtained from $W(CO)_5(en)$ is representative of these complexes and is shown in Figure 1. As a comparison the infrared spectrum of $W(CO)_4(en)$ is also shown. Each $M(CO)_5(en)$ complex exhibits four C-O stretches, consistent with the C_{4v} group of the CO ligand about the metal center.[10] Consequently, these bands are assigned to the A_1^1, B_1, E and A_1^2 modes. It is noted that the formally IR forbidden B_1 mode is observed, and this indicates that the CO ligands are somewhat distorted from idealized C_{4v} symmetry in these complexes. The infrared spectrum obtained from $W(CO)_4(en)$ exhibits bands at 2008 (A_1^{1a}), 1872 (B_1), 1838 (A_1^{1b}), and 1790 cm^{-1} (B_2) and is in agreement with previously reported data.[10b]

Electronic absorption data of each of the $M(CO)_5(en)$ complexes are listed in Table II. The absorption centered at ~400 nm is typical of that observed for a large number of mononuclear metal pentacarbonyl complexes and is therefore assigned to a

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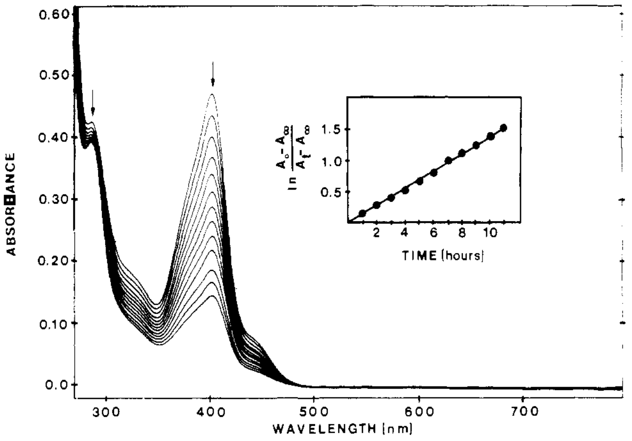

Figure 2. Electronic absorption spectral changes accompanying the thermal reaction of $W(CO)_5(en)$ to form $W(CO)_4(en)$ and CO at 323 K. Spectra were recorded at 1-h intervals. The inset depicts the time-dependent behavior of absorption at 406 nm.

Table III. Observed Rate Constants for the Reaction of $M(CO)_5(en)$ To Form $M(CO)_4(en)$ and CO

M	temp, K	k_{obsd}, s^{-1}
Cr	323	3.0×10^{-4}
Mo	298	3.5×10^{-4}
W	323	4.2×10^{-5}

ligand field (LF) $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$ transition.[11] The energy of this absorption is dependent on the metal center, being ordered Mo > W > Cr, which is also consistent with previous $M(CO)_5L$ spectra.[12] The $W(CO)_5(en)$ complex exhibits another feature as a shoulder at 438 nm, which is assigned to the corresponding $^1A_1(e^4b_2^2) \rightarrow {}^3E(e^3b_2^2a_1^1)$ LF transition. This spin-forbidden band is only observed for the W complex in accordance with the large spin–orbit coupling parameter associated with this metal.[13]

Figure 2 represents the spectral sequence observed when a 1.1×10^{-4} M $W(CO)_5(en)$ solution in chloroform is allowed to stand at 323 K in the dark. Individual spectra were recorded at 1-h intervals. The formation of $W(CO)_4(en)$ (see eq 1) is evidenced

$$W(CO)_5(en) \xrightarrow[323\ K]{\Delta} W(CO)_4(en) + CO \qquad (1)$$

by the smooth spectral conversion to the LF $^1A_1 \rightarrow {}^1A_1, {}^1B_2$ and $^1A_1 \rightarrow {}^3A_1, {}^3B_2$ absorptions characteristic of the product complex.[14] This reaction was also monitored by infrared spectroscopy, which further confirmed the tetracarbonyl product. The rate of this chelation process (eq 1) has been determined by monitoring the time decay of the $^1A \rightarrow {}^1E$ LF absorption of $M(CO)_5(en)$. The absorption decay from A_0 to A_∞ is exponential, and plots of ln $[(A_0 - A_\infty)/(A_t - A_\infty)]$ vs. time exhibited linearity with correlation coefficients typically greater than 0.99 (see Figure 2 inset). Here A_0 is defined as the initial absorbance of the solution, A_t is the absorbance at various time intervals throughout the reaction, and A_∞ is the final absorbance. All absorbance values were recorded at a fixed wavelength in the LF region. The slope of the plotted line is equal to the observed reaction rate constant, k_{obsd}, and values obtained for the $M(CO)_5(en)$ complexes are shown in Table III. The rate data are ordered Mo > Cr > W, consistent with previously reported chelation studies of other $M(CO)_5L$ complexes[8] and both the reactivity[15] and calculated M–C force constants[16] of the parent hexacarbonyls in solution.

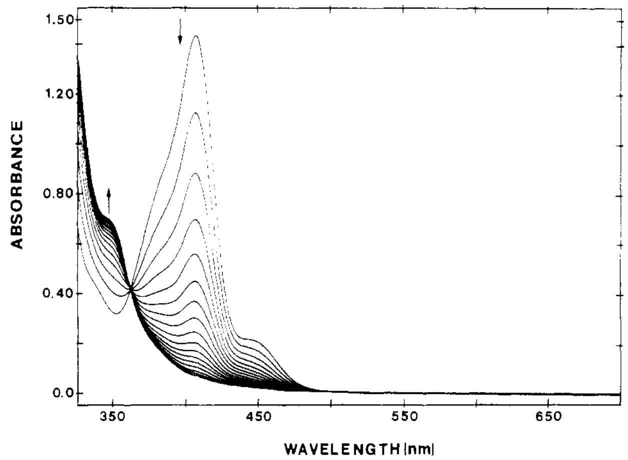

Figure 3. Electronic absorption spectral changes accompanying the 458-nm photolysis of $W(CO)_5(en)$ in isooctane containing 0.1 M PPh_3 at 293 K. Spectra were recorded at 20-s intervals.

The photochemical reactivity of $M(CO)_5(en)$ has been investigated. In the absence of an entering ligand the photochemical processes are apparently intricate, as evidenced by an early loss of isosbestic points during reaction. These processes are thought to involve scavenging of the photoproduced $M(CO)_5$ species by solvent impurities.[8a,b] With an excess of PPh_3 in solution as entering ligand the $W(CO)_5(en)$ complex undergoes ligand photosubstitution typical of $W(CO)_5L$ type complexes (see eq 2).[11b,c] Figure 3 depicts the spectral sequence observed accompanying the 458-nm photolysis of $W(CO)_5(en)$ in isooctane containing 0.1 M PPh_3 at 298 K. The spectra show a clean progression to the spectral features of $W(CO)_5(PPh_3)$. An isosbestic point at 388 nm was maintained throughout the course of the reaction, indicating that the reaction proceeds uncomplicated by side or subsequent reaction. The quantum yield determined for this photosubstitution reaction is 0.07.

$$W(CO)_5(en) \xrightarrow[0.1\ M\ PPh_3\ \text{in isooctane}]{h\nu,\ \lambda\ =\ 458\ nm} W(CO)_5(PPh_3) + en \qquad (2)$$

The formation of the stable monodentate $M(CO)_5(en)$ intermediates described in this paper is somewhat surprising in light of the fact that previous workers have indicated that the en ring closure process is a fast one that does not require further collision between reactants.[17] There are, however, several factors that may contribute to the increased stability of these monodentate $M(CO)_5(en)$ complexes. The basicity of the en ligand is important to consider. However, since the basicity of ethylenediamine ($pK_b = 3.3$)[18] is greater than that of 2,2′-bipyridine ($pK_b = 9.68$),[19] a ligand that is known to form chelated $M(CO)_4L$ complexes readily,[8c,20] it would not appear that this would impede the formation of the metal tetracarbonyl complexes. A second factor to examine is the conformation of the monodentate species. Since free rotation exists around the carbon–carbon bond axis of the en ligand, it is unlikely that the uncoordinated nitrogen atom would be sufficiently sterically constrained in these metal carbonyl de-

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rivatives to hinder chelation. Again, the analogy may be drawn with the $W(CO)_5(bpy)$ or $W(CO)_5(dab)$ (bpy = 2,2′-bipyridine, dab = 1,4-diazabutadiene) complexes, where the N-donor ligands are π-conjugated and yet undergo chelation much more rapidly than these $M(CO)_5(en)$ compounds.[8c] Experimental and theoretical studies on the bpy ligand have concluded that it exists in an approximately s-trans conformation in the solution phase.[21] Thus, the π-conjugation of bpy will, in fact, hinder the rotation about the C_2–C_2' bond necessary to achieve the cis chelation geometry. Correspondingly, the lack of ring closure in these $M(CO)_5(en)$ complexes cannot be attributed solely to the ease of rotation about the en C_2–C_2' bond. A third factor that has been considered is solvation effects on the uncoordinated nitrogen atom of the en ligand. While previous workers have investigated the solvating influence of aqueous and alcoholic solvents on en,[22] it would be difficult, at best, to believe that the chloroform solvent used in this study could provide the necessary solvating power to prevent coordination of the remaining nitrogen. Moreover, we have determined that the $W(CO)_5(en)$ complex is equally stable in room-temperature cyclohexane and isooctane solutions. A fourth factor to consider is hydrogen bonding between the uncoordinated amine groups of en, thereby slowing the rate of chelation. However, at the $\sim 10^{-4}$ M concentrations used in this study, it would seem unlikely that this phenomenon would significantly influence the chelation process.

Thus, other interpretations must be invoked to account for the stability of these $M(CO)_5(en)$ complexes. We view it significant that the en ligand, unlike bpy, is able to undergo free rotation about the C–N bonds and, thus, even when it does achieve a cis geometry, the overlap of the nitrogen lone pair with the metal center may be poor. Also significant may be the tetrahedral environment surrounding the nitrogen atoms of the en ligand, which results in sp^3 hybridization of these orbitals, whereas the hybridization is sp^2 in most other diimine ligands such as 2,2′-bipyridine or 1,10-phenanthroline. The sp^3 hybridization would result in a substantial decrease in orbital angular overlap for the incoming nitrogen atom as it undergoes bond formation and ring closure. We also note that in previous studies where monodentate en complexes have been observed, the metal center possesses a formal charge of +2 or +3.[2-7] These complexes exist only as reaction intermediates and have not been isolated. In contrast, the stable complexes described here have metal centers that possess a formal neutral charge.

In summary, the unusual stability of these $M(CO)_5(en)$ complexes is attributed to the reduction of ligand orbital overlap that is necessary to bring about chelation and to the diminished affinity of the ligand electrons for the metal center.

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Theoretical Analysis of the Cobalt(III)–Cobalt(II) Tris[(±)-1,2-propanediamine] Electron-Transfer Reaction Using Molecular Mechanics Modeling of the Configurational Isomer Distribution in Both Oxidation States

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A theoretical study of the electron-transfer process $[Co\{(\pm)\text{-pn}\}_3]^{3+} + e^- \rightleftharpoons [Co\{(\pm)\text{-pn}\}_3]^{2+}$ (pn = 1,2-propanediamine) based on molecular mechanics modeling of the relative strain energies of the configurational isomers available in each oxidation state leads to the prediction that four different $E°$ values may be expected between isostructural pairs. The four $E°$ values arising from the *lel*$_3$, *lel*$_2$*ob*, *ob*$_2$*lel*, and *ob*$_3$ configurations are calculated to lie within a range of 20 mV. That is, the values of the configurational equilibrium constants are different in the cobalt(III) and cobalt(II) oxidation states. Electrochemical reduction at mercury electrodes of the configurational isomers of $[Co\{(\pm)\text{-pn}\}_3]^{3+}$ demonstrates that the calculated range of $E°$ values is of the correct order of magnitude. However, more detailed theory and experiment correlations could not be made because of lack of resolution of electrochemical measurements and lack of independent experimental information on the numerous equilibrium and/or rate constants that accompany electron transfer. Electrochemical data are extremely dependent not only on the configurational form but also on the electrolyte, which further highlights the complexity of electron-transfer processes involving configurational change when considered in microscopic detail.

Introduction

Electron-transfer processes of the kind

$$A + R \rightleftharpoons B^{n-} + R^{n+} \tag{1}$$

(chemical redox process, R = reductant)

or the equivalent electrochemical process

$$A + ne^- \underset{}{\overset{\text{electrode}}{\rightleftharpoons}} B^{n-} \tag{2}$$

are quantified thermodynamically by an $E°$ value ($E°$ = standard redox potential) and kinetically by a self-exchange homogeneous rate of electron transfer (chemical redox process) or by k_s and α (k_s = standard heterogeneous rate constant for electron transfer at $E°$; α = charge-transfer coefficient) for electrochemical reduction. The theoretical relationship between homogeneous and heterogeneous electron-transfer rates can be described by the Marcus–Hush theory or other models of electron transfer.[4]

Spectroscopic, crystallographic, and other forms of examination of species A and B^{n-} (reactants and products of the electron-transfer process, respectively) reveal that configurational (conformational) changes may be associated with electron transfer in many instances; i.e., A and B^{n-} are not necessarily isostructural.

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(4) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980; references cited therein.

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