$$2\lambda_{\mathrm{ML_2,ML}} = 2\lambda_{\mathrm{ML_2,L}} = k_b[\mathrm{X}]^2 \qquad \text{(A8)}$$

$$\mathrm{d}M_L/\mathrm{d}t = -(\rho_L + k_f[\mathrm{ML}])M_L + \rho_L M^0{}_L + 0.5k_b[\mathrm{X}]^2 M_{\mathrm{ML_2}} \qquad \text{(A9)}$$

$$\mathrm{d}M_{\mathrm{ML}}/\mathrm{d}t = -(\rho_{\mathrm{ML}} + k_f[\mathrm{L}])M_{\mathrm{ML}} + \rho_{\mathrm{ML}} M^0{}_{\mathrm{ML}} + 0.5k_b[\mathrm{X}]^2 M_{\mathrm{ML_2}} \qquad \text{(A10)}$$

$$\mathrm{d}M_{\mathrm{ML_2}}/\mathrm{d}t = -(\rho_{\mathrm{ML_2}} + k_b[\mathrm{X}]^2)M_{\mathrm{ML_2}} + \rho_{\mathrm{ML_2}} M^0{}_{\mathrm{ML_2}} + k_f[\mathrm{L}]M_{\mathrm{ML}} + k_f[\mathrm{ML}]M_L \qquad \text{(A11)}$$

In the inversion-transfer experiment, magnetization at one site is selectively inverted and after some time *t* the magnetization at all the sites is nonselectively detected. For example, if the ML_2 magnetization is inverted then initially

$$M_{\mathrm{ML_2}} = -M^0{}_{\mathrm{ML_2}} \qquad M_L = M^0{}_L \qquad M_{\mathrm{ML}} = M^0{}_{\mathrm{ML}}$$

assuming perfect selectivity and inversion. Thus eqs A9–11 give the initial rates of change:

$$[\mathrm{d}M_L/\mathrm{d}t]_{t=0} = -k_f[\mathrm{ML}]M^0{}_L - 0.5k_b[\mathrm{X}]^2 M^0{}_{\mathrm{ML_2}} \qquad \text{(A12)}$$

$$[\mathrm{d}M_{\mathrm{ML}}/\mathrm{d}t]_{t=0} = -k_f[\mathrm{L}]M^0{}_{\mathrm{ML}} - 0.5k_b[\mathrm{X}]^2 M^0{}_{\mathrm{ML_2}} \qquad \text{(A13)}$$

$$[\mathrm{d}M_{\mathrm{ML_2}}/\mathrm{d}t]_{t=0} = 2\rho_{\mathrm{ML_2}} M^0{}_{\mathrm{ML_2}} + k_b[\mathrm{X}]^2 M^0{}_{\mathrm{ML_2}} + k_f[\mathrm{L}]M^0{}_{\mathrm{ML}} + k_f[\mathrm{ML}]M^0{}_L \qquad \text{(A14)}$$

Similar equations apply to the inversion of the magnetization of the other two resonances.

Exchange of Ni(II) and dppey was assumed to obey the following stoichiometry:

$$[\mathrm{Ni(dppey)X_2}] + \mathrm{dppey} \rightleftharpoons [\mathrm{Ni(dppey)_2X}]^+ + \mathrm{X}^-$$

The initial rate equations are the same as eqs A12–14, except that the concentration of X is not squared.

The experiment measures the initial rates of change of magnetization. The values of ρ_A $(=1/T_{1A})$ were measured independently, and signal intensities in the fully relaxed spectra gave $M^0{}_A$ and also enabled the equilibrium constant, *K*, to be determined. Thus the concentrations of the various species could be calculated from the total amounts added. Since $K = k_f/k_b$ at equilibrium, k_f and k_b could be calculated from eqs A12–14. When the magnetization of ML or L is inverted, two terms cancel in the expression for $(\mathrm{d}M_{\mathrm{ML_2}}/\mathrm{d}t)_{t=0}$ and k_b can be calculated without using the equilibrium constant.

Supplementary Material Available: Tabulations of the elemental analyses, magnetic data, IR data, electronic absorption data, and molar conductivities (6 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36849

Reactions of $[\mathrm{Ni(1,4,7\text{-}triazacyclononane)_2}]^{3+/2+}$ with the Components of Nitrous Acid

M. M. deMaine and D. M. Stanbury*

Received December 20, 1990

The reactions of $[\mathrm{Ni(tacn)_2}]^{3+}$ with some of the components of nitrous acid have been studied in aqueous solution at 25 °C. NO_2^- reacts to form $[\mathrm{Ni(tacn)_2}]^{2+}$ and NO_3^-, and the rate law is $-\mathrm{d}[\mathrm{Ni(tacn)_2}^{3+}]/\mathrm{d}t = k[\mathrm{Ni(tacn)_2}^{3+}][\mathrm{N(III)}]/(1 + [\mathrm{H}^+]/K_a)$ with $k = 212 \pm 7$ $\mathrm{M^{-1}\,s^{-1}}$ and $K_a = (9.6 \pm 1.1) \times 10^{-4}$ M at $\mu = 0.1$ M ($LiClO_4$). Electron transfer from NO_2^- to $[\mathrm{Ni(tacn)_2}]^{3+}$ is proposed as the rate-limiting step. In 0.79 mM NO, $[\mathrm{Ni(tacn)_2}]^{3+}$ reacts with the rate law $-\mathrm{d}[\mathrm{Ni(tacn)_2}^{3+}]/\mathrm{d}t = k'[\mathrm{Ni(tacn)_2}^{3+}] + k''[\mathrm{Ni(tacn)_2}^{3+}]/[\mathrm{H}^+]$ where $k' = (1.02 \pm 0.06) \times 10^{-3}$ $\mathrm{s^{-1}}$ and $k'' = (1.36 \pm 0.07) \times 10^{-4}$ M $\mathrm{s^{-1}}$ at $\mu = 1.0$ M ($LiClO_4$). The k'' pathway leads to destruction of the complex, presumably through nitrosation of the N-deprotonated conjugate base form of the Ni(III) reactant. The k' pathway is interpreted as an outer-sphere electron-transfer reaction between NO and $[\mathrm{Ni(tacn)_2}]^{3+}$.

Introduction

Rapid acid/base equilibria cause solutions of nitrous acid to contain HNO_2, NO_2^-, and NO^+, the relative concentrations depending on pH. Moreover, such solutions are unstable and soon contain significant quantities of NO, NO_2, NO_3^-, and other species. Many of these components of nitrous acid are quite reactive, so that the study of nitrous acid chemistry remains a fertile endeavor. Of interest in this paper are reactions in which the components of nitrous acid react by an outer-sphere electron-transfer mechanism, specifically, reactions in which the NO_2/NO_2^- and NO^+/NO redox couples participate.

Electron-transfer reactions involving the NO_2/NO_2^- couple have been investigated previously, and they serve as important examples of the class of triatomic redox couples. An effective self-exchange rate constant of 2×10^{-2} $\mathrm{M^{-1}\,s^{-1}}$ was derived by applying the cross relationship of Marcus' theory to a series of reactions with substitution-inert coordination compounds.[1] Although there was good consistency between the results for the various metal complexes, there was some basis for concern that the reactions were not truly outer sphere in that all the complexes had exposed lone pairs or π-systems that might interact specifically with the NO_2. More recently, a value of 580 $\mathrm{M^{-1}\,s^{-1}}$ was measured for the actual electron-transfer rate constant between NO_2 and NO_2^-.[2] The significant discrepancy between the effective and actual self-exchange rate constants, combined with the reservations expressed above regarding the nature of the cross-reactions, suggested the need for further study.

Electron-transfer reactions involving the NO^+/NO couple have not been studied as often as those of the NO_2/NO_2^- couple. Potentially, the system is of great interest because of the substantial difference in bond length between NO^+ and NO and because of the high force constants of those bonds. These factors could lead to a high degree of nuclear tunneling in electron-transfer reactions. We reported that the reaction of NO^+ with $IrCl_6^{3-}$ was diffusion-controlled and that this high rate required an inner-sphere mechanism.[3] In that paper, we reviewed the literature evidence for outer-sphere electron transfer involving the NO^+/NO couple and concluded that it was lacking. To our knowledge, the only subsequent report pertains to the reaction of NO^+ with $Re_2(CO)_{10}$ in CH_3CN, but this reaction is complicated by Re–Re bond cleavage.[4] Thus there is considerable motivation for investigating reactions of the NO^+/NO couple that are truly outer sphere.

To investigate genuine outer-sphere electron-transfer reactions of the NO_2/NO_2^- and NO^+/NO couples requires special properties of the redox partner. It must be substitution-inert, a strong oxidant, and a species with a strictly saturated ligand system. The $[\mathrm{Ni(tacn)_2}]^{3+/2+}$ system (tacn = 1,4,7-triazacyclononane) meets these requirements. An added benefit is its low self-exchange rate, which makes the cross-reaction rate constants quite sensitive to the intrinsic barriers of the NO_2/NO_2^- and NO^+/NO couples.

---

(1) Ram, M. S.; Stanbury, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 8136–8142.

(2) Stanbury, D. M.; deMaine, M. M.; Goodloe, G. *J. Am. Chem. Soc.* **1989**, *111*, 5496–5498.

(3) Ram, M. S.; Stanbury, D. M. *Inorg. Chem.* **1985**, *24*, 2954–2962.

(4) Schmidt, S. P.; Basolo, F.; Trogler, W. C. *Inorg. Chim. Acta* **1987**, *131*, 181–189.

0020-1669/91/1330-2104$02.50/0

The chemistry of tacn and related tridentate macrocyclic compounds of main-group and transition-metal elements has been reviewed by Chaudhuri and Wieghardt.[5] A complementary review by Lappin and McAuley[6] focuses on the redox chemistry of nickel. The present paper reports on the reactions of $[Ni(tacn)_2]^{3+}$ with NO_2^- and NO.

Experimental Section

Reagents. Distilled deionized water was obtained from a Barnstead Fi-Streem glass still. Lithium perchlorate ($LiClO_4{\cdot}3H_2O$) was prepared by neutralizing lithium carbonate (Fisher) with concentrated $HClO_4$, and recrystallizing the product three times from water. Solutions of lithium perchlorate were standardized by cation exchange with the acid form of Dowex 50W-X8 cation-exchange resin and titration against standardized NaOH solution. Sodium nitrite (MCB reagent grade) was recrystallized from aqueous ethanol with cooling from 80 to 0 °C. Phthalic acid (Eastman Kodak) was recrystallized from hot water. Argon for deaeration of solutions was purified by passage through a Catalyst Q1 column (Dow) and then through a tower containing water. Nitric oxide (Matheson) was scrubbed free of NO_2 by passing it through 0.5 M aqueous NaOH and a tube of Ascarite. All other materials were of certified or reagent grade.

Synthesis of Nickel Complexes. The method of McAuley et al.[7] was followed to prepare 1,4,7-triazacyclononane trihydrochloride and $[Ni(tacn)_2](ClO_4)_2$. This Ni(II) salt was dissolved in a minimum volume of 0.01 M $HClO_4$, and near-saturated aqueous sodium peroxydisulfate solution was added at 20 °C[8] until there was 0.6 mol of peroxy disulfate for each mole of Ni(II) species. An immediate color change from mauve-pink to yellow-brown was observed. A saturated aqueous solution of $NaClO_4$ was added dropwise with stirring at 20 °C until brown crystals of $[Ni(tacn)_2](ClO_4)_3$ began to form, and then the solution was cooled to 0 °C. The product was filtered, washed with a minimum of ethanol, and recrystallized by cooling a 65 °C saturated solution in 0.001 M $HClO_4$.

Analytical Methods. All UV–visible absorbance data were obtained with an HP 8452A spectrophotometer equipped with 10-mm quartz cells. pH measurements were made at room temperature on a Corning pH meter, Model 130, with a Ross combination electrode filled with 3 M NaCl. Some of the data for the reaction of NO with $[Ni(tacn)_2]^{3+}$ were collected at high ionic strength (μ = 1.0 M) in order to attain high acidities; for these reactions, the concentrations of H^+ were calculated by the titratable acid rather than from measured values of pH.

Quantitative determination of $[Ni(tacn)_2]^{2+}$ in solution (pH ≈ 2) was effected by its conversion to $[Ni(tacn)_2]^{3+}$ via a spectrophotometric titration with a dilute aqueous $KMnO_4$ solution quantitatively diluted from a stock solution, which was standardized with arsenious oxide.[9] To a measured volume of solution containing $[Ni(tacn)_2]^{2+}$ in a spectrophotometer cuvette were added successive 100-μL portions of $KMnO_4$ with absorbance at 312 nm being recorded after each addition. The measured absorbance values were normalized to a volume of 1.0 mL and plotted as a function of added $KMnO_4$. The plot rose steeply during the formation of $[Ni(tacn)_2]^{3+}$ and then more slowly due to the contribution from unreacted $KMnO_4$. $[Ni(tacn)_2]^{2+}$ is also oxidized by ceric ammonium sulfate, but this reaction is not suitable as a titration method because the endpoint is not stable, perhaps because of a reaction of $[Ni(tacn)_2]^{3+}$ with Ce(IV).

Ion chromatography analyses were performed on a Wescan Ion Chromatography System-II consisting of a Wescan Versa-Pump II, a Wescan Model 213 conductivity detector, and a Rheodyne Model 7125 syringe loading system with a 100-μL sample loop. Chromatograms were recorded on an Omni Scribe dual pen recorder. Measurements on aqueous solutions of known concentrations for each ion of interest provided the respective calibration plots. A Wescan Anion/R 25 cm column and 3 mM potassium biphthalate (pH 4) as eluant were used for nitrate and nitrite determinations. A Wescan Standard Cation column with an eluant of 0.5 mM ethylenediamine adjusted to pH 4 with tartaric acid served for Ni^{2+}–hydrate measurements.

Cyclic voltammograms and Osteryoung square wave voltammograms (OSWV)[10] were recorded on a BAS 100 electrochemical analyzer. The working and reference electrodes were glassy carbon and Ag/AgCl filled with 3 M NaCl, respectively. This reference electrode has a potential of 0.196 V vs NHE. Solutions were thermostated at 25.0 ± 0.1 °C. Calibration trials showed that peak current values from OSWV are linear with respect to the sum of the concentrations of $[Ni(tacn)_2]^{2+}$ and $[Ni(tacn)_2]^{3+}$. Interference by nitrite and nitrous acid in OSWV was eliminated by addition of sulfamic acid.

The kinetic data were collected on a Hi-Tech Scientific Model SF-51 stopped-flow apparatus, equipped with a SU-40 spectrophotometer unit and C-400 circulating water bath maintained at 25.0 ± 0.1 °C. The reactions were conducted at μ = 0.10 M ($LiClO_4$) with the buffers indicated in the tables of results. The absorbance decrease at 312 nm (consumption of $[Ni(tacn)_2]^{3+}$) was monitored. There were mixed equal volumes of Ni(III) in $(H/Li)ClO_4$ (μ = 0.1 M) and NO_2^- or NO in $LiClO_4$ plus the buffer salt (μ = 0.1 M) to give reaction mixtures with concentrations of ca. 0.1 mM Ni(III), 0.01 M buffer, 1–25 mM NO_2^-, and 0.87 mM NO (50% saturation).[11,12] For the reactions of NO at 1.0 M ionic strength, solutions of NO and $[Ni(tacn)_2]^{3+}$ were prepared in identical $(Li/H)ClO_4$ media and then mixed in the stopped-flow apparatus. At this ionic strength, the solubility of NO is only 1.58×10^{-3} M/atm, which gives a concentration of 0.79 mM in our reactions at μ = 1.0 M.[11,12]

The output from the SU-40 unit was collected by an On-Line Instrument Systems (OLIS) Model 3820 data acquisition system based on a North Star computer. Pseudo-first-order rate constants were evaluated by exponential fits on the North Star computer with OLIS subroutines. Values presented are averages of at least eight shots. Experiments performed in the later portions of this study employed an OLIS 4300S data acquisition system running on a Zenith 248/12 computer.

For experiments using NO the thermostated water bath surrounding the solution and drive syringes was continuously deaerated with nitrogen. The Ni(III) component solutions were sparged for at least 1 h with Ar. The buffer–ClO_4 component was connected to the gas purification train, and the entire system was flushed for an hour with high-purity N_2 prior to 12 min of vigorous bubbling with NO. Gastight syringes with Teflon Luer tips and platinum needles were employed for transfer of these solutions. The UV-vis spectrum of HNO_2 proved to be a convenient indicator of contamination by O_2, since HNO_2 is the product of the reaction of O_2 with NO. Some of the reactions of NO with $[Ni(tacn)_2]^{3+}$ had half-lives considerably longer than the usual time scale for stopped-flow experiments; the instrument was used nevertheless because of its excellent anaerobic sample handling. For the slowest reactions, data were collected for only the first half-life, and rate constants were obtained by fitting an exponential function constrained to a final absorbance of zero.

A modified version of the Los Alamos nonlinear least-squares computer program[13] (Gauss–Newton method) was used to fit the rate laws to the values of k_{obs}. The data were weighted as the inverse square of the dependent variable. Uncertainties are expressed as 1 standard deviation. A Macintosh II computer was used for the least-squares optimizations.

Results

Properties of the Compounds. Our $[Ni(tacn)_2](ClO_4)_2$ in 1 mM $HClO_4$ showed absorbance maxima at 326, 504, and 800 nm with ϵ = 5.3, 6.0, and 7.8 $M^{-1}\,cm^{-1}$, respectively. λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$), values for this compound were reported by McAuley et al.[7] to be 322 (11), 504 (11), and 799 (16) and, for the chloride salt, by Yang and Zompa[14] to be 310 (12), 500 (9), and 800 (9). We demonstrated a purity exceeding 95% for our $[Ni(tacn)_2](ClO_4)_2$ by spectrophotometric titration with $KMnO_4$. Yang and Zompa[14] noted a slow hydrolysis over a period of hours for solutions of this species in 1 M acid. We confirmed stability for hours via spectra and electrochemically for $[Ni(tacn)_2]^{2+}$ in solutions of neutral pH to pH 2 ($HClO_4$). UV-vis spectra for a 0.017 M solution of $[Ni(tacn)_2]^{2+}$ in 0.4 M $HClO_4$ showed a biphasic decay with $t_{1/2}$ = 50 min for the first phase. The intermediate is $[Ni(tacn)(H_2O)_3]^{2+}$, identified from its published spectrum (λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$) = 334 (5), 574 (4), 877 (sh), 961 (14)).[14] The final product is $[Ni(H_2O)_6]^{2+}$ for which we located a 393-nm peak (ϵ = 4.9 $M^{-1}\,cm^{-1}$) and a less intense very

---

(5) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329–436.
(6) Lappin, A. G.; McAuley, A. *Adv. Inorg. Chem.* **1988**, *32*, 241–295.
(7) McAuley, A.; Norman, P. R.; Olubuyide, O. *Inorg. Chem.* **1984**, *23*, 1938–1943.
(8) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Kuppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953–2956.
(9) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; Macmillan: New York, 1969; p 827.
(10) Osteryoung, J.; O'Dea, J. J. *Electroanal. Chem.* **1986**, *14*, 209–308.
(11) Armor, J. N. *J. Chem. Eng. Data* **1974**, *19*, 82–84.
(12) Schwartz, S. E.; White, W. H. *Adv. Environ. Sci. Eng.* **1981**, *4*, 1–45.
(13) Moore, R. H.; Zeigler, R. K. LSTSQR. Los Alamos National Laboratory, 1959.
(14) Yang, R.; Zompa, L. J. *Inorg. Chem.* **1976**, *15*, 1499–1502.

Table I. Kinetics of the Reaction between NO_2^- and $[Ni(tacn)_2]^{3+}$ [a]

[N(III)], mM	$[H^+]$, M	k_{obs}, s^{-1}	k_{calc}, s^{-1}
1.00	2.40×10^{-5} [b]	0.219	0.207
5.00	2.19×10^{-5} [b]	1.09	1.037
25.0	1.91×10^{-5} [b]	5.35	5.201
1.00	2.69×10^{-5} [b]	0.200	0.2064
5.00	2.51×10^{-5} [b]	1.04	1.034
25.0	2.09×10^{-5} [b]	5.01	5.191
1.00	2.63×10^{-4} [c]	0.159	0.1665
5.00	2.09×10^{-4} [c]	0.735	0.710
25.0	1.02×10^{-4} [c]	4.56	4.794
1.00	1.35×10^{-3} [d]	0.0810	0.08813
5.00	7.94×10^{-4} [d]	0.518	0.5804
25.0	2.19×10^{-4} [d]	3.74	4.318
1.00	5.62×10^{-5} [b]	0.208	0.2004
5.00	1.38×10^{-5} [b]	1.05	1.046
25.0	1.23×10^{-5} [b]	4.96	5.237
1.00	7.94×10^{-7} [e]	0.293	0.2120
5.00	8.32×10^{-7} [e]	1.34	1.060
25.0	8.71×10^{-7} [e]	5.71	5.299
1.00	4.90×10^{-3} [e]	0.0445	0.03473
5.00	2.24×10^{-3} [e]	0.350	0.3181
25.0	2.88×10^{-4} [e]	4.10	4.079

[a] $[Ni(tacn)_2^{3+}]_0$ = 0.1 mM; μ = 0.1 M ($LiClO_4$), 25 ± 0.1 °C. [b] Acetate buffer. [c] Formate buffer. [d] Phthalate buffer. [e] Histidine buffer.

broad band with a poorly defined maximum near 718 nm. Spectral changes for 0.015 M $[Ni(tacn)_2]^{2+}$ in 2.3 M $HClO_4$ showed a faster rate for this biphasic decay. Via Osteryoung square wave voltammetry (OSWV), a $t_{1/2}$ of 5 min was measured for breakdown of 0.5 mM $[Ni(tacn)_2]^{2+}$ in 2.3 M $HClO_4$.

Solutions of $[Ni(tacn)_2]^{3+}$ display equal intensity absorption maxima at 270 and 312 nm with a shallow minimum at 290 nm. The absorptivity at 312 nm for $[Ni(tacn)_2]^{3+}$, determined by spectrophotometric titration of $[Ni(tacn)_2]^{2+}$ with $KMnO_4$ at pH 2 ($HClO_4$), is $(8.8 \pm 0.3) \times 10^3$ M^{-1} cm^{-1}. Titration with $KMnO_4$ showed samples of solid $[Ni(tacn)_2](ClO_4)_3$ to be about 70% pure, with the balance being $[Ni(tacn)_2](ClO_4)_2$. For $[Ni(tacn)_2](ClO_4)_3$ there are published λ_{max}, nm (ϵ, M^{-1} cm^{-1}), values of 312 (10 100 ± 200)[7] and 312 (7200) and 570 (65).[8] Our value of ϵ is intermediate between these two reported values.

Spectral measurements showed $[Ni(tacn)_2]^{3+}$ to be stable in 0.02 M $HClO_4$ for at least several days and in 1 M $HClO_4$ for at least several hours. At pH 3.0, 4.0 ($HClO_4$/acetate), 4.6, and 6.4 (histidine buffer) decomposition was observed to be 5%/day, 3%/h, 10% in 10 min, and 50% in 4 min, respectively.

Electrochemical measurements have been important in understanding this Ni(III/II) system, which shows good reversibility by cyclic voltammetry. OSWV measurement for a solution of 0.1 mM $[Ni(tacn)_2](ClO_4)_2$ in 0.1 M $LiClO_4$–$HClO_4$ at pH 2.3 showed a peak potential of 750 mV vs Ag/AgCl. This gives a formal redox potential of E_f = 952 mV vs NHE, in good agreement with published values of 940,[7] 950,[8] and 947 mV.[15] We noted a slight increase in peak potential at decreased ionic strength that was qualitatively in agreement with the results of Buttafava et al.[16] The value of E_f dropped to 920 mV in 1.0 M $HClO_4$.

Stoichiometry. $[Ni(tacn)_2]^{3+} + NO_2^-$. This reaction was studied from pH 2 to pH 6 by procedures described above. UV–vis spectra showed complete consumption of $[Ni(tacn)_2]^{3+}$ under all conditions. OSWV demonstrated a 100% yield of $[Ni(tacn)_2]^{2+}$ in a system at pH 4.6 with $[Ni(tacn)_2]_0^{3+}$ = 0.1 mM, and $[N(III)]_0$ = 1 mM. Ion chromatography showed the yield of NO_3^- to be $(1.05 \pm 0.05) \times 10^{-4}$ M for a system at pH 4.6 with $[Ni(tacn)_2^{3+}]_0$ = 2.15×10^{-4} M, and $[N(III)]_0$ = 3.0×10^{-3} M.

Thus the overall reaction can be written as

$$2[Ni(tacn)_2]^{3+} + NO_2^- + H_2O \rightarrow 2[Ni(tacn)_2]^{2+} + NO_3^- + 2H^+ \quad (1)$$

Table II. Kinetics of the Reaction of $[Ni(tacn)_2]^{3+}$ with NO[a]

μ = 0.10 M		μ = 1.0 M	
pH	k_{obs}, s^{-1}	$[H^+]$, M	k_{obs}, s^{-1}
0.94	0.00592	1.00	0.00119
1.66	0.0252	0.50	0.00128
2.33	0.0940	0.20	0.00161
3.65[b]	1.83	0.100	0.00235
4.64[c]	17.5	0.050	0.00432
4.69[c]	17.4	0.020	0.00727
		0.010	0.0148

[a] $[Ni(tacn)_2^{3+}]_0$ = 1.0×10^{-4} M, background electrolyte = $LiClO_4$, 25.0 °C. [NO] = 8.7×10^{-4} M at μ = 0.1 M, and [NO] = 7.9×10^{-4} M at μ = 1.0 M. [b] Formate buffer. [c] Acetate buffer.

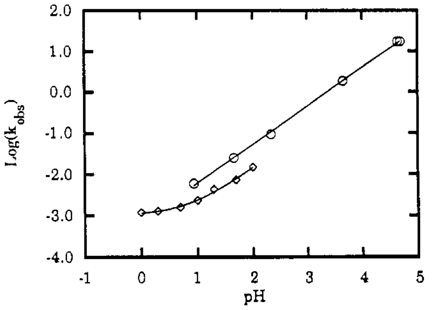

Figure 1. pH dependence of the kinetics of the reaction of NO with $[Ni(tacn)_2]^{3+}$. Conditions: 25.0 °C, [NO] = 8.7×10^{-4} M at μ = 0.1 M and 7.9×10^{-4} M at μ = 1.0 M, $[Ni(tacn)_2^{3+}]_0$ = 1.0×10^{-4} M, background electrolyte = $LiClO_4$. Acetate and formate buffers were used at pH 4.6 and 3.6, respectively. Circles represent data obtained at μ = 0.10 M; the solid line is a linear fit. Diamonds represent data at μ = 1.0 M with pH calculated as $-\log [H^+]$; the solid line is the fit of eq 4.

Kinetics. $2[Ni(tacn)_2]^{3+} + NO_2^-$. Kinetic measurements were conducted under pseudo-first-order conditions with [N(III)] ≫ $2[Ni(tacn)_2^{3+}]$. Semilog plots were linear over more than 5 half-lives. Pseudo-first-order rate constants, k_{obs}, defined by

$$-d[Ni(tacn)_2^{3+}]/dt = k_{obs}[Ni(tacn)_2^{3+}] \quad (2)$$

and obtained from exponential fits of the kinetic data are listed in Table I. The data fit the rate law

$$-\frac{d[Ni(tacn)_2^{3+}]}{dt} = \frac{k[Ni(tacn)_2^{3+}][N(III)]}{1 + [H^+]/K_a} \quad (3)$$

with $k = 212 \pm 7$ M^{-1} s^{-1} and $K_a = (9.6 \pm 1.1) \times 10^{-4}$ M.

Stoichiometry. $[Ni(tacn)_2]^{3+}$ + NO. Measurements on thoroughly deaerated systems (pH 1–4.6) by UV–visible spectra showed total consumption of $[Ni(tacn)_2]^{3+}$ by NO. No new absorbing Ni species were observed. For a system at pH 4.5, $[Ni(tacn)_2]^{2+}$ is at most only a minor product as demonstrated by OSWV and by $KMnO_4$ titration (pH lowered to 2.3 with $HClO_4$ after reaction and prior to titration). By these two techniques it was observed that $[Ni(tacn)_2]^{2+}$ remains unchanged in the reaction procedure with NO, both in the presence and absence of $[Ni(tacn)_2]^{3+}$. Ion chromatography showed $[Ni(H_2O)_6]^{2+}$ is not a product of NO reaction with $[Ni(tacn)_2]^{3+}$ but that there is an unidentified cation product species which elutes soon after $[Ni(H_2O)_6]^{2+}$, which was added to the product mixture as a marker just prior to injection into the ion chromatograph.

No attempt was made to determine the products of the reaction under highly acidic conditions, because the presumed product, $[Ni(tacn)_2]^{2+}$, undergoes hydrolysis on the same time scale as its generation.

Kinetics. $[Ni(tacn)_2]^{3+}$ + NO. Under all conditions investigated the anaerobic reaction of $[Ni(tacn)_2]^{3+}$ with a large excess of NO showed excellent pseudo-first-order kinetics. The data collected at μ = 0.1 M are presented in Table II. A plot of log k_{obs} vs pH, as in Figure 1, shows that this reaction is inverse order with respect to $[H^+]$ (defined as 10^{-pH}), with the slope being 0.94. The order with respect to [NO] was not investigated. The reaction rate at

---

(15) McAuley, A.; Norman, P. R.; Olubuyide, O. *J. Chem. Soc., Dalton Trans.* **1984**, 1501–1505.

(16) Buttafava, A.; Fabrizzi, L.; Perotti, A.; Poggi, A.; Poli, G.; Seghi, B. *Inorg. Chem.* **1986**, *25*, 1456–1461.

pH 4.6 was unaffected by a 5-fold increase in acetate concentration or by the addition of $[Ni(tacn)_2](ClO_4)_2$ at a concentration 10-fold greater than the $[Ni(tacn)_2{}^{3+}]_0$. The deviation of the slope in Figure 1 from unity, coupled with the small systematic deviations from linearity, suggested the presence of a small term in the rate law that is independent of $[H^+]$. A fit of the rate law

$$k_{obs} = k' + k''/[H^+] \tag{4}$$

resulted in values of $k' = (2.66 \pm 0.67) \times 10^{-3}$ s^{-1} and $k'' = (4.03 \pm 0.21) \times 10^{-4}$ M s^{-1} at $\mu = 0.1$ M. Thus, the k' term is of marginal significance but the k'' term is quite well-defined.

By OSWV, it was demonstrated that reaction of a mixture of 0.1 mM $[Ni(tacn)_2]^{3+}$, 8.7×10^{-4} M NO, and 1.0 mM NO_2^- at pH 4.6 does not yield $[Ni(tacn)_2]^{2+}$, the product of reaction with NO_2^- alone. k_{obs} for each of these reducing agents is 15 s^{-1} for NO and 0.22 s^{-1} for NO_2^-. Thus in the mixed system, the faster reaction predominates. This provides assurance that the fit of eq 4 is not affected by the unavoidable minor NO_2^- contaminant introduced during NO saturation.

In order to learn more about the k' term in rate law 4, the reaction was investigated at 1.0 M ionic strength. Under these conditions, the decays also obeyed pseudo-first-order kinetics. However, the rates were systematically lower, as would be expected for a reaction first order in a +3 cation (Ni(III)) and inverse order in a +1 cation (H^+). Moreover, as is shown in Table II and Figure 1, the approach to a limiting rate constant at high acid concentrations became unmistakable. A fit of rate law 4 to data spanning 0.01–1.0 M H^+ (the titratable concentration of H^+) gave values of $k' = (1.02 \pm 0.06) \times 10^{-3}$ s^{-1} and $k'' = (1.36 \pm 0.07) \times 10^{-4}$ M s^{-1} at $\mu = 1.0$ M. The difference between the k' values at the two ionic strengths reflects the high degree of uncertainty in the value at $\mu = 0.1$ M and (presumably) the lower solubility of NO at the higher ionic strength.[11] Because of the difficulties in sample handling, especially for the slower reactions, the dependence on [NO] was not investigated.

Reaction of $[Ni(tacn)_2]^{2+}$ + HNO_2. UV–vis spectra recorded over 30 min showed no formation of $[Ni(tacn)_2]^{3+}$ in a solution containing $[Ni(tacn)_2{}^{2+}]_0 = 8.6 \times 10^{-3}$ M, $[N(III)] = 0.014$ M, and $[HClO_4] = 0.114$ M, but did indicate a 30% decrease in absorbance due to $[Ni(tacn)_2]^{2+}$ decomposition.

Discussion

Reduction by Nitrite. Of the various reactions reported in this paper, the reduction of $[Ni(tacn)_2]^{3+}$ by nitrite is the least unusual. Nevertheless, it is still of interest because it is the first report of electron transfer from NO_2^- in a reaction that is rigorously outer sphere. The presumed mechanism is typical of such reactions and is

$$HNO_2 \rightleftarrows H^+ + NO_2^- \quad K_a \tag{5}$$

$$[Ni(tacn)_2]^{3+} + NO_2^- \rightleftarrows [Ni(tacn)_2]^{2+} + NO_2 \quad k, k_r \tag{6}$$

$$2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \quad k_{dis}\ \text{(fast)} \tag{7}$$

This mechanism leads to the observed stoichiometry, and under the approximation that k_r can be neglected, rate law 3 can also be derived. The value of K_a derived from the fit of rate law 3 to the data gives a value for K_a of 9.6×10^{-4} M, which compares favorably with the literature value of 1.1×10^{-3} M.[1] A value for k_r can be calculated by use of $E_f = 0.952$ V for the $[Ni(tacn)_2]^{3+/2+}$ redox couple and $E° = 1.04$ V for the NO_2/NO_2^- couple.[3,17] These two reduction potentials lead to a value of $k/k_r = 3.3 \times 10^{-2}$, and thus a value of 6.5×10^3 M^{-1} s^{-1} is derived for k_r. In comparison with the literature value of k_{dis} ($=6.5 \times 10^7$ M^{-1} s^{-1}),[18] such a low value of k_r justifies the neglect of k_r in the derivation of rate law 3, and it explains why product inhibition is not observed.

Table III. Marcus Cross-Relationship for NO_2/NO_2^- Reactions[a]

oxidant	$E°$, V	k_{12}, M^{-1} s^{-1}	k_{22}, M^{-1} s^{-1}	r, Å	$k_{11,calc}$, M^{-1} s^{-1}
$[Fe(tmp)_3]^{3+}$	0.84	3.8×10^3	5×10^9	6.5	0.81
$[Fe(bpy)_3]^{3+}$	1.06	6.5×10^4	5×10^8	6.0	0.18
$Fe(CN)_6{}^{3-}$	0.34	2.1×10^{-5}	5×10^3	4.5	0.12
$IrCl_6{}^{2-}$	0.892	19.6	2×10^5	4.4	0.21
$IrBr_6{}^{2-}$	0.843	57	2×10^8	4.7	0.017
$Ru(CN)_6{}^{3-}$	0.92[b]	24[b]	8×10^3 [b]	4.7	0.55
$[Ni(tacn)_2]^{3+}$	0.952[c]	2.1×10^2 [c]	6×10^3 [d]	3.8	5.1

[a] $r_{NO_2} = 1.9$ Å. All data from ref 1 except as noted. [b] Reference 20. [c] This work. [d] Reference 15.

There are reports of oxidation of NO_2^- by other oxidants that have been assigned an analogous mechanism, and notable among these are the oxidations by $[Fe(tmp)_3]^{3+}$ (where tmp = 3,4,7,8-tetramethylphenanthroline),[1] $[Fe(bpy)_3]^{3+}$, $IrCl_6{}^{2-}$, $IrBr_6{}^{2-}$,[19] and $Ru(CN)_6{}^{3-}$.[20] In the reaction of $[Fe(tmp)_3]^{3+}$, a significant inhibitory effect of $[Fe(tmp)_3]^{2+}$ was observed and was accurately simulated by using numerical integration of the complete set of differential equations. These calculations used the literature value for the NO_2 disproportionation rate constant and a reverse rate constant for the electron-transfer step that was required by the known reduction potentials of the two reactants ($k_r = 3 \times 10^6$ M^{-1} s^{-1}). Direct measurement of k_r reported in a subsequent publication confirmed these results.[3] The success of these simulations is probably the most conclusive evidence to date that the general mechanism is correct.

Interest in $[Ni(tacn)_2]^{3+}$ as an oxidant derives from the imposed outer-sphere character of its reactions. This arises from the fact that it is substitution-inert on the time scale of the redox reactions and the fact that it presents a completely saturated ligand environment. Oxidations of nitrite by $[Fe(tmp)_3]^{3+}$, $[Fe(bpy)_3]^{3+}$, $IrCl_6{}^{3-}$, $IrBr_6{}^{2-}$, and $Ru(CN)_6{}^{3-}$ have been reported and have an outer-sphere mechanism by the criterion of ligand substitution. On the other hand, these species do present exposed lone pairs and π-systems, and hence their reactions may still have significant inner-sphere character. Rate constants for these reactions are presented in Table III, along with that for the reaction of $[Ni(tacn)_2]^{3+}$. The reaction of $Fe(CN)_6{}^{3-}$ is also listed in Table III, although the indicated rate constant is actually calculated from the pulse radiolytically measured reverse rate constant.[21] Of all these reactions only that of $[Ni(tacn)_2]^{3+}$ can be confidently assigned a strictly outer-sphere electron-transfer mechanism.

It is of some interest to examine whether the strict imposition of an outer-sphere mechanism in the case of the reaction with $[Ni(tacn)_2]^{3+}$ has any measurable effect. Such an effect would be exhibited as a smaller electron-transfer rate constant than would be observed if the reaction had some inner-sphere character. An alternative treatment is to calculate effective self-exchange rate constants for the NO_2/NO_2^- couple by use of the cross-relationship of the Marcus theory. Inner-sphere character would be expected to lead to increased effective self-exchange rate constants. The usual equations for such calculations are[22]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{8}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln (k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]} \tag{9}$$

$$W_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT] \tag{10}$$

$$w_{ij} = (4.23 \times 10^{-8}Z_iZ_j)/(a(1 + 3.28 \times 10^7 a(\mu^{1/2}))) \tag{11}$$

In these equations k_{11} is the self-exchange rate constant for the NO_2/NO_2^- couple, k_{22} is the analogous value for the metal complex couple, k_{12} is the observed rate constant for electron transfer from NO_2^- to the oxidant, and K_{12} is the cross-elec-

---

[17] Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69–138.

[18] Schwartz, S. E.; White, W. H. In *Trace Atmospheric Constituents: Properties, Transformations, & Fates*; Schwartz, S. E., Ed.; Wiley: New York, 1983; pp 1–116.

[19] Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983**, *51*, 155–179.

[20] Hoddenbagh, J. M. A.; Macartney, D. H. *Inorg. Chem.* **1990**, *29*, 245–251.

[21] Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027–1284.

[22] *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 15, pp 13–47.

tron-transfer equilibrium constant. Z is the collision rate constant, taken as 10^{12} M^{-1} s^{-1}, a is the center-to center distance (cm), and R is the gas constant (kcal mol^{-1} K^{-1}). These equations have been used to calculate the values of k_{11} given in Table III. Similar calculations were previously reported for the first five reactions in Table III,[1] but the derived values of k_{11} are smaller than those presently reported by a factor of about 8. The difference is due to a change in the selected value of $E°$ for the NO_2/NO_2^- couple and a change in the value for Z.

One outlier in Table III is the reaction of $IrBr_6^{2-}$. There is some concern that the value of k_{22} used in this calculation may be in error, because problems related to the facile hydrolysis of $IrBr_6^{3-}$ may not have been eliminated in the original study. The other outlier is the reaction of $[Ni(tacn)_2]^{3+}$, which has a large calculated value of k_{11}. The reason for this deviation cannot be due to inner-sphere character in the other reactions, because this would lead to a smaller rather than a larger value of k_{11}. A plausible explanation may arise from the fact that the value of k_{22} used in the calculation for the reaction of $[Ni(tacn)_2]^{3+}$ was obtained at 1.0 M ionic strength. In any event, the deviation is not large.

One important outcome of these calculations is that there is no evidence for inner-sphere character in any of the reactions analyzed in Table III. Another is that a value of 0.3 M^{-1} s^{-1} is now the best present estimate of the effective self-exchange rate constant for the NO_2/NO_2^- redox couple. This result may be compared with our recent direct determination of the actual self-exchange rate constant between NO_2 and NO_2^- (k_{11} = 580 M^{-1} s^{-1}).[2] An explanation for the 2000-fold increase in rate constant for the direct self-exchange reaction may be that the direct reaction has significant inner-sphere character (strong overlap). A somewhat smaller enhancement of the direct self-exchange rate constant relative to effective values was recently found for the O_2/O_2^- system.[23] These workers attributed the enhancement to nonadditivity of the solvent reorganization barrier for reactions where the ionic radii are highly disparate. It is not yet clear which of these two effects is dominant.

Our upward revision of the self-exchange rate constant for the NO_2/NO_2^- couple[1] affects certain prior discussions of reactions of NO_2^-.[24-26] It reduces the discrepancy between the measured and calculated rate constants for the reaction of ClO_2 with NO_2^-,[25] and it decreases the contribution of solvent reorganization in calculations of the total reorganizational barrier to the NO_2/NO_2^- self-exchange reaction.[24,26]

Reduction by Nitric Oxide. Our study of the reaction of $[Ni(tacn)_2]^{3+}$ with NO was undertaken with the expectation that it would provide an unambiguous example of outer-sphere oxidation of NO. Such a reaction should exhibit pH-independent kinetics. However, our initial studies at low ionic strength revealed a strong inverse-acid dependence. Only at the higher acidities attainable at high ionic strength was an acid-independent term discernible in the rate law. The kinetic dependence on [NO] was not investigated because of the difficulties in sample handling, but if it is assumed that both terms in the rate law are first-order with respect to [NO], then the complete rate-law is

$$-d[Ni(tacn)_2{}^{3+}]/dt = k_1[NO][Ni(tacn)_2{}^{3+}] + k_2[NO][Ni(tacn)_2{}^{3+}]/[H^+] \quad (12)$$

with k_1 = 1.29 ± 0.08 M^{-1} s^{-1} and k_2 = (1.72 ± 0.08) × 10^{-1} s^{-1} at 25 °C and 1.0 M ionic strength.

The probable mechanism for the k_2 pathway is

$$[Ni^{III}(tacn)_2]^{3+} \rightleftarrows [Ni^{III}(tacn)(tacn(-H))]^{2+} + H^+ \quad K_{cb} \quad (13)$$

$$[Ni^{III}(tacn)(tacn(-H))]^{2+} + NO \rightarrow [Ni^{II}(tacn)(tacn\text{-}NO)]^{2+} \quad k_n \quad (14)$$

This mechanism leads to the k_2 term in rate law 12 if $k_2 = K_{cb}k_n$, and it explains the fact that $[Ni(tacn)_2]^{2+}$ is not a reaction product under the pH conditions where the k_2 term is dominant. In this mechanism the species $[Ni^{III}(tacn)(tacn(-H))]^{2+}$ represents the N-deprotonated conjugate base form of $[Ni^{III}(tacn)_2]^{3+}$. A pK_a value of 11.4 has been reported for the analogous deprotonation of $[Fe(tacn)_2]^{3+}$,[27] and a pK_a value of 9-11 has been reported for $[Ru(tacn)_2]^{3+}$.[28] It is entirely reasonable to expect $[Ni(tacn)_2]^{3+}$ to show similar behavior, but the conjugate-base form has not been observed because the complex decomposes in alkaline media.

The second step represents attack of NO on the lone pair of the conjugate base along with internal electron transfer to form a coordinated nitrosamine. A precedent for this reaction is found in the work of Pell and Armor, in which it was reported that $[Ru^{III}(en)_3]^{3+}$ reacts with NO in alkaline media to give $[Ru^{II}(en)_2N_2(H_2O)]^{2+}$ along with decomposition of the coordinated en ligand.[29] Nitrosamines absorb only weakly in the near-UV and visible regions,[30] and this explains why the presumed product in reaction 14 was not detected.

A conceivable alternative mechanism for the k_2 term is

$$NO + OH^- \rightleftarrows HNO_2^- \quad (15)$$

$$HNO_2^- + [Ni(tacn)_2]^{3+} \rightarrow \text{products} \quad (16)$$

A species of the form HNO_2^- has indeed been inferred in certain reactions of HNO_2 and in the pulse radiolysis of HNO_2.[17] However, the most likely products of a reaction between this species and $[Ni(tacn)_2]^{3+}$ would be HNO_2 and $[Ni(tacn)_2]^{2+}$, which definitely are not the actual products of the k_2 term. Moreover, the possibility of hydrolysis of NO as indicated in reaction 15 has been investigated by measuring the solubility of NO in the range from pH 2 to pH 13: no enhanced solubility in base was discovered.[11] For these reasons the mechanism involving nitrosamine formation through the conjugate base form of $[Ni(tacn)_2]^{3+}$ is considered much more likely.

The proposed mechanism for the k_1 term is

$$[Ni(tacn)_2]^{3+} + NO \rightleftarrows [Ni(tacn)_2]^{2+} + NO^+ \quad k_1, k_{-1} \quad (17)$$

$$NO^+ + H_2O \rightarrow HNO_2 + H^+ \quad k_{hyd} \text{ (fast)} \quad (18)$$

Under the approximation that k_{hyd} is fast relative to k_{-1}, the k_1 term in rate law 12 is derived. A value of k_{-1} = 1.0 × 10^5 M^{-1} s^{-1} can be derived from the relation $k_1/k_{-1} = K_{eq}$, the measured value of k_1, and the calculated value for K_{eq} of 1.2 × 10^{-5}. This latter value was obtained from E_f = 0.920 V at μ = 1.0 M for the $[Ni(tacn)_2]^{3+/2+}$ couple and the literature value of 1.21 V for $E°$ for the NO^+/NO couple.[17] The low calculated value of k_{-1} is adequate to justify neglecting k_{-1} relative to k_{hyd}.

This appears to be the first report of outer-sphere electron transfer from nitric oxide. One related study is the report of the reaction of NO with $IrCl_6^{2-}$, in which it was concluded that the reaction was really inner sphere in that there is significant Cl–N bonding in the transition state.[3] Another related study included the reaction of NO with $[Fe(tmp)_3]^{3+}$, where a peculiar pH dependence was observed and the rates were argued to be too fast for an electron-transfer mechanism.[1] Kinetic studies of aqueous NO reactions are quite rare, presumably because of handling difficulties.

Studies of the reverse process, outer-sphere electron transfer to NO^+, are not conclusive. Oxidation of $Re_2(CO)_{10}$ in CH_3CN appears to be an outer-sphere process,[4] but it is complicated by the associated cleavage of the Re–Re bond. Nitrous acid oxidation of $[HFe(CN)_6]^{3-}$ and $[Fe(phen)_2(CN)_2]$ in aqueous solution has been argued to proceed through NO^+,[31,32] but these reactions may

---

(23) Lind, J.; Shen, X.; Merenyi, G.; Jonsson, B. O. *J. Am. Chem. Soc.* **1989**, *111*, 7654–7655.
(24) Bennett, L. E.; Warlop, P. *Inorg. Chem.* **1990**, *29*, 1975–1981.
(25) Stanbury, D. M.; Martinez, R.; Tseng, E.; Miller, C. E. *Inorg. Chem.* **1988**, *27*, 4277–4280.
(26) Stanbury, D. M.; Lednicky, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 2847–2853.
(27) Pohl, K.; Wieghardt, K.; Kaim, W.; Steenken, S. *Inorg. Chem.* **1988**, *27*, 440–447.
(28) Bernhard, P.; Anson, F. C. *Inorg. Chem.* **1988**, *27*, 4574–4577.
(29) Pell, S.; Armor, J. N. *J. Chem. Soc., Chem. Commun.* **1974**, 259–260.
(30) Rao, C. N. R.; Bhaskar, K. R. In *The Chemistry of the Nitro and Nitroso Groups, Part 1*; Feuer, H., Ed.; Robert E. Krieger Publishing Co.: Huntington, NY, 1981; pp 137–163.
(31) Bates, J. C.; Reveco, P.; Stedman, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1487–1488.
(32) Reveco, P.; Stedman, G. *Fresenius' Z. Anal. Chem.* **1979**, *295*, 252–255.

well have significant inner-sphere character. Thus the present reaction, oxidation of NO by [Ni(tacn)$_2$]$^{3+}$, appears to be the best candidate for discussion as an example of outer-sphere electron transfer involving the NO$^+$/NO redox couple.

An analysis of the rate constant for the outer-sphere reaction of NO with [Ni(tacn)$_2$]$^{3+}$ in terms of the cross-relationship of Marcus' theory, as in eqs 8–11, leads to a value of 5 M^{-1} s^{-1} for the effective self-exchange rate constant of the NO$^+$/NO system. For this analysis, a value of 1.77 Å was selected as the radius of NO and NO$^+$. It is inappropriate to give extensive discussion to the magnitude of this self-exchange rate constant until the result is confirmed with other oxidants. However, the low value does imply a significant barrier, and it is qualitatively consistent with the predictions of Eberson and Radner[33] and the electrochemical kinetics results of Lee, Kuchynka, and Kochi.[34]

Conclusions. Nitrite is oxidized by [Ni(tacn)$_2$]$^{3+}$ with rate-limiting electron transfer. This result, combined with a slightly revised potential for the NO$_2$/NO$_2^-$ couple, leads to a revised estimate of the effective self-exchange rate constant for the NO$_2$/NO$_2^-$ couple. The reaction of NO with [Ni(tacn)$_2$]$^{3+}$ is unique in the chemistry of this coordination compound, since it can lead to destruction of the complex via its conjugate-base form. In highly acidic media there is a direct reaction between NO and [Ni(tacn)$_2$]$^{3+}$, and this is interpreted as the first example of outer-sphere electron transfer from NO in homogeneous solution.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant No. CHE-8913734. Thanks are due to Ms. Elizabeth Kage for conducting preliminary studies in this area.

---

(33) Eberson, L.; Radner, F. *Acta Chem. Scand., B* **1984**, *38*, 861–870.

(34) Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196–4204.

Contribution from the Departments of Chemistry, Wayne State University, Detroit, Michigan 48202,
and the University of Wisconsin—Eau Claire, Eau Claire, Wisconsin 54701

Macrocyclic Polyamino Polythiaether Ligands with N_xS_{4-x} and N_xS_{5-x} Donor Sets: Protonation Constants, Stability Constants, and Kinetics of Complex Formation with the Aquocopper(II) Ion

Bryan C. Westerby,[1a] Kerri L. Juntunen,[1a] Gregory H. Leggett,[1a] Virginia B. Pett,[1a]
Michael J. Koenigbauer,[1a] Mark D. Purgett,[1b] Michael J. Taschner,[1b] L. A. Ochrymowycz,[1b]
and D. B. Rorabacher*[,1a]

Received July 3, 1990

The entire series of 14-membered macrocyclic ligands containing the N_xS_{4-x} donor set (where x = 1, 2, 3) with alternating ethylene and propylene bridging groups and two related 15-membered macrocycles with the N_xS_{5-x} donor set (where x = 1, 2) containing only ethylene bridging groups have been characterized in terms of their protonation constants, Cu(II) complex stability constants, and complex formation kinetics with aquocopper(II) ion in aqueous solution at 25 °C. These data are compared to the properties of the corresponding homoleptic ligands [14]aneS$_4$, [14]aneN$_4$ (i.e., cyclam), [15]aneS$_5$, and [15]aneN$_5$ in an attempt to shed further light on the effects of ligand cyclization upon the thermodynamics and the mechanism of metal complex formation. The logarithmic values of the aqueous mixed-mode protonation constants (defined as $K_{\mathrm{H}n}{}^{\mathrm{m}} = [\mathrm{H}_n\mathrm{L}^{n+}]/a_{\mathrm{H}}[\mathrm{H}_{n-1}\mathrm{L}^{(n-1)+}]$) at 25 °C, μ = 0.10 M, are as follows (listed in the order log $K_{\mathrm{H1}}{}^{\mathrm{m}}$ and, where applicable, log $K_{\mathrm{H2}}{}^{\mathrm{m}}$, log $K_{\mathrm{H3}}{}^{\mathrm{m}}$; values in parentheses represent standard deviations within a single determination, while italicized values in braces represent standard deviations among several *replicate* determinations): [14]aneNS$_3$, 8.75 (±0.02); [14]aneN$_2$S$_2$, 9.41 {*±0.23*}, 5.69 {*±0.34*}; [14]aneNSSN, 9.71 {*±0.17*}, 6.60 {*±0.14*}; [14]aneNSNS, 9.78 (±0.12), 8.16 (±0.08); [14]aneN$_3$S, 9.66 (±0.08), 8.24 (±0.12), 2.53 (±0.02); [15]aneNS$_4$, 8.14 (±0.07); [15]aneN$_2$S$_3$, 8.70 (±0.01), 5.16 (±0.01). The corresponding logarithmic stability constants for the Cu$^{\mathrm{II}}$L complexes (log $K_{\mathrm{Cu^{II}L}}$) are as follows: [14]aneNS$_3$, 9.25; [14]aneN$_2$S$_2$, 15.26; [14]aneNSSN, 15.72; [14]aneNSNS, 15.15; [14]aneN$_3$S, >18; [15]aneNS$_4$, 9.80; [15]aneN$_2$S$_3$, 16.02. The specific rate constants for the reaction of aquocopper(II) ion with the various protonated ligand species were resolved as follows (listed in the order $k_{\mathrm{Cu}}{}^{\mathrm{L}}$, $k_{\mathrm{Cu}}{}^{\mathrm{HL}}$, and, where applicable, $k_{\mathrm{Cu}}{}^{\mathrm{H_2L}}$, the superscript indicating the degree of protonation of the ligand; all values in M^{-1} s^{-1}): [14]aneNS$_3$, (3.2 ± 0.2) × 10^6, (1.4 ± 0.3) × 10^2; [14]aneN$_2$S$_2$, (1.6 ± 0.1) × 10^8, (1.3 ± 0.6) × 10^3; [14]aneNSSN, (8.2 ± 0.6) × 10^7, (5 ± 2) × 10^3; [14]aneNSNS, (2.0 ± 0.4) × 10^9, (2.9 ± 0.7) × 10^5; [14]aneN$_3$S, $k_{\mathrm{Cu}}{}^{\mathrm{L}}$ not evaluated, (3.1 ± 0.1) × 10^5, 51 ± 13; [15]aneNS$_4$, (8.4 ± 0.4) × 10^6, (1.4 ± 0.3) × 10^3; [15]aneN$_2$S$_3$, (8 ± 2) × 10^7, (2.5 ± 0.1) × 10^5. For unprotonated ligands containing a single nitrogen donor atom, the rate-determining step in the complex formation with aquocopper(II) ion comes at the point of the first coordinate bond formation involving a nitrogen donor atom, with the values being essentially identical with those for corresponding open-chain ligands. This implies that the increased stability constants commonly observed for macrocyclic ligand complexes arise directly from a reduction of the dissociation rate constants. In the case of monoprotonated ligand species, the complex formation rate constants are generally much smaller than corresponding open-chain species, although this effect varies by several orders of magnitude for ligands with the same donor set, depending upon the specific arrangement of the donor atoms within the macrocyclic ring. The results of the current studies indicate that the reaction kinetics of the unprotonated, mono- and diprotonated species of macrocyclic ligands yield differing information about the fundamental mechanistic consequences of simple ligand cyclization.

Introduction

The enhanced stability of metal ion complexes formed with macrocyclic ligands compared to those formed with analogous open-chain species has been termed the "macrocyclic effect"[2] and has sparked much interest in the study of cyclic ligand complexes. Thermodynamic studies indicate that these stability constant differences arise primarily from two properties associated with the *uncomplexed* macrocyclic ligands: (i) the diminished flexibility of free macrocyclic ligands, resulting in a less negative *entropy* term upon complexation[2-4] and, (ii) in the case of ligands with hydrogen-bonding donor atoms in protolytic solvents, the diminished solvation of the free macrocyclic ligands relative to their

---

(1) (a) Wayne State University. (b) University of Wisconsin—Eau Claire.

(2) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 6540–6541.

(3) Sokol, L. S. W. L.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1981**, *20*, 3189–3195.

(4) Cooper has specifically noted that structural constraints within many macrocyclic ligands may predispose the ligands toward geometries that diminish the entropy associated with complex formation: (a) Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1989**, *72*, 1–72.

0020-1669/91/1330-2109$02.50/0 © 1991 American Chemical Society