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# Diffusive Separation and Associative Electron Transfer in the Oxidation of Thiocyanate by Bis(1,4,7-triazacyclononane)nickel(III)

**Mei-Ling Hung and David M. Stanbury**[*]

Department of Chemistry, Auburn University, Auburn, Alabama 36849

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Oxidation of excess thiocyanate by $[Ni(tacn)_2]^{3+}$ shows kinetic inhibition by the product, $[Ni(tacn)_2]^{2+}$, and with a large excess of Ni(II) the reaction exhibits pseudo-second-order behavior. In the presence of the spin trap DMPO, the rate law is pseudo first order with $k_{obs} = (2k_1[SCN^-] + 2k_2[SCN^-]^2)$ at pH 3, $\mu = 0.1$ M, and 25 °C. The rate constants are $k_1 = 0.046 \pm 0.003$ $M^{-1}\,s^{-1}$ and $k_2 = 2.04 \pm 0.012$ $M^{-2}\,s^{-1}$. Under these conditions inhibition by Ni(II) is significant only at relatively high Ni(II) concentrations. On the basis of a LFER, the magnitude of $k_1$ confirms that it represents electron transfer to form Ni(II) and the SCN radical, with diffusive product separation as the rate-limiting step. The $k_2$ step is interpreted as corresponding to formation of Ni(II) and the radical $(SCN)_2^-$ with electron transfer concerted with S—S bond formation.

## Introduction

About ten years ago we proposed that bimolecular oxidations of small inorganic molecules by substitution-inert complexes could be divided into two classes.[1] One (fast) class comprised oxidations of $I^-$, $N_3^-$, $S_2O_3^{2-}$, and $SCN^-$, while the other (slow) included oxidations of $NO_2^-$ and $SO_3^{2-}$. The first class was characterized by rate constants that were limited by diffusive separation of the electron-transfer products, and the other, by electron transfer per se as the rate-limiting step. These differences were attributed to the electronic states of the free radical intermediates: nonbonding HOMOs led to minimal structural reorganization for the fast class, and antibonding HOMOs in the slow class led to significant reorganizational barriers. This classification has been eroded by the report that several oxidations of $N_3^-$ have rate-limiting electron transfer[2] and by the recent report that the oxidation of $S_2O_3^{2-}$ by $[Ni(tacn)_2]^{3+}$ (tacn = 1,4,7-triazacyclononane) also has rate-limiting electron transfer.[3] The present report, in part, reexamines the reactivity of $SCN^-$ in this context.

Another interesting feature of oxidations of $SCN^-$ by substitution-inert complexes is that they often show overall third-order terms in their rate laws: first order with respect to [oxidant] and second order with respect to $[SCN^-]$;[4] the radical $(SCN)_2^-$ is inferred to be an intermediate in these pathways. The mechanistic issue here is whether electron transfer occurs with simultaneous S—S bond formation or whether these two processes occur consecutively.[4]

As a probe of these two issues, we have chosen to examine the oxidation of $SCN^-$ by $[Ni(tacn)_2]^{3+}$. Our understanding of this oxidant is quite well developed[5–8] because of the discovery of nickel in several enzymes.[9–14] Both $[Ni(tacn)_2]^{3+}$ and $[Ni(tacn)_2]^{2+}$ are substitution-inert, and they constitute a redox couple with a high reduction potential (0.94 V).[15] Since the coordinated tacn ligand provides no potential binding sites, $[Ni(tacn)_2]^{3+}$ can be anticipated to react through outer-sphere electron-transfer mechanisms. Finally, since this redox couple has a relatively low electron self-exchange rate constant ($6 \times 10^3$ $M^{-1}s^{-1}$),[15,16] it could provide a decisive probe of the two mechanistic issues outlined above.

## Experimental Section

**Compounds and Solutions.** Distilled deionized water was obtained from a Barnstead Fi-Streem glass still. NaSCN was recrystallized from hot MeOH (60 °C).[17] $NaClO_4$ (GFS) was recrystallized from $H_2O$/ethanol solution.[17] Ar was purified by passage through a Catalyst Q1 column (Dow) and then through a tower containing water (the same solvent as the solution) to deaerate solutions. The spin trap PBN (*N-tert*-butyl-α-phenylnitrone) was used as supplied by Aldrich, while DMPO (5,5-dimethyl-1-pyrroline *N*-oxide, also from Aldrich), was purified by microdistillation under vacuum and trapped at −78 °C (dry ice/acetone slurry).[18] The purified material was stored in a refrigerator and identified by NMR (Bruker 400 MHz NMR spectrometer) and FTIR (IBM Instruments).[18]

$Ni(ClO_4)_2{\cdot}6H_2O$ (GFS) and free base 1,4,7-triazacyclononane, tacn,[15] were used to synthesize $[Ni(tacn)_2](ClO_4)_2$ (designated as Ni(II)), which was then oxidized by $Na_2S_2O_8$ to form $[Ni(tacn)_2](ClO_4)_3$ as reported previously.[19] After the recrystallization of $[Ni(tacn)_2](ClO_4)_3$ from 1 mM $HClO_4$, the Ni(III) salt obtained (contaminated with some Ni(II)) was used in the reaction studies. It was identified by UV–vis spectroscopy, OSWV (Osteryoung square wave voltammetry), and CV (cyclic voltammetry); the UV–vis spectra were obtained in thermostated quartz cuvettes on an HP 8452A spectrophotometer, and the electrochemical measurements made use of a BAS-100 electrochemical analyzer with Pt wire as an auxiliary electrode, Ag/AgCl as a reference electrode, and Au, Pt, and glassy carbon disks as working electrodes. The amount of Ni(II) contaminant in the purified $[Ni(tacn)_2](ClO_4)_3$ and the extinction coefficient of $[Ni(tacn)_2]^{3+}$ were determined by spectrophotometric titration with a standardized $KMnO_4$ solution as described below. Initial concentrations in this titration were 0.1 mM Ni(III) and 0.52 mM $MnO_4^-$.

Solutions of Ni(III) were prepared freshly to minimize decay. A stock solution of NaSCN was standardized by adding excess $Br_2$ and then

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(1) Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983,** *51,* 155–179.
(2) Ram, M. S.; Stanbury, D. M. *J. Phys. Chem.* **1986,** *90,* 3691–3696.
(3) Sarala, R.; Stanbury, D. M. *Inorg. Chem.* **1992,** *31,* 2771–2777.
(4) Nord, G. *Comments Inorg. Chem.* **1992,** *13,* 221–239.
(5) Krüger, H.-J.; Peng, G.; Holm, R. H. *Inorg. Chem.* **1991,** *30,* 734–742.
(6) Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987,** *26,* 4122–4125.
(7) Brodovitch, J. C.; McAuley, A.; Oswald, T. *Inorg. Chem.* **1982,** *21,* 3442–3447.
(8) Lappin, A. G.; McAuley, A. *Adv. Inorg. Chem.* **1988,** *32,* 241–295.
(9) Walsh, C. T.; Orme-Johnson, W. H. *Biochemistry* **1987,** *26,* 4901–4906.
(10) Hausinger, R. P. *Microbiol. Rev.* **1987,** *51,* 22–42.
(11) *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH: New York, 1988; pp 1–337.
(12) Cammak, R. *Adv. Inorg. Chem.* **1988,** *32,* 297–333.
(13) *Nickel and Its Role in Biology*; Sigel, H., Ed.; Metal Ions in Biological Systems, Vol. 33; Marcel Dekker: New York, 1988; pp 1–488.
(14) Kolodziej, A. F. *Prog. Inorg. Chem.* **1994,** *41,* 493–597.
(15) McAuley, A.; Norman, P. R.; Olubuyide, O. *Inorg. Chem.* **1984,** *23,* 1938–1943.
(16) McAuley, A.; Norman, P. R.; Olubuyide, O. *J. Chem. Soc., Dalton Trans.* **1984,** 1501–1505.
(17) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals,* 3rd ed.; Pergamon: New York, 1988; pp 350, 352.
(18) Ohkuma, T.; Kirino, Y.; Kwan, T. *Chem. Pharm. Bull.* **1981,** *29,* 25–28.
(19) deMaine, M. M.; Stanbury, D. M. *Inorg. Chem.* **1991,** *30,* 2104–2109.

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back-titrating with standardized $Na_2S_2O_3$ iodometrically.[20] The concentration of the NaSCN stock solution was checked by ion chromatography (as described below) after several months, which covered the duration of experimental studies. The conditions for this analysis are the same as those described below for the analysis of $SO_4^{2-}$. The buffer for each reaction was maintained at pH 3 by $HClO_4$ stock solution, which was standardized by titration with NaOH. The $NaClO_4$ stock solution was standardized by passing an aliquot through a cation-exchange column in the acid form, followed by titration with NaOH. A Corning Model 130 pH meter with a Ross combination pH electrode filled with NaCl solution was used in the measurements of pH.

**Stoichiometry.** The yield of $[Ni(tacn)_2]^{2+}$ in the reaction of $SCN^-$ with $[Ni(tacn)_2]^{3+}$ was determined by preparing a stock solution of $[Ni(tacn)_2]^{3+}$. An aliquot was allowed to react with $SCN^-$; the product solution was passed through an anion-exchange column (Dowex 1-X8 in the $Cl^-$ form) to remove excess $SCN^-$ and then titrated spectrophotometrically with $MnO_4^-$ by monitoring the absorbance changes at 270, 312, 526, and 546 nm simultaneously. The end point was easily determined because $MnO_4^-$ absorbs at these wavelengths but $[Ni(tacn)_2]^{3+}$ absorbs at 270 and 312 nm only. Another aliquot of $[Ni(tacn)_2]^{3+}$ stock solution was titrated directly with $MnO_4^-$ (because of the $[Ni(tacn)_2]^{2+}$ contaminant). After corrections for absorption due to excess $MnO_4^-$ and for dilution effects, the yield of $[Ni(tacn)_2]^{3+}$ was calculated by comparing these two titrations. The yield of $[Ni(tacn)_2]^{2+}$ in the reaction with $SCN^-$ was then calculated on the assumption of a 1:1 correspondence between the $[Ni(tacn)_2]^{2+}$ in the product solution and the $[Ni(tacn)_2]^{3+}$ recovered in the titration.

$SO_4^{2-}$ and $CN^-$ were identified and quantitated as products by use of ion chromatography, which was performed on a Wescan ion analyzer, Model 266. The instrument was equipped with a 100-$\mu$L sample loop, a Wescan Versapump-II, a Model 213A electrical conductivity detector, and a Model 271 electrochemical (amperometric) detector with a Pt working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode. Results were recorded by an Omniscribe D-500 strip chart recorder. A 25-cm resin-based anion-exchange column and a 2.0 mL/min eluent flow rate were used for both ions. The eluent was 4.0 mM KHP at pH 4.5 for the $SO_4^{2-}$ analysis (retention time = 5.48 min), while the eluent was 1.0 mM boric acid in 5.0 mM NaOH for the $CN^-$ analysis (pH 12.3, retention time = 14.6 min). For $CN^-$ analysis, the pH of the sample solution was adjusted to the pH of the NaCN calibration solutions. Concentrations of $SO_4^{2-}$ and $CN^-$ were assessed by use of calibration curves based on peak heights, and relative yields were based on initial concentrations of Ni(III) as determined by weight.

**Kinetics.** Solutions were permitted to contact platinum, glass, and Teflon only. Reactions were initiated by mixing equal volumes of the two reactant solutions, both of which were maintained at 0.10 M ionic strength by use of $NaClO_4$ as the background electrolyte. The decay of the absorbance of Ni(III) was monitored at 312 nm, pH 3, and at 25.0 °C by use of thermostated Cary 210 and Hewlett-Packard 8452A spectrophotometers equipped with 1-cm quartz cuvettes or by use of a Hi-Tech SF-51 stopped-flow mixer, SU-40 optical subsystem, and a Zenith-based OLIS 4300S data acquisition system.

Kinetic data from the Hewlett-Packard and Cary instruments were analyzed in order to obtain values of $k_{obs}$ by use of the KaleidaGraph computer application. Stopped-flow data were analyzed by use of the routines provided in the OLIS software. A nonlinear-least-squares program was used to fit rate laws to the values of $k_{obs}$, with weighting as the inverse square of $k_{obs}$.[21]

## Results

The purity of our sample of $[Ni(tacn)_2](ClO_4)_3$ as determined by spectrophotometric titration with $MnO_4^-$ was 66%, the balance being $[Ni(tacn)_2](ClO_4)_2$. Our measured molar absorptivities of Ni(III) are 9300 and 9600 $M^{-1}$ $cm^{-1}$ at 270 and 312 nm, respectively, the value of $\epsilon_{312}$ comparing well with other reported values: 7200, 8800, and 10 100 $M^{-1}$ $cm^{-1}$.[15,19,22]

The reaction of Ni(III) with $SCN^-$ was generally investigated under conditions of a large excess of $SCN^-$, with the absorbance at 312 nm due to Ni(III) providing a convenient measure of the progress of the reaction. None of the other species in solution absorbed appreciably at this wavelength. Because of the instability of Ni(III) in alkaline media,[19] all reactions were conducted in mildly acidic media. Under such conditions the solutions always remained homogeneous and the reactions proceeded with complete consumption of Ni(III).

**Stoichiometry.** The yield of Ni(II), expressed as the ratio $\Delta[Ni(II)]/\Delta[Ni(III)]$, was determined by spectrophotometric titration under the conditions $[Ni(III)]_0 = 2.0 \times 10^{-4}$ M, $[SCN^-] = 6.0 \times 10^{-4}$ M, and pH 3. Values of this ratio were determined in triplicate at both 270 and 312 nm, the results being 0.97 and 0.96, respectively. Thus, we find that $SCN^-$ quantitatively reduces $[Ni(tacn)_2]^{3+}$ to $[Ni(tacn)_2]^{2+}$.

The yield of $SO_4^{2-}$ was determined by use of ion chromatography. For this analysis a sample of product solution was generated at ca. 23 °C from initial conditions of $[Ni(III)]_0 = 1.0$ mM, $[SCN^-] = 5.0$ mM, and pH 3 ($HClO_4$), with no added background electrolyte. From such experiments the ratio $\Delta[Ni(III)]/\Delta[SO_4^{2-}]$ was measured as 5.21. The defect from the theoretical ratio of 6 is tentatively attributed small errors in evaluating the initial concentration of Ni(III). Efforts to determine the yield of $CN^-$ by ion chromatography were not as successful because the peak heights were quite sensitive to pH and not very reproducible. However, under the initial conditions $[Ni(III)]_0 = 0.40$ mM and $[SCN^-] = 7.5$ mM, $CN^-$ was detected qualitatively as a product, with yields roughly comparable to those of $SO_4^{2-}$.

From the above results it is apparent that the overall reaction can be described as

$$6[Ni(tacn)_2]^{3+} + SCN^- + 4H_2O \rightarrow 6[Ni(tacn)_2]^{2+} + SO_4^{2-} + HCN + 7H^+ \quad (1)$$

This stoichiometry is analogous to those reported for the reactions of $SCN^-$ with $[IrCl_6]^{2-}$,[23] $[IrBr_6]^{2-}$,[1] $[Fe(phen)_3]^{3+}$,[24] $[CoW_{12}O_{36}]^{5-}$,[25] $[Os(phen)_3]^{3+}$, and $[Os(bpy)_3]^{3+}$.[26] Reaction 1 is also characteristic of oxidations by $[Ni(tacn)_2]^{3+}$ in that the Ni(III) is reduced by one electron while the ligand environment remains intact, a notable exception to this rule being the reaction of $[Ni(tacn)_2]^{3+}$ with NO in which the ligand system is attacked.[19]

**Kinetics.** All studies were performed with a large excess of $SCN^-$ at $\mu = 0.1$ M and 25 °C. An important feature of the reaction kinetics was immediately apparent from two experiments at 0.1 mM Ni(III) with 0.05 M $SCN^-$ at pH 3. Under these conditions the decay of Ni(III) did not obey the usual pseudo-first-order rate law but rather displayed kinetics that were close to pseudo second order, as shown in Figure 1. This figure also shows the strong inhibitory effect of adding 0.8 mM Ni(II) to the reaction mixture; with this added Ni(II) the fit to pseudo-second-order kinetics was excellent. The rate constant, defined by $-d[Ni(III)]/dt = k_{obs,2}[Ni(III)]^2$, had a value of 152 $M^{-1}$ $s^{-1}$. An immediate conclusion was that the departure from pseudo-first-order kinetics in the first experiment (without added Ni(II)) was due to the accumulation of Ni(II) as an inhibitor during the reaction. Product inhibition of this sort has been reported previously, in the oxidation of $SCN^-$ by $[Os(bpy)_3]^{3+}$,[26] and it is an anticipated consequence of a mechanism involving electron transfer to form the high-energy species SCN and $(SCN)_2^-$.

In the past we have been able to simplify the kinetics of reactions showing product inhibition of this type by adding the spin traps PBN and DMPO.[2,27,28] PBN was found to be unsuitable in the

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(20) Schulek, E. *Z. Anal. Chem.* **1923**, *62*, 337–342; *Chem. Abstr.* **1923**, *17*, 3465–3466.

(21) Moore, R. H.; Zeigler, R. K. *LSTSQR*; Los Alamos National Laboratory: Los Alamos, NM, 1959.

(22) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Kuppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953–2956.

(23) Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715–2722.

(24) Ng, F. T. T.; Henry, P. M. *Can. J. Chem.* **1975**, *53*, 3319–3326.

(25) Olatunji, M. A.; Ayoko, G. A. *Polyhedron* **1984**, *3*, 191–197.

(26) Nord, G.; Pedersen, B.; Farver, O. *Inorg. Chem.* **1978**, *17*, 2233–2238.

(27) Awad, H. H.; Stanbury, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 3636–3642.

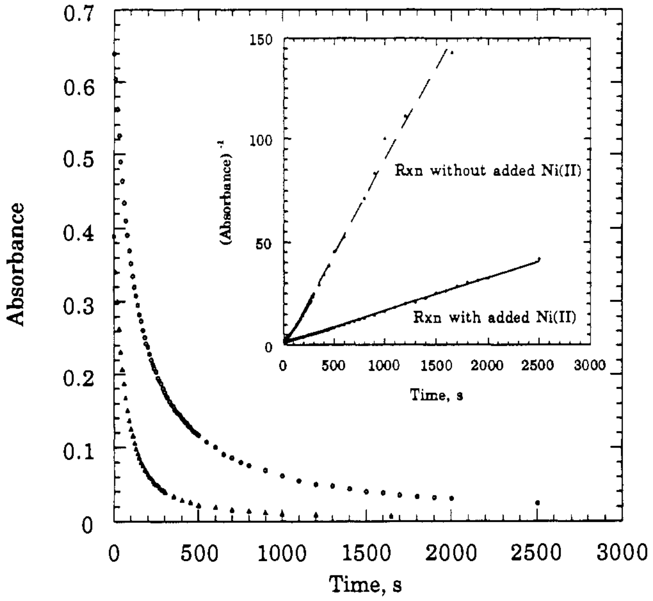

**Figure 1.** Kinetic inhibition by Ni(II) in the reaction of Ni(III) with $SCN^-$ ($[Ni(III)]_0$ = 0.1 mM, $[SCN^-]$ = 50.0 mM, pH 3 ($HClO_4$), $\mu$ = 0.10 M ($NaClO_4$), 25 °C): open circles, without added Ni(II); closed triangles, with 0.8 mM $[Ni(II)]_0$ added.

**Table 1.** Kinetic Effect of DMPO[a]

| [DMPO], mM | $10^3k_{obs}$, $s^{-1}$ | [DMPO], mM | $10^2k_{obs}$, $s^{-1}$ |
|---|---|---|---|
| 1.0 | 5.16 | 4.0 | 1.12 |
| 2.0 | 7.90 | 5.0 | 1.11 |
| 3.0 | 8.18 | | |

[a] $[Ni(III)]_0$ = 0.05 mM, $[SCN^-]$ = 25.0 mM, pH 3 ($HClO_4$), $\mu$ = 0.1 M ($NaClO_4$), 25 °C.

present system because of its high absorbance ($\epsilon \approx 1700$ $M^{-1}$ $cm^{-1}$ at 312 nm) and its relative inefficacy as a trap for SCN.[29] DMPO is more efficient,[29] and its UV absorbance does not overlap with that of Ni(III). Impurities in our sample of DMPO caused the absorbance of Ni(III) in a mixture of 5.0 mM DMPO with 0.05 mM Ni(III) at pH 3 to drop about 5% in first 10 s (although it was stable over the subsequent 100 s). Because of this effect, the first 10 s was disregarded in all subsequent studies.

The effect of DMPO on the reaction of $SCN^-$ with Ni(III) was quite substantial. Pseudo-first-order kinetics was obtained with all residuals less than 2% when the conditions were [DMPO] = 5.0 mM, $[Ni(III)]_0$ = 0.05 mM, $[SCN^-]$ = 30.0 mM, and pH 3. A series of experiments were performed with the same conditions except at 25.0 mM $SCN^-$ and with 1.0–5.0 mM DMPO. The pseudo-first-order rate constants, $k_{obs}$, are collected in Table 1 and show that limiting rates are attained at about 5.0 mM DMPO. Higher concentrations were avoided because of the direct reaction of Ni(III) with impurities in the DMPO.

A series of experiments was performed to examine the effect of added Ni(II) in the presence of 5.0 mM DMPO. In these experiments the concentrations of Ni(II) spanned the range from 0.5 to 2.0 mM, while the initial concentrations of Ni(III) and $SCN^-$ were 0.05 and 30 mM, respectively. The values of $k_{obs}$ systematically decreased with increasing Ni(II) concentrations, as indicated in Table 2. Figure 2 shows that a plot of $1/k_{obs}$ vs $[Ni(II)]_{added}$ is linear as in the relationship

$$\frac{1}{k_{obs}} = \frac{1}{k_a} + \frac{1}{k_b}[Ni(II)] \qquad (2)$$

with $1/k_b = 3.23 \times 10^5$ $M^{-1}$ s and $1/k_a$ = 189 s. Figure 2 also shows that the effect of Ni(II) is insignificant in reactions where it has not been deliberately added.

**Table 2.** Kinetic Inhibition by Ni(II) in the Presence of DMPO[a]

| $[Ni(II)]_{added}$, mM | $10^3k_{obs}$, $s^{-1}$ | $[Ni(II)]_{added}$, mM | $10^3k_{obs}$, $s^{-1}$ |
|---|---|---|---|
| 0.00 | 6.29 | 1.00 | 1.92 |
| 0.50 | 2.86 | 1.50 | 1.48 |
| 0.75 | 2.38 | 2.00 | 1.20 |

[a] $[Ni(III)]_0$ = 0.05 mM, $[SCN^-]$ = 30.0 mM, [DMPO] = 5.0 mM, pH 3 ($HClO_4$), $\mu$ = 0.10 M ($NaClO_4$), 25 °C.

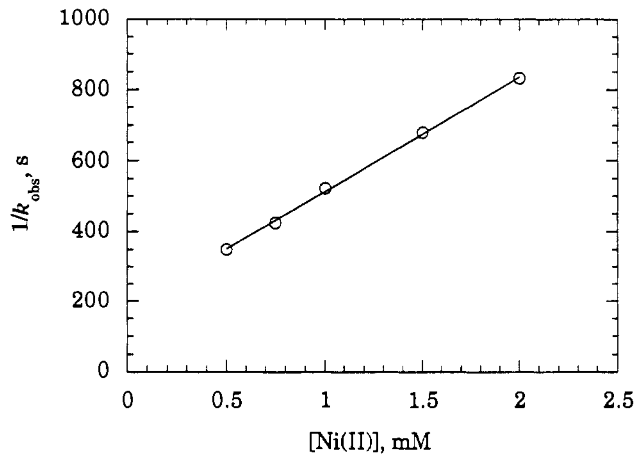

**Figure 2.** Effect of Ni(II) on the reaction of Ni(III) with $SCN^-$ in the presence of DMPO ($[Ni(III)]_0$ = 0.05 mM, $[SCN^-]$ = 30.0 mM, [DMPO] = 5.0 mM, pH 3 ($HClO_4$), $\mu$ = 0.1 M ($NaClO_4$), 25 °C).

**Table 3.** Kinetic Dependence on Concentration of $SCN^-$ [a]

| $[SCN^-]$, mM | $k_{obs}$, $s^{-1}$ | $[SCN^-]$, mM | $k_{obs}$, $s^{-1}$ |
|---|---|---|---|
| 3.0 | $3.05 \times 10^{-4}$ | 40.1 | $9.42 \times 10^{-3}$ |
| 5.2 | $5.90 \times 10^{-4}$ | 49.8 | $1.27 \times 10^{-2}$ |
| 10.0 | $1.40 \times 10^{-3}$ | 60.0 | $2.27 \times 10^{-2}$ |
| 20.1 | $3.65 \times 10^{-3}$ | 70.0 | $2.86 \times 10^{-2}$ |
| 29.7 | $6.29 \times 10^{-3}$ | 80.0 | $3.50 \times 10^{-2}$ |

[a] $[Ni(III)]_0$ = 0.05 mM, pH 3 ($HClO_4$), [DMPO] = 5.0 mM, $\mu$ = 0.10 M ($NaClO_4$), 25 °C.

Kinetic studies of the dependence on the $SCN^-$ concentration covered a 35-fold range for this crucial parameter. These studies were conducted in 5 mM DMPO so as to eliminate effects due to Ni(II). The pseudo-first-order rate constants obtained under initial conditions of 0.05 mM Ni(III) and pH 3 are presented in Table 3. Figure 3 is a plot of $k_{obs}/[SCN^-]$ as a function of $[SCN^-]$, which shows that the rate law is reasonably given as

$$-d[Ni(III)]/dt = k_{obs}[Ni(III)] = (k'[SCN^-] + k''[SCN^-]^2)[Ni(III)] \qquad (3)$$

with both terms quite well defined. A least-squares fit gives rate constants of $k' = (9.23 \pm 0.61) \times 10^{-2}$ $M^{-1}$ $s^{-1}$ and $k'' = 4.08 \pm 0.25$ $M^{-2}$ $s^{-1}$. Prior examples of this rate law include the oxidations of $SCN^-$ by $[IrCl_6]^{2-}$ [23] and by $[Fe(bpy)_3]^{3+}$.[1]

The pH dependence of the reaction was investigated over the range pH 2–4.87, with initial conditions of 0.05 mM Ni(III), 30 mM $SCN^-$, and 5 mM DMPO. The values of $k_{obs}$ are presented in Table 4, and as can be seen, the rate constants increased by a factor of 3 as the pH increased from 2 to 4.87. This very mild pH dependence is not easily incorporated in a simple rate law, but a similar effect was observed in the reaction of $[Ni(tacn)_2]^{3+}$ with $S_2O_3^{2-}$.[3] As in the study with $S_2O_3^{2-}$, we attribute the mild pH dependence to the slow decomposition of $[Ni(tacn)_2]^{3+}$ in solutions that are not highly acidic. Our choice of pH 3 as a standard condition in this work was thus determined by the needs to stabilize Ni(III) and provide for a range of concentrations of $SCN^-$.

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[28] Ram, M. S.; Stanbury, D. M. *Inorg. Chem.* **1985**, *24*, 4233–4234.
[29] Rehorek, D.; Janzen, E. G. *Inorg. Chim. Acta* **1986**, *118*, L29–L30.

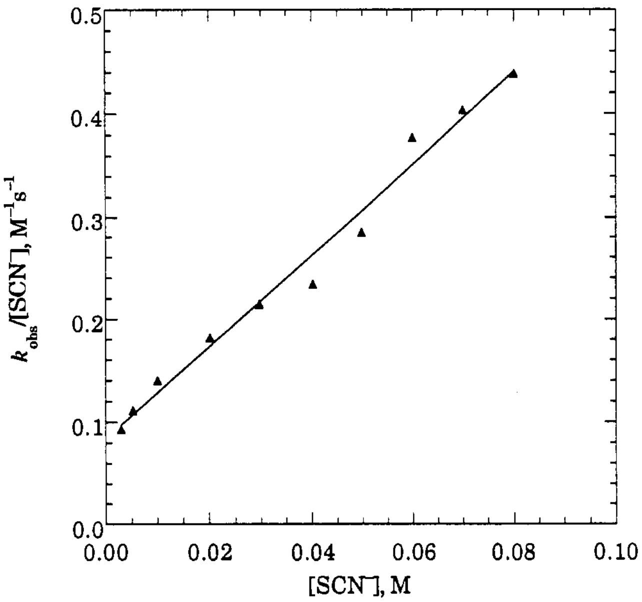

**Figure 3.** Kinetics of the reaction of Ni(III) as a function of [SCN⁻] ($[\mathrm{Ni(III)}]_0$ = 0.05 mM, pH 3 ($HClO_4$), [DMPO] = 5.0 mM, $\mu$ = 0.1 M ($NaClO_4$), 25 °C).

**Table 4.** pH Effect on the Kinetics[a]

| pH | $10^3 k_{obs}$, $s^{-1}$ | pH | $10^2 k_{obs}$, $s^{-1}$ |
|---|---|---|---|
| 1.97[b] | 5.80 | 4.09[c] | 1.37 |
| 2.97[b] | 8.40 | 4.87[c] | 1.65 |

[a] $[\mathrm{Ni(III)}]_0$ = 0.05 mM, [SCN⁻] = 30.0 mM, [DMPO] = 5.0 mM, $\mu$ = 0.10 M ($NaClO_4$), 25 °C. [b] pH adjusted with $HClO_4$. [c] Acetate buffer.

A series of blank experiments showed that $O_2$, $CN^-$, $SO_4^{2-}$, and metal ions had no significant kinetic effects.[30] Tests for the effect of $O_2$ were deemed necessary because an $O_2$ effect was reported in the reaction of $SCN^-$ with $[IrCl_6]^{2-}$.[23] The potential catalytic effect of metal ions was investigated by adding oxalate as a chelate. This is an effective strategy in catalyzed oxidations of $S_2O_3^{2-}$,[3] although the method must be used with caution because oxalate can react with one-electron oxidants.[31-38]

## Discussion

The stoichiometry and kinetic data described above are most easily discussed in terms of an outer-sphere electron-transfer mechanism. This assignment is supported by the identity of the Ni(II) product, which indicates that the coordination sphere of the nickel has not been perturbed by the reaction. It is also supported by the general observation that $[\mathrm{Ni(tacn)_2}]^{3+}$ is substitution-inert and presents no potential binding sites. In this context, the stoichiometry and the rate law are not unusual, relative to prior studies of outer-sphere oxidations of $SCN^-$.[4,23,26]

In these prior studies the proposed mechanism was given by Scheme 1. Such a mechanism will indeed account for our observed stoichiometry. Reaction 8 is already well established.[39-41] The rate constant for association of SCN with $SCN^-$ is approximately diffusion controlled,[42-44] and so eq 7 can be treated as a rapid equilibrium; if steady-state approximations are made for the radical intermediates, the following rate law can be derived:

### Scheme 1

$$\mathrm{M_{ox} + SCN^- \rightleftarrows M_{red} + SCN} \qquad k_1, k_{-1} \qquad (4)$$

$$\mathrm{M_{ox} + 2SCN^- \rightleftarrows M_{red} + (SCN)_2^-} \qquad k_2, k_{-2} \qquad (5)$$

$$\mathrm{M_{ox} + (SCN)_2^- \rightarrow M_{red} + (SCN)_2} \qquad k_3 \qquad (6)$$

$$\mathrm{SCN + SCN^- \rightleftarrows (SCN)_2^-} \qquad k_4, k_{-4}, K_{rad} \qquad (7)$$

$$\mathrm{3(SCN)_2 + 4H_2O \rightarrow 5SCN^- + HCN + SO_4^{2-} + 7H^+} \quad \text{(fast)} \qquad (8)$$

$$-\frac{d[\mathrm{M_{ox}}]}{dt} = \frac{2(k_1[\mathrm{SCN^-}] + k_2[\mathrm{SCN^-}]^2)k_3K_{rad}[\mathrm{M_{ox}}]^2[\mathrm{SCN^-}]}{k_{-1}[\mathrm{M_{red}}] + k_{-2}K_{rad}[\mathrm{SCN^-}][\mathrm{M_{red}}] + k_3K_{rad}[\mathrm{M_{ox}}][\mathrm{SCN^-}]} \qquad (9)$$

This accounts qualitatively for the kinetic inhibition by Ni(II). At high concentrations of $M_{red}$, eq 9 reduces to

$$k_{obs,2} = \frac{2(k_1[\mathrm{SCN^-}] + k_2[\mathrm{SCN^-}]^2)k_3K_{rad}[\mathrm{SCN^-}]}{(k_{-1} + k_{-2}K_{rad}[\mathrm{SCN^-}])[\mathrm{M_{red}}]} \qquad (10)$$

where $k_{obs,2}$ is a pseudo-second-order rate constant, and this is in agreement with the behavior depicted in Figure 1.

Scheme 2 accommodates the results obtained in the presence of DMPO.

### Scheme 2

$$\mathrm{Ni(III) + SCN^- \rightleftarrows Ni(II) + SCN} \qquad k_1, k_{-1}, K_1 \qquad (11)$$

$$\mathrm{Ni(III) + 2SCN^- \rightleftarrows Ni(II) + (SCN)_2^-} \qquad k_2, k_{-2}, K_2 \qquad (12)$$

$$\mathrm{SCN + SCN^- \rightleftarrows (SCN)_2^-} \qquad K_{rad} \qquad (13)$$

$$\mathrm{DMPO + SCN \rightarrow adduct\ 1} \qquad k_{1,\mathrm{DMPO}} \qquad (14)$$

$$\mathrm{DMPO + (SCN)_2^- \rightarrow adduct\ 2} \qquad k_{2,\mathrm{DMPO}} \qquad (15)$$

By applying the steady-state approximations to the concentrations of SCN and $(SCN)_2^-$, it is possible to derive the following rate law

$$\frac{-d[\mathrm{Ni(III)}]}{dt} = \frac{2A(k_1[\mathrm{SCN^-}] + k_2[\mathrm{SCN^-}]^2)[\mathrm{Ni(III)}]}{A + (k_{-1} + k_{-2}K_{rad}[\mathrm{SCN^-}])[\mathrm{Ni(II)}]} \qquad (16)$$

where $A = (k_{1,\mathrm{DMPO}} + k_{2,\mathrm{DMPO}}K_{rad}[\mathrm{SCN^-}])[\mathrm{DMPO}]$. At high

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(30) A full presentation of the rate constants can be found in the M.S. thesis of Mei-Ling Hung, Auburn University, 1993.

(31) Steffan, C. R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 2992–2995.

(32) Nishida, S.; Harima, Y.; Yamashita, K. *Inorg. Chem.* **1989**, *28*, 4073–4077.

(33) Neshvad, G.; Hoffman, M. Z. *J. Phys. Chem.* **1989**, *93*, 2445–2452.

(34) Suwyn, M. A.; Hamm, R. E. *Inorg. Chem.* **1967**, *6*, 142–145.

(35) Dressick, W. J.; Meyer, T. J.; Durham, B.; Rillema, D. P. *Inorg. Chem.* **1982**, *21*, 3451–3458.

(36) Hoffman, M. Z.; Prasad, D. R. *J. Photochem. Photobiol., A* **1990**, *54*, 197–204.

(37) Ogawa, E. *J. Chem. Soc. Jpn.* **1929**, *50*, 248–257.

(38) Chatterjee, U.; Maiti, S.; Sengupta, K. K. *Z. Phys. Chem. (Leipzig)* **1980**, *261*, 1231–1235.

(39) Stedman, G.; Whincup, P. A. E. *J. Chem. Soc. A* **1969**, 1145–1148.

(40) Schöneshöfer, V. M.; Beck, G.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 1011–1015.

(41) Bjerrum, N.; Kirschner, A. *Chem. Abstr.* **1919**, *13*, 1057–1060.

(42) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330–2335.

(43) Chin, M.; Wine, P. H. *J. Photochem. Photobiol., A* **1992**, *69*, 17–25.

(44) Baxendale, J. H.; Bevan, P. L. T.; Stott, D. A. *Trans. Faraday Soc.* **1968**, *64*, 2389–2397.

concentrations of DMPO eq 16 simplifies to

$$-\mathrm{d}[\mathrm{Ni(III)}]/\mathrm{d}t = 2(k_1[\mathrm{SCN^-}] + k_2[\mathrm{SCN^-}]^2)[\mathrm{Ni(III)}] \tag{17}$$

From a comparison of eq 17 with the observed dependence on [SCN$^-$] (eq 3), it is clear that the rate constants are $2k_1 = k' = (9.23 \pm 0.61) \times 10^{-2}$ M$^{-1}$ s$^{-1}$ and $2k_2 = k'' = 4.08 \pm 0.25$ M$^{-2}$ s$^{-1}$ at 25 °C and $\mu = 0.1$ M.

When the reaction is studied at high concentrations of Ni(II) such that its effect is not overwhelmed by that of DMPO, eq 16 leads to

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{2(k_1[\mathrm{SCN^-}] + k_2[\mathrm{SCN^-}]^2)} + \frac{(k_{-1} + k_{-2}K_{\mathrm{rad}}[\mathrm{SCN^-}])[\mathrm{Ni(II)}]}{2A(k_1[\mathrm{SCN^-}] + k_2[\mathrm{SCN^-}]^2)} \tag{18}$$

This expression is in agreement with the observed linear dependence of $1/k_{\mathrm{obs}}$ on [Ni(II)] as in eq 2. Accordingly, we make the following identifications:

$$k_a = 2(k_1[\mathrm{SCN^-}] + k_2[\mathrm{SCN^-}]^2) \tag{19}$$

$$k_a/k_b = \frac{k_{-1} + k_{-2}K_{\mathrm{rad}}[\mathrm{SCN^-}]}{(k_{1,\mathrm{DMPO}} + k_{2,\mathrm{DMPO}}K_{\mathrm{rad}}[\mathrm{SCN^-}])[\mathrm{DMPO}]} \tag{20}$$

Values of $5.3 \times 10^{-3}$ s$^{-1}$ for $k_a$ and $1.7 \times 10^3$ M$^{-1}$ for $k_a/k_b$ can be obtained from the Ni(II) dependence study at 30 mM SCN$^-$ and 5.0 mM DMPO. The value for $k_a$ compares reasonably well with that calculated from the SCN$^-$ dependence study ($6.4 \times 10^{-3}$ s$^{-1}$).

Further analysis of the kinetics depends on accurate one-electron reduction potentials for the redox couples associated with reactions 11 and 12. In the present work, a formal potential ($E_f$) of 0.94 V was obtained for $[\mathrm{Ni(tacn)_2}]^{3+/2+}$ under conditions of ~23 °C, pH 3, and $\mu = 0.10$ M (NaClO$_4$). In previous work we obtained a value of 0.952 V at $\mu = 0.10$ M (LiClO$_4$), pH 2.3, and 25.0 °C.[19] Values reported in other prior studies include 0.947 V (unspecified conditions),[16] 0.940 V at [H$^+$] = 0.1 M (other conditions unspecified),[15] and 0.95 V in 0.1 M LiClO$_4$ at 25.0 °C (pH unspecified).[22] In view of the known sensitivity of this reduction potential to ionic strength,[19] we adopt a value of 0.94 ± 0.01 V in this study.

Values for the potentials involving the SCN and (SCN)$_2^-$ radicals are not as directly obtainable.[45-47] DeFelippis et al. reported a value of 1.29 ± 0.01 V for the (SCN)$_2^-$/2(SCN$^-$) couple.[45] Their result was obtained by measuring pulse-radiolytically the equilibrium position of this couple relative to $[\mathrm{Ru(bpy)_3}]^{3+/2+}$ at $\mu \sim 0.02$ M (KSCN) and 25 °C, and their calculation was based on a potential of 1.28 V for the $[\mathrm{Ru(bpy)_3}]^{3+/2+}$ couple measured at $\mu = 0.1$ M (KCl). DeFelippis et al. compared their result with those obtained previously by less direct methods, and they concluded that the potential lies between 1.29 and 1.32 V. Estimates of the SCN/SCN$^-$ potential based on Schöneshöfer and Henglein's equilibria[48] involving ISCN$^-$ and the potential for the I/I$^-$ couple give a value of 1.60–1.62 V for the SCN/SCN$^-$ formal potential.[46] A similar value, 1.61 V, was calculated by DeFelippis et al. on the basis of their potential for the (SCN)$_2^-$/2(SCN$^-$) couple and the equilibrium constant for reaction 13 ($K_{\mathrm{rad}}$). The potentials selected on the basis of the above considerations are presented in Table 5, but they have uncertainties of about ±10 mV because of the various ionic strengths that were used in their determinations (generally 0.1 M or less).

**Table 5.** Reduction Potentials and Self-Exchange Rate Constants at 25 °C

| redox couple | redn potential, V | $k$, M$^{-1}$ s$^{-1}$ |
|---|---|---|
| Ni(III)/Ni(II) | 0.94[a] | $6 \times 10^3$ [b] |
| SCN/SCN$^-$ | 1.61[c] | $>5 \times 10^4$ [d] |
| (SCN)$_2^-$/2SCN$^-$ | 1.29[e] | 40[d] |

[a] This work. $\mu = 0.10$ M (NaClO$_4$), ~23 °C, pH 3. Measured relative to Ag/AgCl and corrected to NHE by adding 0.197 V. [b] $k$ is $k_{22}$. Reference 16. [c] Reference 46. [d] $k$ is $k_{11}$. This work. [e] Reference 45.

The equilibrium constants, $K_1$ and $K_2$, calculated from the $E_f$ data in Table 5 are $4.9 \times 10^{-12}$ and $1.2 \times 10^{-6}$ M$^{-1}$, respectively, with uncertainties of about a factor of 2. By use of these equilibrium constants, the measured rate constants ($k_1$ and $k_2$), and the principle of detailed balancing, values of $9.7 \times 10^9$ M$^{-1}$ s$^{-1}$ for $k_{-1}$ and $1.7 \times 10^6$ M$^{-1}$ s$^{-1}$ for $k_{-2}$ can be calculated, again with uncertainties of about a factor of 2.

The calculated values of $k_{-1}$ and $k_{-2}$ can be used to examine the Ni(II) dependence in greater detail. As discussed above, the value of $k_a/k_b$ in eq 20 is $1.70 \times 10^3$ M$^{-1}$ at 0.03 M SCN$^-$ and 5.0 mM DMPO. When this result is combined with the calculated values for $k_{-1}$ and $k_{-2}$ and the literature value of $2 \times 10^5$ M$^{-1}$ for $K_{\mathrm{rad}}$,[43,44,47,49-52] a value of $2.3 \times 10^9$ M$^{-1}$ s$^{-1}$ can be calculated for ($k_{1,\mathrm{DMPO}} + k_{2,\mathrm{DMPO}}K_{\mathrm{rad}}[\mathrm{SCN^-}]$). This result is easily satisfied so long as $k_{1,\mathrm{DMPO}}$ is less than $2.3 \times 10^9$ M$^{-1}$ s$^{-1}$ and $k_{2,\mathrm{DMPO}}$ is less than $3.9 \times 10^5$ M$^{-1}$ s$^{-1}$. These rate constants are in qualitative agreement with the results reported for these reactions in acetonitrile.[29]

The pseudo-second-order rate constant obtained in the absence of DMPO can also be examined in greater detail. When this rate constant is inserted into eq 10, along with the above values of $k_1$, $k_{-1}$, $k_2$, $k_{-2}$, and $K_{\mathrm{rad}}$, a value of $2.2 \times 10^7$ M$^{-1}$ s$^{-1}$ can be calculated for $k_3$, rate constant for the oxidation of (SCN)$_2^-$ by Ni(III). A rate constant as large as this is quite reasonable in view of the large driving force for the reaction ($E_f = 0.21$ V for the (SCN)$_2$/(SCN)$_2^-$ couple).[47]

**LFER vs Marcus Theory for $k_1$.** Rate laws with mixed second-order terms analogous to the $k'$ term in eq 3 have been reported for reactions of $[\mathrm{IrCl_6}]^{2-}$,[23] $[\mathrm{Fe(bpy)_3}]^{3+}$,[1] $[\mathrm{CoW_{12}O_{40}}]^{5-}$,[25] $[\mathrm{Ag(OH)_4}]^-$,[53] $[\mathrm{AuBr_4}]^-$,[54] and *trans*-$[\mathrm{Au(NH_3)_2X_{2-n}SCN_n}]^-$ where X = Cl or Br and $n$ = 0, 1, or 2.[55] It has been argued that the reactions of $[\mathrm{Ag(OH)_4}]^-$ and *trans*-$[\mathrm{Au(NH_3)_2X_{2-n}SCN_n}]^-$ have two-electron mechanisms and do not yield free radical intermediates.[53,55] This is quite likely the case for the reaction of $[\mathrm{AuBr_4}]^-$ also. Thus, including our study of $[\mathrm{Ni(tacn)_2}]^{3+}$, there are now four examples of ground-state substitution-inert complexes that may be assumed to oxidize SCN$^-$ directly to the SCN radical through a single-electron-transfer mechanism.

It has been noted previously that values of $k_1$ obey a linear free energy relationship (LFER) of unit slope when plotted as log $k_1$ vs log $K_1$.[4,23,25] Because of the principle of detailed balancing, this requires that all reactions have the same value of $k_{-1}$. This situation arises because $k_{-1}$ is diffusion controlled,[4,23,25] and it implies that the rate-limiting step for the forward process ($k_1$)

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(45) DeFelippis, M. R.; Faraggi, M.; Klapper, M. H. *J. Phys. Chem.* **1990**, *94*, 2420–2424.

(46) Sarala, R.; Rabin, S. B.; Stanbury, D. M. *Inorg. Chem.* **1991**, *30*, 3999–4007.

(47) Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69–138.

(48) Schöneshöfer, M.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 393–398.

(49) Behar, D.; Bevan, P. L. T.; Scholes, G. *J. Phys. Chem.* **1972**, *76*, 1537–1542.

(50) Baxendale, J. H.; Bevan, P. L. T. *J. Chem. Soc. A* **1969**, 2240–2241.

(51) Elliot, A. J.; Sopchyshyn, F. C. *Int. J. Chem. Kinet.* **1984**, *16*, 1247–1256.

(52) Fornier de Violet, P. *Rev. Chem. Intermed.* **1981**, *4*, 121–169.

(53) Kirschenbaum, L. J.; Sun, Y. *Inorg. Chem.* **1991**, *30*, 2360–2365.

(54) Kazakov, V. P.; Konovalova, M. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1968**, *13*, 231–235.

(55) Elmroth, S.; Skibsted, L. H.; Elding, L. I. *Inorg. Chem.* **1989**, *28*, 2703–2710.

is diffusive separation of the products, rather than electron transfer within the encounter complex.[4,23,25] Our calculated value of $k_{-1} = 9.7 \times 10^9$ M$^{-1}$ s$^{-1}$ for the reaction of $[\mathrm{Ni(tacn)_2}]^{3+}$ is essentially diffusion controlled, and thus it conforms to the LFER.

To the degree that the four electron-transfer reactions cited above have outer-sphere mechanisms, Marcus theory is pertinent. However, Marcus theory applies specifically to the electron transfer process, but diffusive product separation is rate limiting for the reactions of $\mathrm{SCN^-}$ conforming to the LFER. Thus, if a self-exchange rate constant for the $\mathrm{SCN/SCN^-}$ couple is calculated by applying the Marcus cross relationship (with appropriate corrections for work terms and solvent barrier nonadditivity), it should be less than the "real" value. The $[\mathrm{Ni(tacn)_2}]^{3+/2+}$ system is of some interest in this context because of its low self-exchange rate constant ($6 \times 10^3$ M$^{-1}$ s$^{-1}$).[16]

The Marcus cross relation is often given as

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{21}$$

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

$$W_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT] \tag{23}$$

$$w_{ij} = (4.23Z_iZ_j)/(a(1 + 0.328a(\mu^{1/2}))) \tag{24}$$

where $k_{12}$ is the second-order electron-transfer rate constant, $K_{12}$ is the equilibrium constant, $k_{11}$ and $k_{22}$ are the self-exchange rate constants for the component redox couples, $Z$ is taken as $1 \times 10^{12}$ M$^{-1}$ s$^{-1}$, $a$ is the center-to-center distance in angstroms when the reactants are in contact, and $R$ is the gas constant (in kilocalories).[56] Values of $k_{11}$ for the free radical couple derived from measured cross-reaction rate constants can then be corrected for solvent barrier nonadditivity; this correction generally increases the calculated value of $k_{11}$.[27]

A calculation of $k_{11}$ (not corrected for solvent barrier nonadditivity) for the $\mathrm{SCN/SCN^-}$ couple was performed on the basis of eqs 21–24. The required value of $a$ was taken as the sum of the radii for $\mathrm{SCN^-}$ and $[\mathrm{Ni(tacn)_2}]^{3+}$, 2.13 and 3.8 Å, respectively.[3,57] The outcome was a value of $5 \times 10^4$ M$^{-1}$ s$^{-1}$ for $k_{11}$. Similar calculations for the reactions of $[\mathrm{IrCl_6}]^{2-}$ and $[\mathrm{Fe(bpy)_3}]^{3+}$ with $\mathrm{SCN^-}$ gave values for $k_{11}$ of $3 \times 10^3$ and $2 \times 10^2$ M$^{-1}$ s$^{-1}$, respectively, based on rate constants and radii given previously.[1] Corresponding calculations for the reaction of $[\mathrm{CoW_{12}O_{40}}]^{5-}$ were not attempted because of difficulties arising from the large negative charge of this oxidant. Nord et al. reported that a self-exchange rate constant of $1 \times 10^7$ M$^{-1}$ s$^{-1}$ gave a satisfactory fit for the reactions of $[\mathrm{IrCl_6}]^{2-}$ and $[\mathrm{Fe(bpy)_3}]^{3+}$;[26] the discrepancy with our calculations arises because they ignored work terms, used an older (larger) value of $k_1$ for the reaction of $[\mathrm{IrCl_6}]^{2-}$, and used a lower value of $k_{22}$ for the $[\mathrm{Fe(bpy)_3}]^{3+/2+}$ couple. If it is accepted that our new calculations are more accurate and that they are lower limits to $k_{11}$ because of the effects of diffusion control, then the inferred value of $k_{11}$ is greater than $5 \times 10^4$ M$^{-1}$ s$^{-1}$. This is in agreement with a recent report on the *exothermic* electron-transfer quenching of $^*[\mathrm{Os^{VI}(tmc)O_2}]^{2+}$ by $\mathrm{SCN^-}$.[58]

The $\mathrm{SCN/SCN^-}$ and $\mathrm{N_3/N_3^-}$ redox couples should have similar self-exchange rate constants because the two couples have the same charge, are of similar sizes, and are isovalent. For both couples the geometric structures in the two oxidation states are very similar because the HOMO is nonbonding,[27,59] and this leads to rapid self-exchange. The value of $5 \times 10^4$ M$^{-1}$ s$^{-1}$ (uncorrected for solvent barrier nonadditivity) reported for $k_{11}$ for the $\mathrm{N_3/N_3^-}$ couple is entirely in agreement with these expectations.[27] An important difference between the two systems is that rate constants for the $\mathrm{N_3^-}$ reactions often are not limited by diffusive product separation because SCN has a much higher reduction potential than $\mathrm{N_3}$ (1.61 vs 1.33 V).[27]

**Table 6.** Kinetics of Third-Order Oxidations of $\mathrm{SCN^-}$ [a]

| oxidant | log $k_2$ | $E_f$, V | $k_{-2}$,[b] M$^{-1}$ s$^{-1}$ | $k_{22}$, M$^{-1}$ s$^{-1}$ | $r$,[j] Å | Marcus log $k_2$ |
|---|---|---|---|---|---|---|
| $[\mathrm{IrBr_6}]^{2-}$ | 0.18[c] | 0.84 | $6.1 \times 10^7$ | $2.0 \times 10^8$ | 4.7 | 0.17 |
| $[\mathrm{Fe(bpy)_3}]^{3+}$ | 3.88[d] | 1.06 | $5.8 \times 10^7$ | $5.0 \times 10^8$ | 6 | 3.76 |
| $[\mathrm{Fe(phen)_3}]^{3+}$ | 4.15[e] | 1.06 | $1.1 \times 10^8$ | $5.0 \times 10^8$ | 6.5 | 3.02 |
| $[\mathrm{Fe(5\text{-}Cl(phen))_3}]^{3+}$ | 5.28[e] | 1.11[i] | $2.1 \times 10^8$ | $5.0 \times 10^8$ | 6.5 | 3.48 |
| $[\mathrm{Fe(5\text{-}Br(phen))_3}]^{3+}$ | 5.23[e] | 1.13 | $8.6 \times 10^7$ | $5.0 \times 10^8$ | 6.5 | 3.66 |
| $[\mathrm{Fe(5\text{-}Me(phen))_3}]^{3+}$ | 3.85[e] | 1.02 | $2.6 \times 10^8$ | $5.0 \times 10^8$ | 6.5 | 2.64 |
| $[\mathrm{Fe(4,7\text{-}Me_2(phen))_3}]^{3+}$ | 1.70[e] | 0.86 | $9.3 \times 10^8$ | $5.0 \times 10^8$ | 7 | 1.00 |
| $[\mathrm{Os(bpy)_3}]^{3+}$ | 1.40[f] | 0.86 | $4.7 \times 10^8$ | $1.8 \times 10^8$ | 6.7 | 1.40 |
| $[\mathrm{Os(phen)_3}]^{3+}$ | 1.03[g] | 0.84 | $4.4 \times 10^8$ | $3.1 \times 10^8$ | 6.7 | 0.72 |
| $[\mathrm{IrCl_6}]^{2-}$ | –0.33[c] | 0.89 | $2.7 \times 10^6$ | $2.0 \times 10^5$ | 4.4 | –0.76 |
| $[\mathrm{Ni(tacn)_2}]^{3+}$ | 0.30[h] | 0.94 | $1.7 \times 10^6$ | $6.0 \times 10^3$ | 3.8 | 0.83 |

[a] $\mu = 0.1$ M, 25 °C. $E_f$ values obtained from references cited for rate constants. [b] Calculated from $k_{-2} = k_2/K_2$ with $E_f = 1.29$ V for $\mathrm{(SCN)_2^-/2(SCN^-)}$. [c] Reference 23. [d] Reference 1. [e] Reference 24; in 1 M $\mathrm{H_2SO_4}$. [f] Reference 61. [g] Reference 26; $\mu = 1$ M. [h] This work. [i] Reference 71, p 113. [j] Estimated.

**LFER vs Marcus Theory for $k_2$.** Oxidations of $\mathrm{SCN^-}$ by substitution-inert complexes usually have terms in their rate laws corresponding to $k_2$: i.e., terms that are second order with respect to $[\mathrm{SCN^-}]$ and first order with respect to [oxidant]. Table 6 summarizes these data and also gives values of $k_{-2}$ calculated from $k_2$ and $K_2$ by the principle of detailed balancing. In those cases where these calculated rate constants can be compared with values obtained directly by pulse radiolysis,[60,61] the agreement is adequate. Additional values for $k_{-2}$ can be found in pulse radiolysis studies of the reactions with $[\mathrm{Fe(CN)_6}]^{4-}$, $[\mathrm{Mo(CN)_8}]^{4-}$, $[\mathrm{W(CN)_8}]^{4-}$, $[\mathrm{Ru(bpy)_3}]^{2+}$, $[\mathrm{Os(terpy)_3}]^{2+}$, $[\mathrm{Fe(tacn)_2}]^{2+}$, and a series of substituted ferrocenes.[60,62,63] With the exception of that for the reaction with the good reducing agent $[\mathrm{Fe(tacn)_2}]^{2+}$, the values of $k_{-2}$ are substantially less than diffusion controlled, as has been noted by Nord.[4]

Nord has proposed that a good LFER can be derived from the data in Table 6 (not including those for $[\mathrm{Ni(tacn)_2}]^{3+}$) by constructing a plot of log $k_2$ vs log $K_2$.[4] Her LFER is given as

$$k_2 = (6.3 \times 10^8) \exp[38.93(E_{\mathrm{f,ox}} - 1.331)] \tag{25}$$

and is equivalent to a statement that $k_{-2}$ is $6.3 \times 10^8$ M$^{-1}$ s$^{-1}$. As the results for $k_{-2}$ in Table 6 show, the reactions of $[\mathrm{IrCl_6}]^{2-}$ and $[\mathrm{Ni(tacn)_2}]^{3+}$ are conspicuously slow. Nord argued that the point for $[\mathrm{IrCl_6}]^{2-}$ could be disregarded because it probably represented a catalyzed inner-sphere reaction. However, such a process introduces an additional term in the rate law and would be expected to yield an anomalously large rate constant rather than the low value observed. In any event, we believe that the data for $[\mathrm{IrCl_6}]^{2-}$ do not suffer from this complication and properly represent the mechanism given in Scheme 1. The new result, for $[\mathrm{Ni(tacn)_2}]^{3+}$, further weakens the support for this LFER. As is shown by the values of $k_{-2}$ in Table 7, four additional outliers can be found in the pulse-radiolysis literature.

A mechanism that was proposed for oxidations of iodide[64] was recently invoked in support of the LFER in eq 25.[4] It is given

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(56) *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH: Deerfield Beach, FL, 1986; Vol. 15, pp 13–47.

(57) Jenkins, H. D. B.; Thakur, K. P. *J. Chem. Educ.* **1979**, *56*, 576–577.

(58) Schindler, S.; Castner, E. W., Jr.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1993**, *32*, 4200–4208.

(59) Bradforth, S. E.; Kim, E. H.; Arnold, D. W.; Neumark, D. M. *J. Chem. Phys.* **1993**, *98*, 800–810.

(60) DeFelippis, M. R.; Murthy, C. P.; Faraggi, M.; Klapper, M. H. *Biochemistry* **1989**, *28*, 4847–4853.

(61) Nord, G.; Pedersen, B.; Floryan-Løvborg, E.; Pagsberg, P. *Inorg. Chem.* **1982**, *21*, 2327–2330.

(62) Shoute, L. C. T.; Alfassi, Z. B.; Neta, P.; Huie, R. E. *J. Phys. Chem.* **1991**, *95*, 3238–3242.

(63) Pohl, K.; Wieghardt, K.; Kaim, W.; Steenken, S. *Inorg. Chem.* **1988**, *27*, 440–447.

(64) Raycheba, J. M. T.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 45–51.

**Table 7.** Kinetics of Reduction of $(SCN)_2^-$

| reductant | $E_f$,[a] V | $k_{22}$, $M^{-1}\,s^{-1}$ | $k_{-2}$, $M^{-1}\,s^{-1}$ | $k_{-2,calc}$,[b] $M^{-1}\,s^{-1}$ | $r$,[i] Å |
|---|---|---|---|---|---|
| $[Fe(tacn)_2]^{2+}$ | 0.05 | $4.6 \times 10^3$ [c] | $5.9 \times 10^9$ [d] | $1.9 \times 10^{11}$ | 3.8 |
| $[Ru(bpy)_3]^{2+}$ | 1.27 | $4.0 \times 10^8$ [e] | $1.4 \times 10^7$ [f] | $8.0 \times 10^5$ | 6.5 |
| $[Mo(CN)_8]^{4-}$ | 0.84 | $3.0 \times 10^4$ [g] | $3.5 \times 10^6$ [h] | $7.4 \times 10^6$ | 4.7 |
| $[Fe(CN)_6]^{4-}$ | 0.46 | $3.0 \times 10^2$ [g] | $2.4 \times 10^7$ [h] | $4.8 \times 10^7$ | 4.5 |

[a] Potentials from references cited for corresponding values of $k_{-2}$. [b] Calculated as described in text using $k_{11} = 40\ M^{-1}\,s^{-1}$. [c] Reference 72. [d] Reference 63. [e] Reference 73. [f] Reference 60. [g] Reference 74. [h] Reference 62. [i] Estimated.

by the first two reactions in Scheme 3,

**Scheme 3**

$$M_{ox} + SCN^- \rightleftarrows M_{red},SCN \qquad K_{1,et} \qquad (26)$$

$$M_{red},SCN + SCN^- \rightarrow M_{red},(SCN)_2^- \qquad k_{sc} \qquad (27)$$

$$M_{red},SCN \rightleftarrows M_{red} + SCN \qquad k_{diff}, k_{-diff}, K_D \qquad (28)$$

which describe the $k_2$ steps as an electron-transfer preequilibrium followed by rate-limiting scavenging of the caged radical by $SCN^-$ such that $k_2 = K_{1,et}k_{sc}$. This mechanism could lead to a LFER if $k_{sc}$ were a constant. The addition of reaction 28 (cage escape) contributes the $k_1$ term in the rate law according to $k_1 = K_{1,et}k_{diff}$; this is in agreement with our understanding that the $k_1$ terms are, in general, limited by diffusive product separation. Scheme 3 also requires that $K_1$ be equal to $K_{1,et}k_{diff}/k_{-diff}$. This leads to the relationship

$$k_{sc} = k_2K_D/K_1 \qquad (29)$$

$K_1$ can be calculated from $E_f$ for the oxidants and $E_f$ for SCN, and a reasonable estimate of 7 M can be made for $K_D$.[65] Values of $k_{sc}$ calculated in this way for the reactions in Table 6 range from $3 \times 10^{12}\ M^{-1}\,s^{-1}$ (for the reaction of $[Ni(tacn)_2]^{3+}$) to $2 \times 10^{15}\ M^{-1}\,s^{-1}$ for the reaction of $[Fe(4,7\text{-}Me_2(phen))_3]^{3+}$. These calculated rate constants exceed the diffusion-controlled limit by a considerable margin, and so we can reject the proposal that the $k_2$ paths represent scavenging of caged SCN.

An alternative approach is to propose that electron transfer to $SCN^-$ is assisted by a second molecule of $SCN^-$, and this leads to a Marcus-type correlation of the $k_2$ rate constants. This approach has been considered qualitatively by Ng and Henry[24] and quantitatively by us and by Nord et al.[4,23,26,61] All of these quantitative treatments applied the simple cross relationship of Marcus theory (eqs 21 and 22 without work terms). To test Marcus theory properly in these systems, work terms should be included because of the various charges of the oxidants. Moreover, as we have discussed previously,[66] the cross relationship is not directly applicable to reactions of this type because the self-exchange rate constant involving $(SCN)_2^-$ would be third order and this is incompatible with the formulation of $\ln f_{12}$ in eq 22. The issue of dimensionality can by resolved by envisioning the reaction as occurring in two steps:

$$2SCN^- \rightleftarrows (SCN)_2^{2-} \qquad K_{ip} \qquad (30)$$

$$M_{ox} + (SCN)_2^{2-} \rightarrow M_{red} + (SCN)_2^- \qquad k_{et} \qquad (31)$$

This would lead to the measured rate constant, $k_2$, being the product $K_{ip}k_{et}$. The self-exchange reaction would then be defined in terms of an ion pair:

$$^*(SCN)_2^{2-} + (SCN)_2^- \rightarrow {}^*(SCN)_2^- + (SCN)_2^{2-} \qquad k_{11} \qquad (32)$$

This would lead to $k_{11}$ being a second-order rate constant. If the cross relationship is applied, $k_{12}$ would be $k_{et}$ in reaction 31 and $K_{12}$ would be the equilibrium constant for reaction 31, calculated as $K_2/K_{ip}$.

Formation of an ion pair between two molecules of $SCN^-$ rests on firm theoretical grounds.[67] As a reasonable approximation, the value of $K_{ip}$ may be taken as $0.035\ M^{-1}$, which is the value estimated for the corresponding reaction of $I^-$ at $\mu = 0.1$ M.[66] A rough estimate of 3.2 Å can be made for the effective radii of $(SCN)_2^{2-}$ and $(SCN)_2^-$; this estimate is based on the calculated structure of $(SCN)_2^-$.[68] Table 6 shows that a value of $40\ M^{-1}\,s^{-1}$ for $k_{11}$ leads to a fine correlation of the data obtained at $\mu = 0.1$ M. In particular, this treatment accounts for the deviations from the LFER for the reactions of $[Ni(tacn)_2]^{3+}$ and $[IrCl_6]^{2-}$, which arise from relatively low self-exchange rate constants for the coordination complexes. The correlation is not as good for the reactions of $[Fe(phen)_3]^{3+}$ and its derivatives; these reactions were studied at high ionic strength (1 M $H_2SO_4$), and so the values of $k_{11}$ and $E_f$ for $(SCN)_2^-$ may not be appropriate.

Further tests of Marcus theory are shown in Table 7 as calculated values of $k_{-2}$ for the reactions of $[Fe(tacn)_2]^{2+}$, $[Mo(CN)_8]^{4-}$, $[Fe(CN)_6]^{4-}$, and $[Ru(bpy)_3]^{2+}$. The result for the $[Fe(tacn)_2]^{2+}$ reaction indicates that it should be diffusion controlled (in agreement with experiment) because of this reaction's highly favorable driving force. The relatively low value of $k_{-2}$ for $[Ru(bpy)_3]^{2+}$ is also reproduced, this time because of the unfavorable driving force. In the cases of $[Mo(CN)_8]^{4-}$ and $[Fe(CN)_6]^{4-}$, the low $k_{-2}$ values can be traced to the low self-exchange rate constants for these complexes.

The value of $40\ M^{-1}\,s^{-1}$ derived for the $(SCN)_2^-/(SCN)_2^{2-}$ self-exchange reaction may be compared with the value of $3 \times 10^4\ M^{-1}\,s^{-1}$ derived previously for the corresponding iodide system.[66] We have argued that the dissociation energy of $X_2^-$ is an important factor in the reorganizational energies for such processes,[66] and Savéant has developed this concept for dissociative electron transfer of alkyl halides.[69] Savéant finds a good correlation using gas-phase dissociation energies for RX,[70] while we find that aqueous dissociation energies are required for acceptable results in the $X_2^-$ systems.[66] The difference, of course, is that dissociation of $X_2^-$ is strongly assisted by the solvent. A test of this is not presently possible in the case of the $(SCN)_2^-$ system because the gas-phase dissociation energy is unknown. However, the aqueous dissociation enthalpies are known for both $I_2^-$ and $(SCN)_2^-$, with $(SCN)_2^-$ being about 8 kJ $mol^{-1}$ more stable.[50,51] This energy difference qualitatively accounts for the lower intrinsic reactivity of the thiocyanate system.

In summary, the LFER achieves moderate empirical success in correlating the values of $k_2$ and $k_{-2}$, but its explanation in terms of a cage-scavenging mechanism is not viable. Moreover, the LFER provides no rationale for the deviations for reactions having the same mechanism. Marcus theory, on the other hand, is

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(65) Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: New York, 1991; p 210.

(66) Stanbury, D. M. *Inorg. Chem.* **1984**, *23*, 2914–2916.

(67) Gao, J.; Boudon, S.; Wipff, G. *J. Am. Chem. Soc.* **1991**, *113*, 9610–9614.

(68) Jensen, N. H.; Wilbrandt, R.; Pagsberg, P.; Hester, R. E.; Erstbrunner, E. *J. Chem. Phys.* **1979**, *71*, 3326–3329.

(69) Savéant, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 6788–6795.

(70) Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 10595–10602.

(71) Schilt, A. A. *Analytical Applications of 1,10-Phenanthroline and Related Compounds*; Pergamon: New York, 1969; pp 36, 107, 122.

(72) Küppers, H.-J.; Wieghardt, K.; Steenken, S.; Nuber, B.; Weiss, J. *Z. Anorg. Allg. Chem.* **1989**, *573*, 43–62.

(73) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113–127.

(74) Campion, R. J.; Purdie, N.; Sutin, N. *Inorg. Chem.* **1964**, *3*, 1091–1094.

somewhat more cumbersome in that it requires additional data on self-exchange rates, but it accounts for deviations from the LFER in a systematic manner. The success of Marcus theory is taken in support of a detailed mechanism for the $k_2$ process, in which the three reactants become assembled as an ion triplet (alternatively viewed as an ion pair between the oxidant and $(SCN)_2^{2-}$), which then undergoes outer-sphere electron transfer with concerted S—S bond formation. This is entirely analogous to the mechanism that we have discussed for oxidations of iodide.[66]

**$k_3$ Analysis.** We are aware of only one other report of a rate constant for a reaction in which $(SCN)_2^-$ is oxidized to $(SCN)_2$ by an "outer-sphere" oxidant, and that is for the reaction with $[Os(bpy)_3]^{3+}$ ($k_3 = 1 \times 10^{10}$ M$^{-1}$ s$^{-1}$).[61] This rate constant is about 3 orders of magnitude greater than our result for the $[Ni(tacn)_2]^{3+}$ reaction, despite the somewhat greater driving force of the latter. Marcus theory again provides a rationale for this behavior, since the self-exchange rate constant for the Ni(III/II) system is 5 orders of magnitude lower than for the Os(III/II) system. A significant contribution to the barrier would also be expected from the $(SCN)_2/(SCN)_2^-$ couple because of the major structural reorganization involved.[68]

**Summary.** The reaction of $[Ni(tacn)_2]^{3+}$ with SCN$^-$ is somewhat unusual in that it shows substantial product inhibition and a measurable value for the second-order rate constant $k_1$. The product inhibition supports the assignment of electron-transfer mechanisms for both the $k_1$ and $k_2$ paths. Values of $k_1$ for a series of oxidants adhere strictly to a simple LFER that requires the rate-limiting step to be diffusive product separation. This is consistent with the predictions of Marcus theory because of the low reorganizational energies involved as well as the high endothermicity of the reactions. The third-order $k_2$ rate constants show systematic variations depending on the driving force and the self-exchange rate constants. They are described by a mechanism involving associative electron transfer, in which S—S bond formation and electron transfer occur as a concerted process.

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