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# Articles

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## Bromine Oxidation of a Nickel(II) Bis(oxime-imine) Complex. Evidence for a Single-Step Outer-Sphere Two-Electron Transfer?

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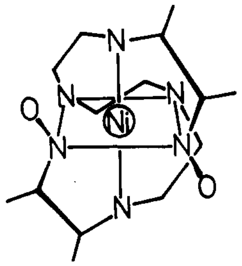
The kinetics and mechanism of the two-electron oxidation of the sexidentate bis(oxime-imine) complex of nickel(II), $[Ni^{II}L]$ (I), by bromine have been investigated in bromide ion media over the pH range 3.1-7.6 at 25 °C and 1.0 M ionic strength. In the presence of an excess of bromine or nickel(II), oxidation is monophasic, and the initial product is $[Ni^{IV}L]^{2+}$, a formal nickel(IV) species that undergoes subsequent reactions to give an unknown oxidation product with excess bromine at pH >6 or to give $[Ni^{III}L]^+$ by comproportionation with excess nickel(II) at pH >5. The sole kinetically important oxidant is $Br_2$, and second-order rate constants for reaction of $[Ni^{II}L]$ and its protonated form $[Ni^{II}LH]^+$ are $2.1 \times 10^7$ and $7.1 \times 10^5$ $M^{-1}$ $s^{-1}$, respectively. These rate constants are in line with a rate-determining single-electron-transfer reaction, and the proposed mechanism involves formation of a transient ion pair $[Ni^{III}L^+,Br_2^-]$ in which the rate of subsequent electron transfer is comparable with the rate of ion-pair dissociation. In addition, the pulse-radiolysis technique has been used to investigate the reactions of nickel(II) with $Br_2^-$ to give $[Ni^{III}L]^+$, and rate constants for $[Ni^{II}L]$ and $[Ni^{II}LH]^+$ are $8.5 \times 10^8$ and $2.7 \times 10^8$ $M^{-1}$ $s^{-1}$, respectively, at 21 °C.

### Introduction

The electron-transfer chemistry of the nickel(IV) bis(oxime-imine) complex $[Ni^{IV}L]^{2+}$ where $LH_2$ is 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime has been well studied. Reactions with one-electron[1-3] and two-electron[4-6] reductants lead to the formation of nickel(III) intermediates and eventually to the nickel(II) products. Studies of the oxidation of the corresponding nickel(II) complexes, I, by one-electron oxidants have also been reported.[7-10] However, no reactions with potential two-electron oxidants have yet been examined. The role of nickel(III) in such reactions is of considerable interest. At higher pH, oxidation of nickel(III) to nickel(IV), eq 1, is thermodynamically less favorable[1,11,12] than the corresponding oxidation of nickel(II) to nickel(III), eq 2, while at lower pH, the reduction potentials of nickel(IV) and nickel(III) are comparable, eq 3.



I

$$[Ni^{IV}L]^{2+} + e^- \rightleftharpoons [Ni^{III}L]^+ \qquad E° = 0.64\ V \qquad (1)$$

$$[Ni^{III}L]^+ + e^- \rightleftharpoons [Ni^{II}L] \qquad E° = 0.42\ V \qquad (2)$$

$$[Ni^{III}LH]^{2+} + e^- \rightleftharpoons [Ni^{II}LH]^+ \qquad E° = 0.65\ V \qquad (3)$$

A complicating feature of the oxidation of the nickel(II) complexes is the presence of a variety of protonation equilibria,[12] eq 4 and 5. In addition, the nickel(III) intermediate is also subject

$$[Ni^{II}LH_2]^{2+} \rightleftharpoons [Ni^{II}LH]^+ + H^+ \qquad pK_4 = 5.90 \qquad (4)$$

$$[Ni^{II}LH]^+ \rightleftharpoons [Ni^{II}L] + H^+ \qquad pK_5 = 7.80 \qquad (5)$$

to protonation,[1] eq 6. However, the behavior of these complexes,

$$[Ni^{III}LH]^{2+} \rightleftharpoons [Ni^{III}L]^+ + H^+ \qquad pK_6 = 4.05 \qquad (6)$$

including reactivity toward electron transfer is relatively well understood,[13] enabling detailed mechanistic investigations to be undertaken.

Bromine is a potent oxidant with a reduction potential[14] sufficient to oxidize nickel(II) to nickel(IV) over a wide pH range, eq 7. It is subject to various hydrolytic equilibria which are

$$Br_2 + 2e^- \rightleftharpoons 2Br^- \qquad E° = 1.087\ V \qquad (7)$$

relatively well characterized,[15,16] eq 8 and 9, and the reduction

$$H_2O + Br_2 \rightleftharpoons HOBr + H^+ + Br^- \qquad K_8 = 9.6 \times 10^{-9}\ M^2 \qquad (8)$$

$$HOBr \rightleftharpoons OBr^- + H^+ \qquad pK_9 = 8.62 \qquad (9)$$

potentials of the hydrolyzed species are also known, eq 10 and 11. The oxidations of a number of metal ion complexes by these bromine species have been reported.[17-20]

$$HOBr + H^+ + 2e^- \rightleftharpoons Br^- + H_2O \qquad E° = 1.33\ V \qquad (10)$$

$$OBr^- + H_2O + 2e^- \rightleftharpoons Br^- + 2OH^- \qquad E° = 0.70\ V \qquad (11)$$

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[†] Department of Chemistry.

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(1) Lappin, A. G.; Laranjeira, M. C. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1861-1865.

(2) Lappin, A. G.; Laranjeira, M. C. M.; Peacock, R. D. *Inorg. Chem.* **1983**, *22*, 786-791.

(3) Macartney, D. H.; McAuley, A. *Inorg. Chem.* **1983**, *22*, 2062-2066.

(4) Lappin, A. G.; Laranjeira, M. C. M.; Youde-Owei, L. *J. Chem. Soc., Dalton Trans.* **1981**, 721-725.

(5) Macartney, D. H.; McAuley, A. *J. Chem. Soc., Dalton Trans.* **1984**, 103-107.

(6) Munn, S. F.; Lannon, A. M.; Laranjeira, M. C. M.; Lappin, A. G. *J. Chem. Soc., Dalton Trans.* **1984**, 1371-1375.

(7) Macartney, D. H.; McAuley, A. *Can. J. Chem.* **1982**, *60*, 2625-2628.

(8) Macartney, D. H.; McAuley, A. *Can. J. Chem.* **1983**, *61*, 103-108.

(9) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3510-3524.

(10) Allan, A. E.; Lappin, A. G.; Laranjeira, M. C. M. *Inorg. Chem.* **1984**, *23*, 477-482.

(11) Mohanty, J. G.; Singh, R. P.; Chakravorty, A. *Inorg. Chem.* **1975**, *14*, 2178-2183.

(12) Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1976**, *15*, 2912-2916.

(13) Lappin, A. G.; Martone, D. P.; Osvath, P. *Inorg. Chem.* **1985**, *24*, 4187-4191.

(14) Latimer, W. N. *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 62.

(15) Pink, J. M. *Can. J. Chem.* **1970**, *48*, 1169-1171.

(16) Anbar, M.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 1073-1077.

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During studies of the oxidation of $[Ni^{II}LH]^{2+}$ by $Br_2$ at pH 5.7 with the reductant in excess, conditions in which $[Ni^{III}L]^+$ is the thermodynamic product, it was noted that the reaction involved the formation of $[Ni^{IV}L]^{2+}$ as an intermediate. The implication is that a single-step two-electron transfer may be involved. A detailed mechanistic study was therefore undertaken.

## Experimental Section

**Materials.** The compounds $[Ni^{IV}L](ClO_4)_2$ and $[Ni^{II}LH_2](ClO_4)_2$ were prepared as outlined previously.[11] Solutions of nickel(IV) were standardized spectrophotometrically with the use of literature[11] absorption coefficients ($\epsilon_{500}$ = 6300 $M^{-1}$ $cm^{-1}$) while nickel(II) solutions were prepared by dissolving accurately weighed amounts of the crystalline solid. The nickel(III) complex $[Ni^{III}L]^+$ was generated by mixing equimolar amounts of $[Ni^{IV}L]^{2+}$ and $[Ni^{II}L]$ at pH >5.

Bromine solutions were prepared from elemental bromine (Fisher, ACS) and were standardized spectrophotometrically at 390 nm ($\epsilon$ = 179 $M^{-1}$ $cm^{-1}$)[20] or at the isosbestic point of $Br_2$ and $Br_3^-$, 457 nm ($\epsilon$ = 98 $M^{-1}$ $cm^{-1}$).[18] Sodium perchlorate (Fluka, puriss) and sodium bromide (Fisher, ACS) were used as supplied, as were the other reagents, which were of ACS reagent grade quality or better.

**Methods.** Unless otherwise noted, kinetic measurements were made in $1.0 \times 10^{-2}$ M buffer solutions at 1.0 M ionic strength with use of $NaClO_4$ as background electrolyte. Reactions were monitored at 500 nm with a Durrum D-110 stopped-flow spectrophotometer thermostated at 25.0 ± 0.1 °C. Data were collected with a Nicolet 3091 digital oscilloscope. The pH of solutions was determined immediately after reaction with a Beckman SelectIon 2000 multimeter equipped with a Corning combination glass electrode with saturated calomel (NaCl) reference.

Steady-state radiolyses were carried out in a Gammacell 200 $^{60}Co$ source with a dose rate of 4 krd $min^{-1}$. Pulse-radiolysis kinetic and spectrophotometric measurements were made with a computer-controlled instrument described previously.[21] The dose was calibrated with an aqueous $N_2O$-saturated KSCN solution before each set of experiments. The differential extinction coefficients for the transient spectra ($\Delta\epsilon'$) were calculated from the relation $\Delta\epsilon' = AK/DG$ where $A$ is the difference in absorbance after and before the pulse, $D$ the dose supplied by the pulse, $G$ the radiation yield, and $K$ a calibration factor chosen such that $G\Delta\epsilon'$ for the $(SCN)_2^-$ radical is $4.56 \times 10^4$ molecules $(100\ eV)^{-1}$ $M^{-1}$ $cm^{-1}$ [22] at 480 nm in $N_2O$-saturated solutions of $10^{-2}$ M KSCN. Radiolysis experiments were carried out at 21 ± 1 °C.

Radiolysis of water or aqueous solution results in the formation of $e_{aq}^-$, OH, H, and molecular products, eq 12. In the presence of nitrous oxide,

$$H_2O \rightsquigarrow 2.8e^- + 2.8OH + 0.6H \qquad (12)$$

strongly reducing solvated electrons are converted into oxidizing OH radicals, eq 13, which in the presence of bromide ions react to give the

$$e^- + N_2O \rightarrow OH + OH^- + N_2 \qquad (13)$$

$Br_2^-$ radical,[23] eq 14 and 15. The formation of $Br_2^-$ by the mechanism

$$OH + Br^- \rightarrow BrOH^- \qquad (14)$$

$$BrOH^- + Br^- \rightarrow Br_2^- + OH^- \qquad (15)$$

is fast, $\geq 8 \times 10^8$ $M^{-1}$ $s^{-1}$ at pH $\leq 11$. Studies of the reaction of the nickel(II) complex with OH reveal that it is also rapid, accelerating with increasing pH from $3 \times 10^9$ $M^{-1}$ $s^{-1}$ at pH 7.0 to $6 \times 10^9$ $M^{-1}$ $s^{-1}$ at pH 10.0, but leads to different products from those found with $Br_2^-$. This competing reaction is avoided by using a ratio $[Br^-]/[Ni(II)] \geq 50$, and under the conditions used ($[Br^-] = 1 \times 10^{-2}$ M), essentially all the OH radicals are converted into $Br_2^-$ with a half-life of less than 0.1 μs.

## Results

The oxidation of nickel(II) by bromine is kinetically a very complex reaction involving species that undergo a variety of protic and complexation processes. Equilibrium constants for most of these processes are well documented but not in general for the conditions, 1.0 M $NaBr/NaClO_4$, used in the present work. Where satisfactory fits to experimental data were obtained using the literature constants, no attempt was made to remeasure the constants. Most of the constants used together with reduction potentials for the species involved in the various reactions are presented in the introduction.

**(a) Stoichiometry and Reaction Products.** The stoichiometry of the oxidation of nickel(II) by $Br_2$ in bromide media at pH <6 was investigated spectrophotometrically by measuring the nickel(IV) produced by mixing standard solutions of nickel(II) and $Br_2$, and was found to be 1:1, eq 16, as might be predicted from

$$[Ni^{II}LH_2]^{2+} + Br_2 \rightarrow [Ni^{IV}L]^{2+} + 2H^+ + 2Br^- \qquad (16)$$

the reduction potentials. Between pH 5 and 6 with an excess of nickel(II), the product is nickel(III), eq 17, but acidification leads

$$2[Ni^{II}LH]^+ + Br_2 \rightarrow 2[Ni^{III}L]^+ + 2H^+ + 2Br^- \qquad (17)$$

to disproportionation. At higher pH, and particularly at low bromide ion concentrations, conditions favorable for the formation of HOBr, the formation of nickel(IV) is followed by a decomposition reaction in which a novel oxidized transient with a broad absorption maximum around 490 nm is formed. It has not proved possible to identify this species but it is thought to be the product of the reaction of HOBr with $[Ni^{IV}L]^{2+}$ in which ligand attack has taken place. Detailed studies of this reaction are not the subject of this paper.

**(b) Kinetics of Oxidation of Nickel(II) by $Br_2$.** The kinetics of oxidation of nickel(II) by $Br_2$ were examined under pseudo-first-order conditions with excess bromine in the presence of bromide ion over the pH range 3–6 by monitoring the rate of production of the highly colored $[Ni^{IV}L]^{2+}$ at 500 nm. Some data were also obtained with an excess of nickel(II). The reaction traces are monophasic, first order for more than 3 half-lives, and observed rate constants, $k_{obsd}$, are presented in Table I. The reaction is first-order in both [Ni(II)] and $[Br_2]$, and the second-order rate constants, $k_{so}$, decrease in the presence of bromide ion for data at two pH values. This $[Br^-]$ dependence is due to the formation of $Br_3^-$, eq 18. The rate constants can be fit to eq 19, where $k_a$

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad K_{18} \qquad (18)$$

$$k_{so} = \frac{k_a + k_b K_{18}[Br^-]}{1 + K_{18}[Br^-]} \qquad (19)$$

and $k_b$ are the rate constants for reactions of nickel(II) with $Br_2$ and $Br_3^-$ respectively. The best fit parameters are $k_a = (1.96 \pm 0.04) \times 10^4$ $M^{-1}$ $s^{-1}$, $k_b = 0 \pm 5$ $M^{-1}$ $s^{-1}$, and $K_{18} = 14.6 \pm 0.4$ $M^{-1}$ at pH 4.40 and $k_a = (1.59 \pm 0.02) \times 10^5$ $M^{-1}$ $s^{-1}$, $k_b = 50 \pm 100$ $M^{-1}$ $s^{-1}$, and $K_{18} = 14.4 \pm 0.4$ $M^{-1}$ at pH 5.30. Spectrophotometric titration of $Br_2$ with $Br^-$ at 390 nm confirms that $K_{18} = 14.4 \pm 0.2$ $M^{-1}$ ($\epsilon_{Br_2} = 173 \pm 4$ $M^{-1}$ $cm^{-1}$, $\epsilon_{Br_3^-} = 741 \pm 25$ $M^{-1}$ $cm^{-1}$) under the conditions of the study. The value is close to values reported in the literature for different conditions ($K_{18}$ = 16.9).[15] Good agreement in the values of $K_{18}$ at different pH values suggests that the equilibrium involving HOBr has little effect on the reaction kinetics below pH 5.3, even at relatively low (0.01 M) $[Br^-]$ concentrations. Second-order rate constants for reactions of $Br_3^-$ are negligible and in the subsequent analysis of the pH dependence of the reaction were set at zero.

The second-order rate constant at $[Br^-]$ = 0.01 M increases with pH, reaching a maximum around pH 6.3, and subsequently decreases. This behavior can be explained by consideration of the various protonation and hydrolysis reactions involved. At low pH, the strong increase in rate with increasing pH can be explained by a mechanism involving oxidation of the different protonated forms of nickel(II), eq 20–22. Above pH 6, hydrolysis of bromine

$$[Ni^{II}LH_2]^{2+} + Br_2 \rightarrow [Ni^{IV}L]^{2+} + 2H^+ + 2Br^- \quad k_{20} \qquad (20)$$

$$[Ni^{II}LH]^+ + Br_2 \rightarrow [Ni^{IV}L]^{2+} + H^+ + 2Br^- \quad k_{21} \qquad (21)$$

$$[Ni^{II}L] + Br_2 \rightarrow [Ni^{IV}L]^{2+} + 2Br^- \quad k_{22} \qquad (22)$$

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[17] Woodruff, W. H.; Margerum, D. W.; Milano, M. J.; Pardue, H. L.; Santini, R. E. *Inorg. Chem.* **1973**, *12*, 1490–1494.

[18] Woodruff, W. H.; Burke, B. A.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2573–2577.

[19] Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2578–1585.

[20] Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38–43.

[21] Patterson, L. K.; Lilie, J. J. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 129–141; *Chem. Abstr.* **1975**, *83*, 3037s.

[22] Baxendale, J. H.; Bevan, P. L. T.; Stott, D. A. *Trans. Faraday Soc.* **1968**, *64*, 2389–2397.

[23] Schuler, R. H.; Patterson, L. K.; Janata, E. *J. Phys. Chem.* **1980**, *84*, 2088–2089.

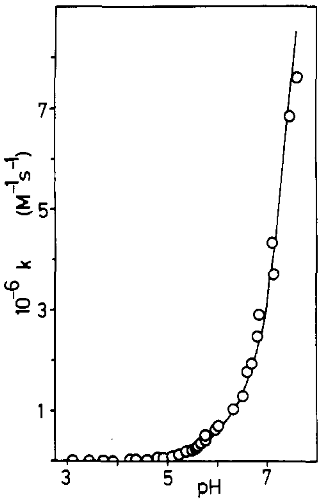

**Figure 1.** Plot of the second-order rate constant for bromine oxidation, corrected for the actual $[Br_2]$ concentration as a function of pH at 25 °C and 1.0 M ionic strength.

is important and the reactions of HOBr and $OBr^-$ must be considered. These result in a reduction in rate, implying that HOBr and $OBr^-$ are much less reactive than $Br_2$. To simplify the analysis, only contributions from the most reactive nickel(II) complex, $[Ni^{II}L]$, were considered, eq 23 and 24.

$$[Ni^{II}L] + HOBr \rightarrow [Ni^{IV}L]^{2+} + OH^- + Br^- \quad k_{23} \qquad (23)$$

$$[Ni^{II}L] + OBr^- \xrightarrow{(H^+)} [Ni^{IV}L]^{2+} + OH^- + Br^- \quad k_{24} \qquad (24)$$

In the subsequent analysis it was found that the rate constants $k_{23}$ and $k_{24}$ were negligible (for example $k_{23} \leq 10^3$ $M^{-1}$ $s^{-1}$, which is within the experimental error for $k_{22}$) and that the data are well represented by the second-order rate expression given in eq 25.

$$k_{so} = (k_{20}[H^+]^4[Br^-] + k_{21}K_4[H^+]^3[Br^-] + k_{22}K_4K_5[H^+]^2[Br^-] + k_{23}K_4K_5K_8[H^+] + k_{24}K_4K_5K_8K_9)/ ([H^+]^2 + K_4[H^+] + K_4K_5)([H^+]^2[Br^-] + K_{18}[H^+]^2[Br^-]^2 + K_8[H^+] + K_8K_9) \qquad (25)$$

Best fit parameters (weighting $1/k_{so}$) are $k_{20} = (2 \pm 4) \times 10^3$ $M^{-1}$ $s^{-1}$, $k_{21} = (7.1 \pm 1.3) \times 10^5$ $M^{-1}$ $s^{-1}$, and $k_{22} = (2.1 \pm 0.5) \times 10^7$ $M^{-1}$ $s^{-1}$ for the equilibrium constants reported elsewhere in the paper. This fit shows a significant deviation for data at higher pH and high $[Br^-]$ where HOBr formation, eq 8, is suppressed, suggesting that the hydrolysis constant used, $K_8$, is inappropriate. However, other complications including the subsequent decomposition of the nickel(IV) product and the approach of the first-order rate constants for the redox process to the rate of interconversion of $Br_2$ and HOBr (110 $s^{-1}$)[24] may affect the accuracy of the data in this regime.[25] Figure 1 shows a plot of all the second-order rate constants corrected for the actual bromine ($Br_2$) concentration as a function of pH. Agreement with the calculated curve is very good.

Above pH 6 and at lower bromide ion concentrations, conditions which favor the formation of HOBr, the oxidation of nickel(II) to nickel(IV) is followed by two slower processes. The first of these is an increase in absorbance ($t_{1/2}$ = 1.5 s at pH 6.5 and $[Br_2]_T = 1.5 \times 10^{-4}$ M) to give a transient absorbing at 490 nm, and this is followed by the slower decomposition of the oxidized nickel complex. Both rates show a strong dependence on increasing oxidant concentrations, and both increase with increasing pH. It is thought that the reaction involves attack of HOBr on the oxime–imine ligand structure of $[Ni^{IV}L]^{2+}$, but detailed investigations were not carried out.

**Table I.** Pseudo-First-Order Rate Constants for the Oxidation of Nickel(II) by Bromine at 25 °C and 1.00 M Ionic Strength

| $pH^a$ | $[Br^-]$, M | $10^4[Br_2]_T$,$^g$ M | $10^5$[Ni(II)], M | $k_{obsd}$, $s^{-1}$ | $k_{calcd}$,$^h$ $s^{-1}$ |
|---|---|---|---|---|---|
| 3.15 | 1.00 | 1.43 | 1.03 | 0.0095 | 0.0117 |
| 3.46 | 1.00 | 1.43 | 1.03 | 0.0235 | 0.0240 |
| 3.97 | 1.00 | 1.43 | 1.03 | 0.074 | 0.077 |
| 4.43 | 1.00 | 1.43 | 1.03 | 0.20 | 0.219 |
| 4.94 | 1.00 | 1.43 | 1.03 | 0.64 | 0.679 |
| 5.25 | 1.00 | 1.43 | 1.03 | 1.34 | 1.31 |
| 5.56 | 1.00 | 1.43 | 1.03 | 2.42 | 2.42 |
| $5.65^b$ | 1.00 | 1.38 | 1.05 | 2.87 | 2.77 |
| $5.83^b$ | 1.00 | 1.38 | 1.05 | 3.76 | 3.84 |
| $5.98^b$ | 1.00 | 1.38 | 1.05 | 5.5 | 5.0 |
| 3.00 | 1.00 | 0.089 | 24.9 | 0.0133 | 0.0145 |
| 4.25 | 1.00 | 0.089 | 24.9 | 0.17 | 0.25 |
| 4.64 | 1.00 | 0.089 | 24.9 | 0.60 | 0.61 |
| 5.11 | 1.00 | 0.089 | 24.9 | 1.43 | 1.70 |
| 5.45 | 1.00 | 0.089 | 24.9 | 2.96 | 3.40 |
| 5.73 | 1.00 | 0.089 | 24.9 | 5.6 | 5.79 |
| 5.79 | 1.00 | 0.089 | 24.9 | 8.2 | 6.5 |
| 4.14 | 0.99 | 74 | 1.03 | 7.8 | 5.93 |
| 4.25 | 0.99 | 2.94 | 1.03 | 0.36 | 0.30 |
| 4.26 | 0.99 | 7.4 | 1.03 | 0.89 | 0.78 |
| 4.26 | 0.99 | 14.6 | 1.03 | 1.77 | 1.54 |
| 4.26 | 0.99 | 22.2 | 1.03 | 2.69 | 2.34 |
| 4.26 | 0.99 | 44.4 | 1.03 | 5.1 | 4.68 |
| 4.36 | 0.50 | 1.48 | 1.03 | 0.34 | 0.364 |
| $5.30^c$ | 0.50 | 1.43 | 1.03 | 2.92 | 2.72 |
| 4.40 | 0.30 | 1.48 | 1.03 | 0.55 | 0.614 |
| $5.33^c$ | 0.30 | 1.43 | 1.03 | 4.6 | 4.45 |
| 4.40 | 0.10 | 1.48 | 1.03 | 1.25 | 1.34 |
| $5.33^c$ | 0.10 | 1.43 | 1.03 | 10.7 | 9.6 |
| 4.40 | 0.03 | 1.48 | 1.03 | 2.05 | 2.26 |
| $5.33^c$ | 0.03 | 1.43 | 1.03 | 16.8 | 15.9 |
| 3.46 | 0.01 | 1.51 | 1.03 | 0.134 | 0.339 |
| 3.76 | 0.01 | 1.51 | 1.03 | 0.50 | 0.67 |
| 3.98 | 0.01 | 1.51 | 1.03 | 0.94 | 1.11 |
| 4.40 | 0.01 | 1.48 | 1.03 | 2.54 | 2.79 |
| 4.43 | 0.01 | 1.51 | 1.03 | 2.48 | 3.05 |
| 4.81 | 0.01 | 1.51 | 1.03 | 5.5 | 6.9 |
| 5.30 | 0.01 | 1.51 | 1.03 | 17.5 | 17.6 |
| $5.30^c$ | 0.01 | 1.43 | 1.03 | 18.7 | 16.7 |
| $5.30^c$ | 0.01 | 1.43 | 1.03 | 18.3 | 16.7 |
| $5.42^d$ | 0.01 | 1.43 | 1.03 | 18.5 | 20.4 |
| $5.49^e$ | 0.01 | 1.43 | 1.03 | 18.2 | 22.6 |
| 5.58 | 0.01 | 1.51 | 1.03 | 28.8 | 27.0 |
| 6.02 | 0.01 | 1.51 | 1.03 | 49 | 42 |
| 6.33 | 0.01 | 1.48 | 1.03 | 46 | 46 |
| $6.54^f$ | 0.01 | 1.48 | 1.03 | 42 | 48 |
| $6.60^f$ | 0.01 | 1.48 | 1.03 | 52 | 48 |
| $6.71^f$ | 0.01 | 1.48 | 1.03 | 46 | 47 |
| $6.82^f$ | 0.01 | 1.48 | 1.03 | 48 | 46 |
| $6.85^f$ | 0.01 | 1.48 | 1.03 | 53 | 46 |
| $7.11^f$ | 0.01 | 1.48 | 1.03 | 46 | 42 |
| $7.15^f$ | 0.01 | 1.48 | 1.03 | 36 | 41 |
| $7.44^f$ | 0.01 | 1.48 | 1.03 | 31 | 32 |
| $7.60^f$ | 0.01 | 1.48 | 1.03 | 26 | 29 |

[a] Buffer: unless otherwise noted [acetate] = 0.01 M. [b] [acetate] = 0.02 M. [c] [acetate] = 0.054 M. [d] [acetate] = 0.128 M. [e] [acetate] = 0.50 M. [f] [phosphate] = 0.01 M. [g] $[Br_2]_T$ refers to $[Br_2] + [Br_3^-] + [HOBr] + [OBr^-]$. [h] $k_{calcd}$ is the rate constant calculated by using eq 25 and the parameters in the text.

**(c) Kinetics of Oxidation of Nickel(III) by $Br_2$.** Solutions of $[Ni^{III}L]^+$ are thermodynamically stable above pH 5,[1] and in the presence of an excess of $[Ni^{IV}L]^{2+}$ (to ensure that no nickel(II) is present), the kinetics of the oxidation by $Br_2$ can be examined. Rate data are presented in Table II. As with the corresponding reaction of nickel(II), the second-order rate constants $k'_{so}$ decrease with increasing bromide ion concentration due to the formation of unreactive $Br_3^-$. The data at pH 5.08 were fit to eq 19, and values of $k'_a = (9.3 \pm 0.3) \times 10^4$ $M^{-1}$ $s^{-1}$, $k'_b = (7 \pm 3) \times 10^2$ $M^{-1}$ $s^{-1}$ were obtained with $K_{18} = 14.4$ $M^{-1}$.

When $[Ni^{III}L]^+$ reacts in an acidic solution of $Br_2$ at pH 2, the only reaction that is detected is the slow disproportionation[13] of $[Ni^{III}LH]^{2+}$, indicating that the protonated complex has little

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[24] Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355–1361.

[25] A better fit to the data at high bromide ion concentrations was obtained with $k_{21} = (5.8 \pm 0.9) \times 10^5$ $M^{-1}$ $s^{-1}$ and $k_{22} = (3.9 \pm 0.7) \times 10^7$ $M^{-1}$ $s^{-1}$, not substantially different.

**Table II.** Pseudo-First-Order Rate Constants for the Oxidation of Nickel(III) by Bromine at 25 °C and 1.00 M Ionic Strength

| pH | $[Br^-]$, M | $10^4[Br_2]_T$,[c] M | $10^5$[Ni(III)], M | $k_{obsd}$, $s^{-1}$ |
|---|---|---|---|---|
| 4.38 | 0.50 | 1.48 | 1.31[a] | 0.83 |
| 4.78 | 0.50 | 1.48 | 1.31[a] | 1.45 |
| 4.78 | 0.50 | 7.55 | 1.05[a] | 5.7 |
| 5.08 | 0.50 | 1.48 | 1.31[a] | 1.74 |
| 5.08 | 0.50 | 7.55 | 1.05[b] | 9.0 |
| 5.08 | 0.30 | 1.48 | 1.31[a] | 2.84 |
| 5.08 | 0.10 | 1.48 | 1.31[a] | 5.6 |
| 5.08 | 0.03 | 1.48 | 1.31[a] | 9.9 |
| 5.08 | 0.01 | 1.48 | 1.31[a] | 11.7 |

[a] In the presence of $2.2 \times 10^{-5}$ M $[Ni^{IV}L]^{2+}$. [b] In the presence of $1.0 \times 10^{-5}$ M $[Ni^{IV}L]^{2+}$. [c] $[Br_2]_T = [Br_2] + [Br_3]^- + [HOBr] + [^-OBr]$.

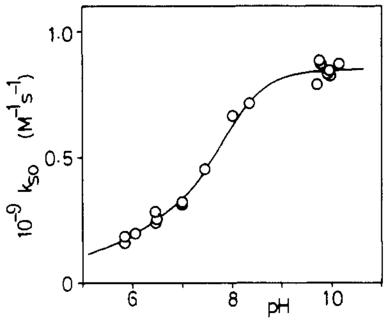

**Figure 2.** Plot of the second-order rate constant for the $Br_2^-$ oxidation as a function of pH at 21 °C.

reactivity with $Br_2$ and allowing evaluation of the second-order rate constant for oxidation of $[Ni^{III}L]^+$, eq 26, as $k_{26} = 1.2 \times 10^5$ $M^{-1}$ $s^{-1}$. Confirmation of this decrease in reactivity with protonation was also obtained from studies between pH 4 and 5.

$$[Ni^{III}L]^+ + Br_2 \rightarrow [Ni^{IV}L]^{2+} + Br_2^- \quad k_{26} \qquad (26)$$

**(d) Kinetics of Oxidation of Nickel(II) by $Br_2^-$.** Radiolysis of nickel(II) in $N_2O$-saturated solutions containing $10^{-2}$ M bromide ion over the pH range 5.5–11 results in the formation of $[Ni^{III}L]^+$, eq 27, which has a characteristic absorption spectrum. There is

$$[Ni^{II}L] + Br_2^- \rightarrow [Ni^{III}L]^+ + 2Br^- \qquad (27)$$

competition with the second-order disproportionation of $Br_2^-$, eq 28, which has a rate constant of $4 \times 10^9$ $M^{-1}$ $s^{-1}$. However, the

$$2Br_2^- \rightarrow Br_2 + 2Br^- \qquad (28)$$

kinetics of formation of $[Ni^{III}L]^+$ are largely unaffected except at lower pH, and good first-order behavior was observed for several half-lives. First-order rate constants are presented in Table III, from which it can be seen that the reaction is first order in $[Ni^{II}L]$ and shows a strong dependence on pH, Figure 2.

The data are consistent with the mechanism shown in eq 29–31 and were fit to the corresponding rate law, eq 32. Best fit

$$[Ni^{II}LH_2]^{2+} + Br_2^- \rightarrow [Ni^{III}L]^+ + 2H^+ + 2Br^- \quad k_{29} \qquad (29)$$

$$[Ni^{II}LH] + Br_2^- \rightarrow [Ni^{III}L]^+ + H^+ + 2Br^- \quad k_{30} \qquad (30)$$

$$[Ni^{II}L] + Br_2^- \rightarrow [Ni^{III}L] + 2Br^- \quad k_{31} \qquad (31)$$

$$k''_{so} = \frac{k_{29}[H^+]^2 + k_{30}K_4[H^+] + k_{31}K_4K_5}{[H^+]^2 + K_4[H^+] + K_4K_5} \qquad (32)$$

parameters are $k_{29} = (9 \pm 2) \times 10^7$ $M^{-1}$ $s^{-1}$, $k_{30} = (2.7 \pm 0.1) \times 10^8$ $M^{-1}$ $s^{-1}$, and $k_{31} = (8.45 \pm 0.23) \times 10^8$ $M^{-1}$ $s^{-1}$ from values for the acidity constants published in the literature.

## Discussion

The oxidation of nickel(II) by bromine solutions leads cleanly to the formation of the substitution-inert ion $[Ni^{IV}L]^{2+}$, with no evidence for adduct formation except at higher pH in the presence of HOBr. It might be concluded from this that the rate-limiting reaction is outer sphere in nature. However, two electrons are transferred, and it is possible that a labile, bromine-containing nickel(III) intermediate is formed and that the subsequent oxidation is outer sphere.

**Table III.** Pseudo-First-Order Rate Constants for the Oxidation of Nickel(II) by $Br_2^-$ at 21 °C[a]

| pH | $[Br^-]$, M | $10^5$[Ni(II)], M | $10^{-4}k_{obsd}$, $s^{-1}$ | $10^{-8}k_{so}$, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| 5.85 | 0.01 | 7.67 | 1.45 | 1.89 |
| 5.85 | 0.01 | 21.23 | 3.33 | 1.57 |
| 6.05 | 0.01 | 13.12 | 2.58 | 1.97 |
| 6.45 | 0.01 | 13.12 | 3.21 | 2.86 |
| 6.50 | 0.01 | 7.68 | 2.04 | 2.66 |
| 6.50 | 0.01 | 10.14 | 2.36 | 2.33 |
| 6.50 | 0.01 | 13.06 | 3.32 | 2.54 |
| 6.50 | 0.01 | 16.93 | 4.06 | 2.40 |
| 7.00 | 0.005 | 5.62 | 1.78 | 3.18 |
| 7.00 | 0.01 | 13.12 | 4.11 | 3.13 |
| 7.45 | 0.01 | 13.12 | 5.92 | 4.51 |
| 8.00 | 0.01 | 13.12 | 8.74 | 6.66 |
| 8.35 | 0.01 | 13.12 | 9.35 | 7.12 |
| 9.70 | 0.01 | 13.12 | 10.4 | 7.90 |
| 9.75 | 0.01 | 13.12 | 11.6 | 8.84 |
| 9.80 | 0.01 | 16.66 | 14.7 | 8.82 |
| 9.90 | 0.01 | 4.85 | 4.02 | 8.30 |
| 9.90 | 0.01 | 6.72 | 5.66 | 8.42 |
| 9.90 | 0.01 | 12.86 | 10.9 | 8.48 |
| 10.0 | 0.01 | 9.58 | 7.89 | 8.23 |
| 10.30 | 0.01 | 9.70 | 8.44 | 8.70 |

[a] $[Br_2^-] = (2–3) \times 10^{-6}$ M. $k_{so} = k_{obsd}/[Ni(II)]$

Over the whole pH range studied (3–7) the mechanistic behavior is very simple with $Br_2$ as the only kinetically important oxidant. Comparison of this observation with results from studies of the bromine oxidation of $[Fe(edta)]^{2-}$, $[Co(edta)]^{2-}$, and $[Mn(edta)]^{2-}$[19] is of interest. In these studies both $Br_2$ and $Br_3^-$ are kinetically important, and the ratio of rate constants for reaction of these two species, $k_a/k_b$, lies in the range 2–31. In the present case, this ratio is >1000 despite the positive charge on the reductant, which should favor reaction of $Br_3^-$. The ion $Br_3^-$ is a slightly less powerful oxidant and is expected to be less reactive than $Br_2$. Large $k_a/k_b$ ratios are achieved for inner-sphere reactions where the greater Lewis basicity of $Br_3^-$ predominates. This suggests that the reactions with the nickel(II) complexes are outer sphere in nature, supporting the evidence from product analysis. In the case of the oxidation of $[Ni^{III}L]^+$ by $Br_2$, similar arguments can be made for an outer-sphere process.

Oxidation of nickel(II) by $Br_2^-$ is a much simpler process because it involves a single step. The product is cleanly $[Ni^{III}L]^+$ although at lower pH (<6), where disproportionation of $Br_2^-$ limits investigation, the conversion to nickel(III) is small. For all cases examined, therefore, the electron transfer reactions would seem to be outer sphere, not unexpected in view of the reported behavior of the nickel oxime–imine system.[1,13]

Since the oxidation of nickel(II) by $Br_2$ is a two-electron process, the question arises as to whether the rate-limiting step involves the transfer of both electrons in a single event or whether there are two discrete electron-transfer processes, with rate-limiting formation of reactive intermediates.[26] This latter possibility is much more likely because outer-sphere two-electron-transfer steps, though not impossible, are extremely unlikely as the structural changes involved in a two-electron transfer, and hence the Franck–Condon barriers, are generally much greater than those for a one-electron process.

However, evidence for an apparent single-step two-electron-transfer reaction comes from observations made on the reaction at pH 5.73 in conditions of excess nickel(II) ([Ni(II)] = $2.49 \times 10^{-4}$ M, $[Br_2]_T = 8.9 \times 10^{-6}$ M) where the thermodynamic product is $[Ni^{III}L]^+$. With the stopped-flow technique, at 500 nm, the absorbance shows an increase of the order expected for the formation of $[Ni^{III}L]^+$, but this is followed by a slower absorption decrease corresponding to 3 ± 0.5% of the total absorbance change,

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[26] See: Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980; pp 84–96.

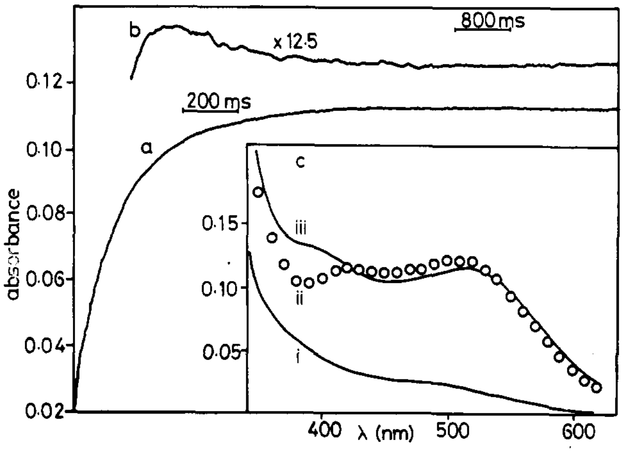

**Figure 3.** Plot of absorbance against time for the oxidation of nickel(II) ($2.49 \times 10^{-4}$ M) by bromine ($8.9 \times 10^{-6}$ M) at pH 5.73 showing (a) the initial formation of nickel(IV) followed by (b) reaction of nickel(IV) with excess nickel(II) to give nickel(III). The inset (c) shows the spectra of the mixed reactants (i), the reaction mixture at 1 s showing characteristics of nickel(IV) (ii), and the spectrum of nickel(III) at the end of the reaction (iii). Nickel(IV) has absorption maxima at 500 and 430 nm and a trough at 390 nm that is obscured by the presence of nickel(III).

Figure 3. The spectrum of the intermediate shows characteristics of nickel(IV). At 360 nm, only the slower process is detected as an absorbance increase with a pseudo-first-order rate constant of 1.1 $s^{-1}$. When the bromine is replaced by a comparable concentration of $[Ni^{IV}L]^{2+}$, the behavior at 360 nm is almost identical with a psuedo-first-order rate constant of 1.2 $s^{-1}$.[27] In other words, reaction of $Br_2$ with $[Ni^{II}LH]^+$ at pH 5.7 produces $[Ni^{IV}L]^{2+}$ as a reaction intermediate, eq 33 and 34. At 500 nm the extinction

$$2[Ni^{II}LH]^+ + Br_2 \rightarrow [Ni^{IV}L]^{2+} + [Ni^{II}LH]^+ + 2Br^- + H^+ \quad (33)$$

$$[Ni^{IV}L]^{2+} + [Ni^{II}LH]^+ \rightarrow 2[Ni^{III}L]^+ + H^+ \quad (34)$$

coefficient of $[Ni^{IV}L]^{2+}$ exceeds twice the value for $[Ni^{III}L]^+$ by around 5%;[1] hence, the 3% absorbance change for the slower reaction implies that in excess of 60% of the reaction proceeds by this mechanism. The errors in this estimate are large, and the pathway may be quantitative.

These observations rule out a single-electron-transfer mechanism of the type given in Scheme I, where the first two reactions are rate-limiting.

**Scheme I**

$$[Ni^{II}L] + Br_2 \rightarrow [Ni^{III}L]^+ + Br_2^- \qquad 2.1 \times 10^7\ M^{-1}\ s^{-1}$$

$$[Ni^{II}LH]^+ + Br_2 \rightarrow [Ni^{III}LH]^{2+} + Br_2^- \qquad 7.1 \times 10^5\ M^{-1}\ s^{-1}$$

$$[Ni^{II}L] + Br_2^- \rightarrow [Ni^{III}L]^+ + 2Br^- \qquad 8.5 \times 10^8\ M^{-1}\ s^{-1}$$

$$[Ni^{II}LH]^+ + Br_2^- \rightarrow [Ni^{III}LH]^{2+} + 2Br^- \qquad 2.7 \times 10^8\ M^{-1}\ s^{-1}$$

$$[Ni^{III}LH]^{2+} \rightleftharpoons [Ni^{III}L]^+ + H^+ \qquad 8.9 \times 10^{-5}\ M$$

$$[Ni^{III}L]^+ + Br_2 \rightarrow [Ni^{IV}]^{2+} + Br_2^- \qquad 1.2 \times 10^5\ M^{-1}\ s^{-1}$$

$$2[Ni^{III}L]^+ \rightarrow [Ni^{IV}L]^{2+} + [Ni^{II}L] \qquad 38\ M^{-1}\ s^{-1}$$

$$[Ni^{III}LH]^{2+} + [Ni^{III}L]^+ \rightarrow [Ni^{IV}L]^{2+} + [Ni^{II}LH]^+ \qquad 3.4 \times 10^3\ M^{-1}\ s^{-1}$$

$$2Br_2^- \rightarrow Br_2 + 2Br^- \qquad 4 \times 10^9\ M^{-1}\ s^{-1}$$

$$[Ni^{III}L]^+ + Br_2^- \rightarrow [Ni^{IV}L]^{2+} + 2Br^- \qquad 10^9\ M^{-1}\ s^{-1}\ \text{(estimate)}$$

Disproportionation of nickel(III) is slow, and above pH 5.5, the rate constant for oxidation of nickel(II) exceeds that for oxidation of $[Ni^{III}L]^+$. If the mechanism in Scheme I is operating, the $[Ni^{III}L]^+$ concentration should build up, allowing detection as an intermediate. Since no such intermediate is detected, the mechanism can be ruled out as a dominant pathway though small amounts of the pathway are possible. The only unknown quantity in Scheme I is the rate of oxidation of $[Ni^{III}L]^+$ by $Br_2^-$, which can be estimated[13] to be around $10^9$ $M^{-1}$ $s^{-1}$, an order of magnitude faster than the corresponding reaction of $[Ni^{II}LH]^+$.

If a mechanism involving one-electron-transfer processes and the formation of discrete nickel(III) intermediates can be eliminated on the basis of these observations, then mechanisms involving synchronous two-electron transfer may seem more plausible. However, it is highly unlikely that the rapid rate constants for the reactions of $[Ni^{II}L]$ and $[Ni^{II}LH]^+$ with $Br_2$ can be explained by the synchronous transfer of two electrons from nickel to bromine. Although $[Ni^{II}L]$ and $[Ni^{IV}L]^{2+}$ have similar structures,[28] Ni–N bond length changes are substantial.[13] Likewise partial cleavage of the Br–Br bond would prohibit facile two-electron transfer in bromine. It is not possible to distinguish between a single-step two-electron-transfer process and two discrete single-electron-transfer processes if the reaction intermediate cannot be detected. Clearly $[Ni^{III}L]^+$ will not serve as a reasonable intermediate. An ion pair containing $[Ni^{III}L]^+$ may serve this role.

The proposed mechanism for the reaction is shown in Scheme II. In the rate-limiting step, there is one-electron transfer between nickel(II) and bromine to give an ion pair $\{[Ni^{III}L^+, Br_2^-\}$ in which the subsequent electron transfer is more rapid than the diffusion apart to form free $[Ni^{III}L]^+$ and $Br_2^-$. An ion-pairing constant around 1 $M^{-1}$ might be assumed,[29] which means that the estimate for electron transfer within this ion pair is $10^9$ $s^{-1}$, at least an order of magnitude smaller than the rate of dissociation to form the free ions. However, if the electron-transfer step has associated with it a significant steric factor, enhancement of this step would be expected since a favorable juxtaposition of the reactants results from the initial electron transfer forming $\{Ni^{III}L^+, Br_2^-\}$. It seems most likely that electron transfer and dissociation compete at comparable rates and that small amounts of free $[Ni^{III}L]^+$ remain undetected in the reaction mixture.[30]

**Scheme II**

$$[Ni^{II}L] + Br_2 \rightarrow \{[Ni^{III}L]^+, Br_2^-\}$$

$$[Ni^{II}LH]^{2+} + Br_2 \rightarrow \{[Ni^{III}L]^+, Br_2^-\} + H^+$$

$$\{[Ni^{III}L]^+, Br_2^-\} \rightarrow [Ni^{IV}L]^{2+} + 2Br^- \quad \textit{major}$$

$$\{[Ni^{III}L]^+, Br_2^-\} \rightarrow [Ni^{III}L]^+ + Br_2^- \quad \textit{minor}\ \text{(Scheme I)}$$

Margerum and co-workers[31] have estimated the one-electron potentials for bromine reduction, eq 35 and 36. The large driving

$$Br_2 + e^- \rightleftharpoons Br_2^- \qquad E^\circ = 0.51\ V \quad (35)$$

$$Br_2^- + e^- \rightleftharpoons 2Br^- \qquad E^\circ = 1.67\ V \quad (36)$$

force for reduction of $Br_2^-$ is certainly consistent with a high rate for electron transfer within the ion pair. With use of the one-electron potential for reduction of $Br_2$ and an estimate of the self-exchange rate for the $Br_2/Br_2^-$ reaction, it should be possible to calculate the rate constants for nickel(II) oxidation by using the Marcus expression,[32] eq 37 and 38, where $k_{ab}$ is the calculated

$$k_{ab} = (k_{aa}k_{bb}K_{ab}f_{ab})^{1/2} \quad (37)$$

$$\log f_{ab} = (\log K_{ab})^2/4[\log (k_{aa}k_{bb}/Z^2)] \quad (38)$$

cross-reaction rate constant, $K_{ab}$ is the equilibrium constant for

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(27) The difference in reaction rates is due partly to the small difference in [nickel(IV)] concentrations for the comproportionation experiments, and partly to a slightly higher pH (5.76) for the reaction with $[Ni^{IV}L]^{2+}$.

(28) Korvenranta, J.; Saarinen, H.; Näsäkkälä, M. *Inorg. Chem.* **1982**, *21*, 4296–4300.

(29) Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1957**, *79*, 3304–3310.

(30) $[Ni^{III}L]^+$ should be easiest to detect at higher pH, but the subsequent adduct formation reactions with HOBr obscure small deviations from first-order kinetic behavior.

(31) Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1973**, *12*, 962–964.

(32) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196.

**Table IV.** Comparison of Experimental Rate Constants with Those Calculated by Using Marcus Theory for the Oxidations of Nickel(II) and Nickel(III) by $Br_2$ and $Br_2^-$

| reacn | $k_{so}$,[a] $M^{-1}\ s^{-1}$ | $k_{so}$(calcd),[b] $M^{-1}\ s^{-1}$ |
|---|---|---|
| $[Ni^{II}L] + Br_2$ | $2.1 \times 10^7$ | $8 \times 10^6$ |
| $[Ni^{II}LH]^+ + Br_2$ | $7.1 \times 10^5$ | $4 \times 10^4$ |
| $[Ni^{II}LH_2]^{2+} + Br_2$ | $\leqslant 2 \times 10^3$ | $2 \times 10^{-1}$ |
| $[Ni^{III}L]^+ + Br_2$ | $1.2 \times 10^5$ | $4 \times 10^5$ |
| $[Ni^{II}L] + Br_2^-$ | $8.5 \times 10^8$ | $8 \times 10^8$ |
| $[Ni^{II}LH]^+ + Br_2^-$ | $2.7 \times 10^8$ | $4 \times 10^7$ |
| $[Ni^{II}LH_2]^{2+} + Br_2^-$ | $\leqslant 9 \times 10^7$ | $2 \times 10^4$ |
| $[Ni^{III}L]^+ + Br_2^-$ | $10^9$ (estimate) | $3 \times 10^8$ |

[a] Experimentally derived value. [b] Calculated by using eq 37 and reduction potentials, association constants, and rate constants documented in the text.

the reaction, $k_{aa}$ is the self-exchange rate for the oxidant, $k_{bb}$ is the corresponding rate for the reductant, and $Z$ is the collision frequency for neutral molecules in solution ($10^{11}\ M^{-1}\ s^{-1}$). A value for $k_{aa}$ of $1 \times 10^9\ M^{-1}\ s^{-1}$ was chosen, in line with values for other radical species, and the results of these calculations are presented in Table IV. The calculated rates are all within an order of magnitude of the values observed, certainly consistent with the mechanism shown in Scheme II (or indeed in Scheme I). Similar calculations were performed for the oxidation of $[Ni^{III}L]^+$ with $Br_2$; again, agreement is good. Thus, a number of features of the oxidation of nickel(II) by $Br_2$ point to an apparent two-electron outer-sphere process: the detection of $[Ni^{IV}L]^{2+}$ as an intermediate in the reaction with nickel(II) in excess and failure to detect $[Ni^{III}L]^+$ in the reaction with $Br_2$ in excess. Nevertheless an explanation involving sequential two-electron transfer within a single ion pair is preferred. The reaction rates are in line with the theoretical treatment for single-electron transfer and would be expected to be much lower for a two-electron process. However, a problem with this explanation is the relatively low rate predicted for electron transfer from $Br_2^-$ to $[Ni^{III}L]^+$ within the ion pair compared with ion dissociation. This prediction relies on estimates of both the second-order rate constant for reaction of $Br_2^-$ with $[Ni^{III}L]^+$ and the ion-pair association constant. Both estimates are subject to considerable uncertainty.

Stanbury[33] has suggested that it is possible to consider electronic self-exchange between species such as $Br_2^-$ and the ion pair $(Br,Br)^{2-}$, eq 39 and 40, where the asterisks are used to denote

$$2Br^- \rightleftharpoons (Br,Br)^{2-} \quad K_{38} \tag{39}$$

$$Br_2^- + (^*Br^-,^*Br^-) \rightleftharpoons {}^*Br_2^- + (Br^-,Br^-) \tag{40}$$

the different bromine pairs. A value of $K_{39} = 0.05\ M^{-1}$ was estimated[31] for the conditions in this study from which the self-exchange rate, eq 40, can be estimated to be around $1\ M^{-1}\ s^{-1}$. This value is 4 orders of magnitude lower than the corresponding number for the $I_2^-/(I^-,I^-)$ self-exchange rate,[33] in line with the expected trend in bond stretching energies,[34] which determine the Franck–Condon barriers to electron transfer. However the accuracy of the calculations and lack of comparable data in the literature preclude more detailed comment.

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**Registry No.** $Ni^{II}L$, 59980-38-0; $[Ni^{II}LH]^+$, 60306-03-8; $Br_2$, 7726-95-6; $Br_2^-$, 24959-67-9.

**Supplementary Material Available:** Table V, showing the amount of nickel(IV) produced on mixing aliquots of standard nickel(II) and bromine solutions (1 page). Ordering information is given on any current masthead page.

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[33] Stanbury, D. M. *Inorg. Chem.* **1984**, *23*, 2914–2916.

[34] Tripathi, G. N. R.; Schuler, R. H.; Fessenden, R. W. *Chem. Phys. Lett.* **1985**, *113*, 563–568.

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# Ligand Design for Enhanced Stereoselectivity in the Electron-Transfer Reactions between Nickel(IV) Bis(oxime-imine) Complexes and $[Co(edta)]^{2-}$

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A number of derivatives of the sexidentate bis(oxime–imine) ligand 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $Me_2L(1)H_2$, have been prepared in which the methyl groups on the oxime–imine chromophores are replaced by more bulky phenyl groups, $MePhL(1)H_2$ and $PhMeL(1)H_2$, or chiral (*S*) methyl (L(2)) and benzyl (L(3)) groups are attached on the amine backbone at the 5- and 12-positions. Nickel(II) complexes of the ligands can be oxidized to the corresponding nickel(III) and nickel(IV) derivatives, and the effect of changing ligand structure on the reduction potentials of the complexes is small. Self-exchange rate constants for the nickel(IV)/nickel(III) change have been estimated from the rates of the cross-reactions between $[Ni^{III}MePhL(1)]^+$ and $[Ni^{III}PhMeL(1)]^+$ and their chiral (5*S*,12*S*)-dimethyl nickel(IV) derivatives to be $8 \times 10^5$ and $4 \times 10^6\ M^{-1}\ s^{-1}$, respectively, at 25 °C and 0.1 M ionic strength. The kinetics and mechanisms of reduction of $[Ni^{IV}MePhL(1)]^{2+}$ and $[Ni^{IV}PhMeL(1)]^{2+}$ and $[Co(edta)]^{2-}$ have also been investigated. The reactions are biphasic with initial rapid reduction of nickel(IV) to give a nickel(III) transient, which is subsequently reduced. Nickel(IV) reduction is outer sphere in nature, and the rates are in general agreement with the predictions of Marcus theory; however, the nickel(III) step is complicated by disproportionation. Binding of the chiral ligand systems to the nickel ions is deduced from circular dichroism studies to be stereospecific, giving the $\Lambda$ absolute configuration around the metal in all cases. Stereoselectivity in the oxidation of $[Co(edta)]^{2-}$ by nickel(IV) has been investigated by using these chiral complexes, and in all cases the preferred isomer of the product $[Co(edta)]^-$ is $\Delta$ with enantiomeric excesses of 7%, 21%, 22%, and 46% for the complexes $[Ni^{IV}PhMeL(2)]^{2+}$, $[Ni^{IV}MePhL(2)]^{2+}$, $[Ni^{IV}Me_2L(3)]^{2+}$, and $[Ni^{IV}MePhL(3)]^{2+}$, respectively. The stereoselectivities are explained by a model that takes into account steric factors in the reactions, in which the $C_2$ oxime–imine face of the nickel(IV) complex exerts a controlling influence.

## Introduction

There is a considerable number of reports of chiral induction in outer-sphere electron-transfer reactions between metal ion complexes in solution.[1-6] The effects are generally modest, around 30% in the most favorable cases, although in the presence of chiral catalysts such as DNA,[7] high stereoselectivity can be attained.

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[1] Geselowitz, D. A.; Taube, H. *J. Am. Chem. Soc.* **1980**, *102*, 4525–4526.

[2] Kondo, S.; Sasaki, Y.; Saito, K. *Inorg. Chem.* **1981**, *20*, 429–433.

[3] Lappin, A. G.; Laranjeira, M. C. M.; Peacock, R. D. *Inorg. Chem.* **1983**, *22*, 786–791.

[4] Martone, D. P.; Osvath, P.; Eigenbrot, C.; Laranjeira, M. C. M.; Peacock, R. D.; Lappin, A. G. *Inorg. Chem.* **1985**, *24*, 4693–4699.

0020-1669/87/1326-3094$01.50/0