# Mechanisms of Reduction of a Nickel(IV) Oxime Complex by 1,2- and 1,4-Dihydroxybenzene Compounds in Aqueous Perchlorate Media

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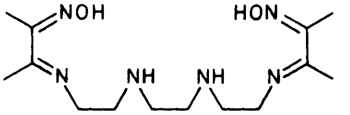
The kinetics of the reduction of a nickel(IV) oxime complex, $[Ni^{IV}L]^{2+}$($H_2L$ = 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime), by catechol, hydroquinone, and 2-methylhydroquinone ($H_2Q$) have been investigated in aqueous perchlorate media in the pH range 3.5—6. Below pH 4.5 the reaction is monophasic with the $Ni^{IV}$–$Ni^{III}$ step rate-determining. Above pH 4.7 a biphasic process is observed with a rapid $Ni^{IV}$–$Ni^{III}$ reduction followed by a slower reaction of the nickel(III) intermediate. A complex pH dependence is attributed to reaction pathways involving several reductant and oxidant species related by proton equilibria. For the principal reaction pathways involving $[Ni^{IV}L]^{2+}$ and $HQ^-$, rate constants fall in the range *ca.* $10^7$—$10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$. With $H_2Q$ as reductant, rate constants are *ca.* $10^5$—$10^6$ times smaller. The specific rate parameters compare favourably with the rate constants determined by Marcus theory calculations.

There has been considerable interest recently in the higher oxidation states of nickel.[1] Numerous complexes of nickel(III), and a lesser number of nickel(IV)[2] have been reported. Nickel(III) complexes frequently contain nitrogen donor ligands, such as tetra-aza macrocycles. The stabilization of the nickel(IV) oxidation state has been achieved with the use of deprotonated oxime ligands.[3] The sexidentate ligand 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime ($H_2L$) forms pseudo-octahedral complexes with $Ni^{II}$, $Ni^{III}$, and $Ni^{IV}$.[4] In aqueous solution $[Ni^{IV}L]^{2+}$ is an oxidizing agent ($Ni^{IV}$–$Ni^{III}$, $E^\ominus = 0.65$ V) and its redox reactions with organic[5] and inorganic[6,7] reductants have been reported. With metal-ion reductants[6] in acidic solution, the one-electron reduction of $[Ni^{IV}L]^{2+}$ is the rate-determining step with no evidence for any long-lived nickel(III) species. Kinetic investigations at higher pH, using ascorbic acid[5] and $[Co(phen)_3]^{2+}$(phen = 1,10-phenanthroline) as reductants, have revealed separate one-electron processes involving $[Ni^{IV}L]^{2+}$ and a detectable $Ni^{III}$ intermediate.



$H_2L$

In this paper, the results of a kinetic study of the reduction of $[NiL]^{2+}$ by catechol ($H_2$cat) (1,2-dihydroxybenzene), hydroquinone ($H_2$quin) (1,4-dihydroxybenzene), and 2-methylhydroquinone ($H_2$mquin) are presented. Rate constants were determined over the range pH 3.5—6 at 25 °C to obtain further information on the nature and reactivity of the nickel(III) and nickel(IV) species in solution.

## Experimental

*Materials.*—The nickel(II) oxime perchlorate, $[Ni(H_2L)][ClO_4]_2$, was prepared by addition of $H_2L$ to a methanol solution of nickel(II) perchlorate.[3] The nickel(IV) oxime, $[NiL][ClO_4]_2$, was isolated after oxidation of $[Ni(H_2L)][ClO_4]_2$ in concentrated nitric acid, as described previously.[3] Analysis of the product was satisfactory (Found: C, 29.25; H, 4.65; N, 15.05. $C_{14}H_{26}Cl_2N_6NiO_{10}$ requires C, 29.60; H, 4.60; N, 14.80%). The concentration of aqueous $[NiL]^{2+}$ solutions was determined spectrophotometrically at 500 ($\varepsilon$ = 6 300) and 430 nm ($\varepsilon$ = 5 960 dm$^3$ mol$^{-1}$ cm$^{-1}$).[3]

Hydroquinone (Aldrich), catechol (Fisher) and 2-methylhydroquinone (Eastman) were recrystallized from ethanol and diethyl ether and stored at 0 °C. Acetate buffers (0.01 mol dm$^{-3}$) were used to control acid concentrations between pH 3.5 and 6, with appropriate amounts of $HClO_4$ employed at higher acidities. In some instances at higher pH's, phosphate buffers were used with no significant differences observed in rates. Sodium (lithium) perchlorate was added to maintain the ionic strength at 0.10 (1.0) mol dm$^{-3}$. Nitrogen saturated solutions of the reductants were prepared just prior to use.

*Kinetic Measurements.*—The kinetic experiments were carried out using a stopped-flow apparatus described previously.[8] The reduction of $[NiL]^{2+}$ (*ca.* $5 \times 10^{-5}$ mol dm$^{-3}$) was followed at 500 nm under pseudo-first-order conditions of excess reductant (1.5—5) × $10^{-3}$ mol dm$^{-3}$. At pH < 4.5 plots of ln $(A_t - A_\infty)$ against time were linear for at least three half-lives. Above pH 4.5 the decay curve was biphasic, with approximately equal decreases in absorbance at 500 nm for each step. The rate constants for the initial process were *ca.* 15 times greater than those of the second step. Rate data for the first reaction were derived from the first 70% of reaction. For the slower step, rate calculations were performed on the final 80% of reaction, where there is no interference from the first step.

## Results

The stoicheiometries of the reduction of $[Ni^{IV}L]^{2+}$ ($4.0 \times 10^{-4}$ mol dm$^{-3}$) by $H_2$cat, $H_2$quin, and $H_2$mquin [(1—10) × $10^{-5}$ mol dm$^{-3}$] were determined by spectrophotometric titrations (500 nm) at pH 4.3. The ratios of nickel(IV) consumed to reductant added were, for $H_2$cat 0.96 ± 0.04 : 1.00, for $H_2$quin 0.98 ± 0.04 : 1.00, and for $H_2$mquin 1.01 ± 0.04 : 1.00. The overall reactions may therefore be expressed by equation (1), where Q is the corresponding quinone.

$$[Ni^{IV}L]^{2+} + H_2Q \longrightarrow [Ni^{II}(H_2L)]^{2+} + Q \qquad (1)$$

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**Table 1.** Rate constants [a] for the reduction of the nickel(IV) ($k_a$) and nickel(III) ($k_b$) oxime complexes by benzene diols: $T = 25.0$ °C, $I = 0.10$ mol dm$^{-3}$ ($NaClO_4$)

| Reductant | pH | $10^{-2}k_0$/ dm$^3$ mol$^{-1}$ s$^{-1}$ | pH | $10^{-3}k_a$/ dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^{-2}k_b$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| $H_2$cat | 3.37 | 1.09 | 4.87 | 1.42 | 0.70 |
| | 4.20 | 1.47 | 5.11 | | $0.79_6$ |
| | | | 5.30 | 3.56 | 0.81 |
| | | | 5.58 | 6.66 | 0.91 |
| | | | 5.78 | 10.80 | 1.05 |
| | | | 5.96 | 15.70 | 1.22 |
| | | | 4.75 [b] | | 0.76 |
| | | | 5.25 [b] | | 0.84 |
| | | | 5.55 [b] | | 0.91 |
| $H_2$quin | 3.37 | 3.43 | 4.69 | 0.45 | 1.84 |
| | 3.80 | 3.53 | 5.12 | 1.35 | 1.91 |
| | 4.25 | 3.88 | 5.60 | 3.71 | 2.09 |
| | | | 5.64 | | 2.26 |
| | | | 5.83 | 5.80 | 2.22 |
| | | | 6.08 | 11.0 | 2.59 |
| | | | 6.19 | | 2.59 [c] |
| | | | $6.44_5$ | | 3.44 [c] |
| $H_2$mquin | 3.47 | 6.03 | 4.98 | 1.99 | 5.65 |
| | 3.86 | 6.74 | 5.30 | 3.30 | 5.75 |
| | 4.24 | 9.30 | 5.62 | 7.10 | 5.97 |
| | 4.63 | 14.0 | 5.92 | 14.1 | 6.38 |
| | (4.83 | 15.6) [d] | | | |
| $H_2$mquin [b] | 3.49 | 8.44 | 4.89 | 1.90 | |
| | 3.61 | 8.94 | 5.05 | 2.45 | 6.30 |
| | 3.81 | 9.30 | | | |
| | 3.87 | 9.50 | 5.36 | 3.80 | 6.10 |
| | 4.21 | 11.84 | 5.85 | 4.80 | 6.55 |
| | 4.47 | 13.4 | | | |
| | 4.50 | 13.9 | | | |
| | 4.61 | $16.2_6$ | | | |

[a] $[Ni^{IV}] = (2.1—5.7) \times 10^{-5}$ mol dm$^{-3}$. Reductant concentrations in the ranges $(1.78—4.64) \times 10^{-3}$ mol dm$^{-3}$ ($H_2$cat), $(1.95—3.81) \times 10^{-3}$ mol dm$^{-3}$ ($H_2$quin), and $(2.73—3.37) \times 10^{-3}$ mol dm$^{-3}$ ($H_2$mquin). [b] $I = 1.0$ mol dm$^{-3}$ ($LiClO_4$). [c] Phosphate buffer. [d] Though the pH > 4.7, the rate difference was such that we could not see a definite second process.

Pseudo-first-order rate constants, measured using excess [$H_2Q$], showed a first-order dependence on the reductant concentration. The overall second-order rate constants, measured at 25 °C over the entire pH range are presented in Table 1.

Below pH 4.7 the decay of the $[Ni^{IV}L]^{2+}$ absorbance at 500 nm is monophasic. The rate law for the stoicheiometric two-electron reduction is given by equation (2). The second-

$$-d[NiL^{2+}]/dt = k_0[NiL^{2+}][H_2Q]_{tot} \quad (2)$$

order rate constants, $k_0$, increased with decreasing acid concentrations. In additional experiments carried out at much lower pH's, it was found that the hydrogen-ion dependence was not a simple inverse relationship. In some instances there was evidence for a slight induction period, indicating other possible reactions. Above pH *ca.* 3.5, however, good first-order decay curves were observed.

Above pH *ca.* 4.7 the decay of the absorbance at 500 nm separates into two stages. As the pH is increased the faster initial step is more easily identified from the slower second step. The absorbance changes in the two steps are roughly equal over the range $\lambda = 430—550$ nm. Lappin and Laranjeira [7] reported the spectrum of a nickel(III) intermediate in the reduction of $[NiL]^{2+}$ by $[Co(phen)_3]^{2+}$ with maxima at 505 and 398 nm and ε values of 2 890 and 3 000 dm$^3$ mol$^{-1}$ cm$^{-1}$, respectively. The intermediate observed in this study appears to be the same $Ni^{III}$ complex.

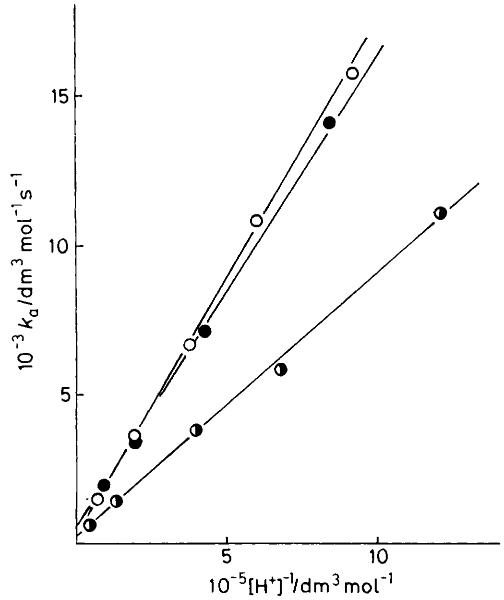

**Figure 1.** Inverse acid dependence of $k_a$ for the reduction of $[Ni^{IV}L]^{2+}$ by catechol (○), hydroquinone (◑), and 2-methylhydroquinone (●)

The rate laws for the consecutive (one-electron) reductions of the nickel(IV) and nickel(III) species are given in equations (3) and (4). The $k_a$ and $k_b$ values measured between pH 4.6

$$-d[NiL^{2+}]/dt = 2k_a[NiL^{2+}][H_2Q]_{tot} \quad (3)$$

$$-d[Ni^{III}]dt = 2k_b[Ni^{III}][H_2Q]_{tot} \quad (4)$$

and 6.1 at 25 °C are presented in Table 1. In this range both the $[Ni^{IV}L]^{2+}$ and $[Ni^{III}L]^{+}$ reactions exhibit $[H^+]^{-1}$ dependences (see Figures 1 and 2) although for the $[Ni^{III}L]^{+}$ reduction a hydrogen-ion independent pathway is also observed. Studies were also made at higher ionic strength (1.0 mol dm$^{-3}$), the most extensive using 2-methylhydroquinone as reductant. Rates are generally *ca.* 10% higher than at $I = 0.1$ mol dm$^{-3}$ but the general behaviour observed is similar to that described above (see Table 1).

## Discussion

The results of the present kinetic study indicate that at low pH (<4.5) the one-electron reduction of $[NiL]^{2+}$ by the dihydroxybenzene compounds is slower than the subsequent reduction of the $Ni^{III}$ intermediate, while at higher pH $[NiL]^{2+}$ is more rapidly reduced than the $Ni^{III}$ species. These observations are the result of protonation equilibria involving both oxidant and reductant species. With the reductants employed in this work the 'crossover' occurs between pH 4 and 5. In a kinetic study using $[Co(phen)_3]^{2+}$ as a reductant, Lappin and Laranjeira [7] reported biphasic reactions at pH > 3. For the reductions of $[NiL]^{2+}$ by metal ions [6] such as $Fe^{2+}$ in acidic solutions (pH < 2), no nickel(III) intermediate was detectable using stopped-flow spectrophotometry. It is interesting to note

**Table 2.** Proton equilibrium constants and reduction potentials for the benzene diols

| Reductant | p$K_1$ [a] | p$K_2$ [a] | p$K_{r_1}$ [b] | p$K_{r_2}$ [c] | $E_1$ [d]/V | $E_2$ [d]/V | $E_3$ [e]/V |
|---|---|---|---|---|---|---|---|
| $H_2$cat [f] | 9.24 | 13.0 | *ca.* −1 | 5.0 | 1.12 | 0.49 | 0.043 |
| $H_2$quin [g] | 9.85 | 11.4 | *ca.* −1 | 4.1 | 1.09 | 0.45 | 0.023 |
| $H_2$mquin [g] | 10.05 | 11.6 | *ca.* −1 | 4.4 | 1.03 | 0.38 | −0.05 |

[a] Refs. 11, 16, and 17. [b] Ref. 11. [c] Refs. 11 and 16. [d] Calculated using equations (30) and (31). [e] From ref. 16 or extrapolation using data therein. [f] $I$ = 1.0 mol dm$^{-3}$ ($NaClO_4$). [g] $I$ = 0.65 mol dm$^{-3}$ ($NaClO_4$).

**Table 3.** Comparison of observed and calculated specific rate constants

| Oxidant | Reductant | $\Delta E^0$/V | $\Delta G_c{}^0$/ kJ mol$^{-1}$ | $\Delta G_{obs.}{}^*$/ kJ mol$^{-1}$ | $k_{obs.}$/ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_{calc.}$/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| $[Ni^{IV}L]^{2+}$ | $H_2$cat | −0.47 | 46.5 | 52.4 | 60 | 30 |
| | $H_2$quin | −0.44 | 43.6 | 49.0 | 270 | 70 |
| | $H_2$mquin | −0.38 | 37.70 | 47.3 | 480 | 360 |
| | Hcat$^-$ | 0.15 | −12.5 | 20.9 | $4.8 \times 10^7$ | $6.8 \times 10^7$ |
| | Hquin$^-$ | 0.20 | −17.3 | 20.2 | $6.4 \times 10^7$ | $1.6 \times 10^8$ |
| | Hmquin$^-$ | 0.27 | −26.1 | 17.6 | $1.8 \times 10^8$ | $6.4 \times 10^8$ |
| $[Ni^{III}(HL)]^{2+}$ | $H_2$cat | −0.48 | 47.1 | | | 6 |
| | $H_2$quin | −0.45 | 44.4 | | | 13 |
| | $H_2$mquin | −0.39 | 38.6 | | | 65 |
| | Hcat$^-$ | 0.14 | −11.5 | 22.7 | $1.5 \times 10^7$ | $1.1 \times 10^7$ |
| | Hquin$^-$ | 0.19 | −16.3 | 17.9 | $1.7 \times 10^8$ | $2.6 \times 10^7$ |
| | Hmquin$^-$ | 0.26 | −25.1 | 14.0 | $7.9 \times 10^8$ | $1.0 \times 10^8$ |
| $[Ni^{III}L]^+$ | Hcat$^-$ | −0.08 | 8.70 | 34.0 | $1.1 \times 10^5$ | $1.3 \times 10^5$ |
| | Hquin$^-$ | −0.03 | 3.9 | 31.5 | $4.1 \times 10^5$ | $3.6 \times 10^5$ |
| | Hmquin$^-$ | 0.04 | −2.85 | 29.2 | $1.0 \times 10^6$ | $1.4 \times 10^6$ |

that in cyclic voltammetry studies of the nickel–oxime system the separation of a single two-electron pattern {$[Ni^{IV}L]^{2+} + 2e^- + 2H^+ \longrightarrow [Ni^{II}(H_2L)]^{2+}$, $E^{\ominus} = 0.95$ V} at low pH into two one-electron processes at higher pH occurs in the region of pH 4—5.[4,6,7]

*Reductions of* $[Ni^{IV}L]^{2+}$.—Kinetic[6] and electrochemical studies[4] have shown that the nickel(IV) species is $[NiL]^{2+}$ at pH > 0 with p$K < -1$ for the protonation of $[NiL]^{2+}$ in aqueous solution, $[Ni^{IV}L]^{2+} + H^+ \rightleftharpoons [Ni^{IV}(HL)]^{3+}$. The dependence of $k_a$ on $[H^+]$ has been attributed, therefore, to proton equilibria involving the reductants.

In neutral and acidic media the benzene diols are undissociated species ($H_2Q$). In general p$K_1$ lies in the range 9—10 and the second dissociation takes place with p$K_2$ in the range 11—13 (Table 2).[9] A reaction scheme for the reduction of $[NiL]^{2+}$ by hydroquinone and the other reductants in the pH range 3.5—6 may be expressed by equations (5)—(7).

$$H_2Q \overset{K_1}{\rightleftharpoons} HQ^- + H^+ \qquad (5)$$

$$[NiL]^{2+} + H_2Q \xrightarrow{k_1} [NiL]^+ + H_2Q^{\cdot +} \qquad (6)$$

$$[NiL]^{2+} + HQ^- \xrightarrow{k_2} [NiL]^+ + HQ^{\cdot} \qquad (7)$$

If $H_2Q^{\cdot +}$ and $HQ^{\cdot}$ react rapidly[10] with $[NiL]^{2+}$, then the rate law for the reduction of $[NiL]^{2+}$ according to the mechanism is given in equation (8). In the pH range under consideration

$$\frac{-d[NiL^{2+}]}{dt} = \frac{2(k_1 + k_2K_1/[H^+])\,[NiL^{2+}][H_2Q]_{tot}}{(1 + K_1/[H^+])} \qquad (8)$$

where $K_1 \ll [H^+]$, $k_a$ may be expressed in the form given in equation (9).

$$k_a = k_1 + k_2K_1[H^+]^{-1} \qquad (9)$$

Above pH 4, $k_a$ exhibited a linear inverse dependence on $[H^+]$, as shown in Figure 1. The specific rate constants $k_1$ and $k_2$ were derived from the slopes and intercepts of the $[H^+]^{-1}$ dependence plots. The rate constants for the reaction of $[NiL]^{2+}$ with the three benzene diols and their anionic forms are presented in Table 3. The greater reactivity of $HQ^-$ relative to $H_2Q$, $k_2/k_1$ *ca.* $10^5$—$10^6$, has been observed in previous kinetic studies of the oxidation of hydroquinone in neutral solutions.[11,12]

*Reduction of* $Ni^{III}$ *Species*.—The separation of the nickel(III) reduction step (above pH 4.5) from the rapid initial reaction of $[NiL]^{2+}$ is sufficiently great that studies for this reaction may be made. Pseudo-first-order rate constants were measured between 4.6 and 6.1. An inverse acid dependence was again observed, attributable to the $HQ^-$ oxidation pathway. The oxime protons on the nickel(III) complex are less acidic than those on nickel(IV) and a p$K_a$ of $\leqslant 3.9$ has been determined[7] for the equilibrium (10).

$$[Ni(HL)]^{2+} \overset{K_a}{\rightleftharpoons} [NiL]^+ + H^+ \qquad (10)$$

A reaction scheme for the reduction of the nickel(III) intermediate is outlined in equations (11)—(14).

$$[Ni(HL)]^{2+} + H_2Q \xrightarrow{k_3} [Ni(HL)]^+ + H_2Q^{\cdot +} \qquad (11)$$

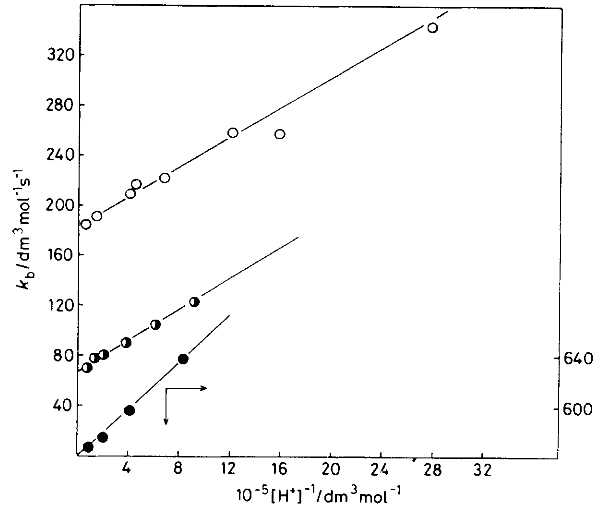

**Figure 2.** Plots of $k_b$ against $[H^+]^{-1}$ in the reduction of $[Ni^{III}L]^+$ by catechol (○), hydroquinone (◑), and 2-methylhydroquinone (●) [equation (17)]

$$[Ni(HL)]^{2+} + HQ^- \xrightarrow{k_4} [Ni(HL)]^+ + HQ^{\cdot} \qquad (12)$$

$$[NiL]^+ + H_2Q \xrightarrow{k_5} NiL + H_2Q^{\cdot +} \qquad (13)$$

$$[NiL]^+ + HQ^- \xrightarrow{k_6} NiL + HQ^{\cdot} \qquad (14)$$

The semiquinone radicals produced in equations (6) and (7) and (11)—(14) react rapidly with a second $Ni^{IV}$ or $Ni^{III}$ ion. If the radicals decay in part *via* disproportionation[11] [equation (15)] then the simple stoicheiometry observed would not be expected. The rate law for the disappearance of $Ni^{III}$ is given in equation (16).

$$HQ^{\cdot} + HQ^{\cdot} \longrightarrow H_2Q + Q \qquad (15)$$

$$\frac{-d[Ni^{III}]}{dt} = 2\frac{(k_3[H^+]/K_a + k_4K_1/K_a + k_5 + k_6K_1/[H^+])}{([H^+]/K_a + 1)(1 + K_1/[H^+])}[Ni^{III}][H_2Q]_{tot} \qquad (16)$$

For the evaluation of the specific rate constants it was assumed that $k_4/k_3$ and $k_6/k_5$ were in the region of $10^5$—$10^6$ as observed previously.[11] In the reduction of $[Ni^{III}(HL)]^{2+}$ and $[Ni^{III}L]^+$ by $[Co(phen)_3]^{2+}$ and ascorbic acid, Lappin and Laranjeira[7] observed that $[Ni(HL)]^{2+}$, a stronger oxidant ($E^\ominus = 0.64$ V), was 20—40 times more reactive than $[NiL]^+$ ($E^\ominus = 0.42$ V). If only $k_4$ and $k_6$ contribute to the reaction rate, the rate law may be expressed in the form (17) under conditions of higher pH where $K_a > [H^+]$.

$$k_b = k_4K_1/K_a + k_6K_1/[H^+] \qquad (17)$$

The hydrogen-ion dependence of the rates is shown in Figure 2. The specific rate constants (Table 3) are again large (*ca.* $10^5$—$10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$).

The rate constant for an outer-sphere electron-transfer reaction may be predicted by use of Marcus theory equations.[13] This correlation establishes a relationship between the free energy of reaction ($\Delta G_{12}^\ominus$) and the free energies of activation for the cross reactions ($\Delta G_{12}^*$) and reductant and oxidant self-exchange reactions ($\Delta G_{11}^*$ and $\Delta G_{22}^*$).

$$k_{12} = Ze^{-(\Delta G_{12}^*/RT)} \qquad (18)$$

$$\Delta G_{12}^* = w_{12} + \frac{\lambda_{12}}{4} + \frac{\Delta G_c^\ominus}{2} + \frac{(\Delta G_c^\ominus)^2}{4\lambda_{12}} \qquad (19)$$

$$\lambda_{12} = 2(\Delta G_{11}^* - w_{11} + \Delta G_{22}^* - w_{22}) \qquad (20)$$

$$\Delta G^\ominus = \Delta G_{12}^* + w_{21} - w_{12} \qquad (21)$$

The work terms $w_{12}$ and $w_{21}$ correspond to the energy associated with bringing the reactants and products, respectively, to a separation distance $r$ in the activated complex. The terms $w_{11}$ and $w_{22}$ similarly apply to the self-exchange reactions. In aqueous solution at 25 °C and an ionic strength of 0.10 mol dm$^{-3}$, the Debye–Hückel expression for the work term[14] is given by equation (22).

$$w_{12} = \frac{4.24Z_1Z_2}{r(1 + 0.104r\sqrt{I})} \qquad (22)$$

In order to calculate the specific cross reaction rate constants for the reactions a knowledge is necessary of the reactant reduction potentials and rate constants for the individual self-exchange processes. Both the reductants and oxidants in this study have pH dependent redox equilibria.

The electrochemistry of the $Ni^{II}$,$Ni^{III}$,$Ni^{IV}$–oxime system has been investigated by means of cyclic voltammetry techniques.[4,6,7] Below pH 5 a single two-electron wave is observed with a potential of 0.95 V (*versus* normal hydrogen electrode) [equation (23)].

$$[Ni^{IV}L]^{2+} + 2e^- + 2H^+ \rightleftharpoons [Ni^{II}(H_2L)]^{2+} \qquad (23)$$

Above pH 5, two one-electron processes are identified. The equilibria of interest in this study [equations (24)—(26)] have

$$[Ni^{IV}L]^{2+} + e^- \rightleftharpoons [Ni^{III}L]^+ \qquad (24)$$

$$[Ni^{III}(HL)]^{2+} + e^- \rightleftharpoons [Ni^{II}(HL)]^+ \qquad (25)$$

$$[Ni^{III}L]^+ + e^- \rightleftharpoons [Ni^{II}L] \qquad (26)$$

potentials of 0.65,[4] 0.64,[7] and 0.42 V,[4] respectively. At higher acidities (0.1—1.0 mol dm$^{-3}$) the couple $[Ni(H_2L)]^{3+/2+}$ ($E^\ominus = 1.23$ V) has been shown to be important in redox processes.[6] Contributions at pH ~ 1 from this reactant may be a reason for the more rapid $Ni^{III}$–$Ni^{II}$ reduction under these conditions leading to the observation of only one process.

The redox equilibria involved in the hydroquinone/semiquinone self-exchange reactions are outlined in equations (27)—(29).

$$\begin{tikzcd}
H_2Q \arrow[r, rightleftharpoons, "E_1^\circ"] \arrow[d, rightleftharpoons, "+H^+"', "pK_1"] & H_2Q^{\cdot +} + e^- \arrow[d, rightleftharpoons, "+H^+"', "pKr_1"] & (27) \\
HQ^- \arrow[r, rightleftharpoons, "E_2^\circ"] \arrow[d, rightleftharpoons, "+H^+"', "pK_2"] & HQ^{\cdot} + e^- \arrow[d, rightleftharpoons, "+H^+"', "pKr_2"] & (28) \\
Q^{2-} \arrow[r, rightleftharpoons, "E_3^\circ"] & Q^{\cdot -} + e^- & (29)
\end{tikzcd}$$

The potentials for the $H_2Q^{\cdot -}/H_2Q$ and $HQ^{\cdot}/HQ^-$ couples may be determined from the proton equilibrium constants and the $Q^{\cdot -}/Q^{2-}$ reduction potentials using equations (30) and (31).

$$E_1{}^{\circ} = E_3{}^{\circ} + 0.059(\mathrm{p}K_1 + \mathrm{p}K_2 - \mathrm{p}K_{r_1} - \mathrm{p}K_{r_2}) \quad (30)$$

$$E_2{}^{\circ} = E_3{}^{\circ} + 0.059(\mathrm{p}K_2 - \mathrm{p}K_r) \quad (31)$$

The $E_3{}^{\circ}$ [15] and p$K$ values [10,16] employed in equations (30) and (31) were determined experimentally or extrapolated from values for similar compounds using a linear relationship between $E^{\circ}$ and p$K$.[10,17] The equilibrium constants and potentials for the reductants are listed in Table 2.

Previous studies of the oxidation of hydroquinone and related complexes have resulted in an estimate of $\Delta G_{11}{}^*$ for the $H_2Q^{\cdot +}/H_2Q$ self-exchange reaction of 18.8 kJ mol$^{-1}$ ($k_{11} = 5 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$).[10] A similar value was assumed for the $HQ^{\cdot}/HQ^-$ couple. The self-exchange rate constants for the $Ni^{IV}$–$Ni^{III}$ and $Ni^{III}$–$Ni^{II}$ reactions have been determined independently in this laboratory [6] and by Lappin and Laranjeira [7] with good agreement. For the $[NiL]^{2+/+}$, $[Ni(HL)]^{2+/+}$, and $[NiL]^{+/0}$ couples, exchange rate constants of $6 \times 10^4$, $2 \times 10^3$, and $1 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively, have been employed.

The calculated specific rate constants for reductions of the $Ni^{III}$ and $Ni^{IV}$ oximes by the benzene diols are presented in Table 3. Reasonable agreement, within an order of magnitude in most cases, is observed between the experimental and calculated values. The discrepancies may be due to uncertainties in the reduction potentials and self-exchange parameters of the species involved. Calculations have been made of the rate for reaction ($k_3$) [equation (11)] between the protonated complex $[Ni^{III}(HL)]^{2+}$ and the neutral substrates $H_2Q$. The values obtained are generally $<10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$ and inspection of the data reveals that inclusion of pathway (11) would contribute $<10\%$ towards the acid-independent parameter in equation (17). It is of interest to note that, as with the nickel(IV) systems, the rates of reaction of the anionic form of the reductant are *ca.* $10^6$ times greater than for the neutral species. Substrates of this type are well known as electron-transfer agents in naturally occurring systems.[18] The rapid rates of redox reactions involving the anions in the present study confirm the importance of dissociation phenomena, not only of the negatively charged reductants but also of the anion radicals formed as the immediate reaction products. Further studies are in progress on the reactions of hydroquinone and related compounds with other $Ni^{IV}$ oxime complexes and $Ni^{III}$ monoxime species. These investigations may provide more information on the nature and reactivity of the $Ni^{IV}$ and $Ni^{III}$ species in solution.

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