

One-electron Reduction of Nickel(IV) Oxime Complexes †

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The kinetics of reduction of two nickel(IV)-oxime complexes by the organic radicals $\text{H}_2\dot{\text{C}}\text{OH}$, $(\text{CH}_3)\text{H}\dot{\text{C}}\text{OH}$, $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, $\dot{\text{C}}\text{O}_2^-$, and $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ have been examined in aqueous solution using the pulse radiolysis technique. Difference spectra indicate that the electron is transferred to the metal centre and spectroscopic characterization of the nickel(III) transients is presented.

The nickel(IV) complex with the sexidentate bis(oxime-imine) ligand 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioximate, $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$, has been studied in aqueous solution.¹⁻³ It is substitution inert, even in concentrated acid solution and can be optically resolved.⁴ Kinetic studies of the reduction of $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ to the corresponding nickel(II) complex show dominant pathways involving consecutive one-electron transfers with the formation of nickel(III) intermediates.^{5,6} These nickel(III) complexes can be prepared independently.

In contrast, although nickel(III) intermediates have been proposed in corresponding reductions^{7,8} of tris(dimethylglyoximate)nickelate(IV), $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$, and have been detected⁹ using e.s.r. techniques, they have eluded the spectrophotometric characterization necessary to determine their kinetic role. Information on these species is important in assigning mechanism.

The pulse radiolysis technique provides a means for producing low concentrations of powerful single-electron reducing agents on the microsecond time-scale. This rapid time resolution facilitates the detection of reactive transients. Accordingly, pulse radiolysis studies of the reduction of $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ and $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ have been carried out to compare the reactivity of these two complexes and to allow characterization of the nickel(III) transients.

Experimental

The complexes $[\text{Ni}^{\text{II}}(\text{H}_2\text{L})][\text{ClO}_4]_2$ and $[\text{Ni}^{\text{IV}}\text{L}][\text{ClO}_4]_2$ were obtained as described previously.¹ Solutions of $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ were prepared^{9,10} by the reaction of a suspension of nickel(IV) oxide with a slight excess of dmg^{2-} in aqueous KOH solution, followed by purification on an anion-exchange column (Dowex 1-8 x; 400 mesh), eluting with 0.02 mol dm^{-3} KCl solution adjusted to pH 11.6 with KOH. All other reagents were Baker analysed or Fisher ACS reagent grade. Water was purified with a Millipore Milli-Q system.

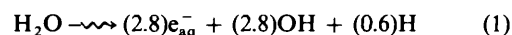
Steady-state radiolyses were carried out in a Gammecell 200 ^{60}Co source with a dose rate of 40 Gy min^{-1} . Pulse radiolysis kinetic and spectrophotometric measurements were made with a computer-controlled instrument described previously.¹¹ The linear accelerator (ARCO LP-7) supplies 5–50 ns pulses of 8 MeV electrons. The dose used (3–5 Gy per pulse) produced 2–3 $\mu\text{mol dm}^{-3}$ concentration of radicals. At this concentration, the radical-radical recombination reaction does not take place to any significant extent compared to the process under investigation. The dose was calibrated with an aqueous N_2O -saturated KSCN solution before each set of experiments. The differential absorption coefficients for the transient spectra ($\Delta\epsilon'$) were calculated from the relation $\Delta\epsilon' = AK/DG$ where A is the

differential 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 $(\text{SCN})_2^-$ radical is 4.56×10^4 molecules $(100 \text{ eV})^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ¹² at 480 nm in N_2O -saturated solutions of $10^{-2} \text{ mol dm}^{-3}$ KSCN. Radiolysis experiments were carried out at $21 \pm 1^\circ\text{C}$.

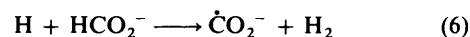
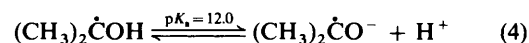
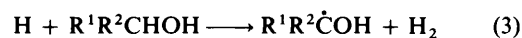
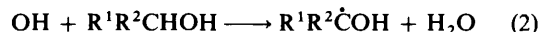
Absorption spectra were recorded on a Cary 219 spectrophotometer interfaced with a PDP 11/55 computer or on a Varian DMS 100 spectrophotometer. Kinetic measurements were made using a Durrum D-110 spectrophotometer⁶ thermostatted at $25.0 \pm 0.1^\circ\text{C}$.

Results and Discussion

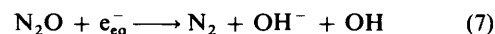
Radiolysis of water or aqueous solution results in the formation of e_{aq}^- , OH, H and molecular products, equation (1). In acidic



solutions, reduction of H^+ also takes place and in order to study a clean reduction it is necessary to scavenge these radicals and convert them into reducing species.¹³ Various alcohols $\text{R}^1\text{R}^2\text{CHOH}$, methanol ($\text{R}^1 = \text{R}^2 = \text{H}$), ethanol ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$), isopropyl alcohol ($\text{R}^1 = \text{R}^2 = \text{CH}_3$), and formate ion have been used for this purpose, equations (2)–(6). These



radicals are known to be efficient one-electron reducing agents. In N_2 -purged solution, rapid reduction by e_{aq}^- is observed followed by a slower reduction by the organic radicals. For rate studies, it is advantageous to use N_2O as an electron scavenger, equation (7), so that reduction takes place with the organic radicals only.



Reduction of $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ by the radical species $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, $(\text{CH}_3)\text{H}\dot{\text{C}}\text{OH}$, $\text{H}_2\dot{\text{C}}\text{OH}$, and $\dot{\text{C}}\text{O}_2^-$ at pH < 4 results in quantitative formation of a reduced product with a broad featureless absorption at 500 nm ($\epsilon_{500} \approx 3000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), Figure 1. This spectrum is characteristic^{3,14} of the

† Non-S.I. unit employed: $\text{eV} \approx 1.60 \times 10^{-19} \text{ J}$.

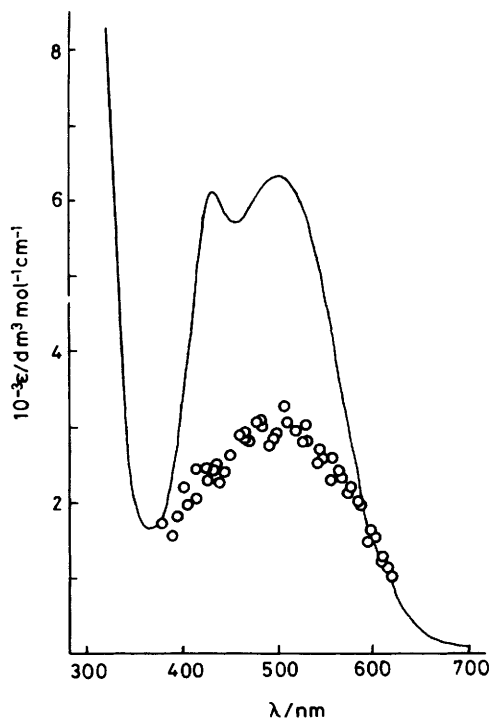


Figure 1. Initial (—) and final (O) absorbance spectrum, 75 ms after pulse for the reaction of $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ with $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ at pH 2.5, 10% $(\text{CH}_3)_2\text{CHOH}$, and 21 °C

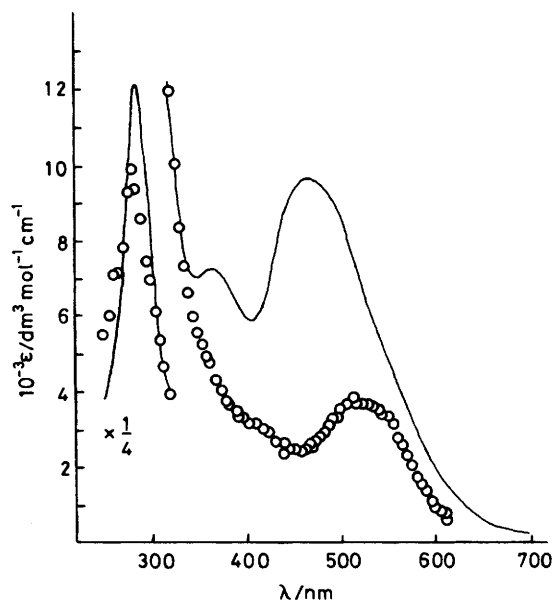


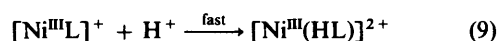
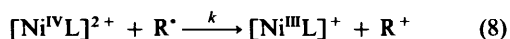
Figure 2. Initial (—) and final (O) absorbance spectrum 0.1 ms after the pulse for the reaction of $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ with $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ at pH 12.5, 10% $(\text{CH}_3)_2\text{CHOH}$, and 21 °C

Table. Second-order rate constants for reduction of nickel(IV) oxime complexes

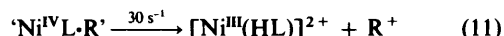
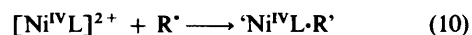
Reaction	pH	$10^9 k_{\text{so}} / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
$[\text{Ni}^{\text{IV}}\text{L}]^{2+} + \text{H}_2\dot{\text{C}}\text{OH}$	2.5	3.54 ± 0.09
$[\text{Ni}^{\text{IV}}\text{L}]^{2+} + (\text{CH}_3)\dot{\text{H}}\text{COH}$	2.3–2.5	3.54 ± 0.07
$[\text{Ni}^{\text{IV}}\text{L}]^{2+} + (\text{CH}_3)_2\dot{\text{C}}\text{OH}$	2.5–3.7	2.65 ± 0.10
$[\text{Ni}^{\text{IV}}\text{L}]^{2+} + \dot{\text{C}}\text{O}_2^-$	2.2–4.1	11.8 ± 0.5
$[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-} + (\text{CH}_3)_2\dot{\text{C}}\text{O}^-$	12.5	1.74 ± 0.04

nickel(III) complex $[\text{Ni}^{\text{III}}(\text{HL})]^{2+}$, indicating that reduction takes place at the metal centre.

The kinetics of the reaction, monitored at 500 or 430 nm, can be analysed by a pseudo-first-order treatment and the rate constants are linearly dependent on the reagent in excess, $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ (ca. 20–170 $\mu\text{mol dm}^{-3}$ range studied, typically 6–12 solutions). Second-order rate constants (Table) are independent of pH in the range shown and can be identified with the reactions (8) and (9), where R^{\cdot} is a reducing radical. In



the case of the alcohol radicals, a slow phase, accounting for ca. 10% of the total absorbance change, occurs on the millisecond time-scale with a first-order rate constant of $30 \pm 5 \text{ s}^{-1}$, independent of pH and the initial $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ concentration. This small absorbance change is consistent with a minor production pathway involving an intermediate adduct, equations (10) and (11), or may indicate a slow rearrangement of the nickel(III) product. However this latter explanation can be



eliminated since no comparable absorbance change is detected in the generation of $[\text{Ni}^{\text{III}}(\text{HL})]^{2+}$ within the mixing chamber of a stopped-flow spectrophotometer by protonation of $[\text{Ni}^{\text{III}}\text{L}]^{+}$ ¹⁴ or by reduction using $[\text{Fe}(\text{CN})_6]^{4-}$.^{*} Disproportionation of $[\text{Ni}^{\text{III}}(\text{HL})]^{2+}$ does take place, but over a much longer time-scale.¹⁴

The complex $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ is unstable at low pH but can be examined above pH 12.^{9,10} Reduction by the radical $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ was studied in the pH range 12.5–13.0 (Figure 2). The reaction, monitored at a variety of wavelengths, is rapid, substantially pH-independent and first-order in both $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ and $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ concentrations with a second-order rate constant at the high-pH limit of $(2.39 \pm 0.15) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. A previously undetected species, presumably $[\text{Ni}^{\text{III}}(\text{dmg})_3]^{3-}$ is formed in the reaction with absorption maxima at 280 ($\epsilon_{280} = 29\,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 520 nm ($\epsilon_{520} = 3\,700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The species is stable on the millisecond time-scale.

In an attempt to characterize higher oxidation state nickel-dimethylglyoximate species, Lati and Meyerstein¹⁵ examined the oxidation of $[\text{Ni}^{\text{II}}(\text{Hdmg})_2]$ by OH and NH_2 radicals in basic solution. The products are nickel(III) species with absorption maxima at 440 (NaOH) or 470 nm (NH_4OH), considerably different from the results of reduction of $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$. It seems likely that the nickel(III) complexes obtained in the earlier study have a lower co-ordination number since the nickel(II) reactant is square planar.

Direct comparison of the reactivities of $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ and $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ is not possible. Reductions of the former by $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ and of the latter by $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ occur at comparable rates. However, the deprotonated radical generally

* Rate constants for the reduction of $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$, $[\text{Ni}^{\text{III}}\text{L}]^{+}$, and $[\text{Ni}^{\text{III}}(\text{HL})]^{2+}$ by $[\text{Fe}(\text{CN})_6]^{4-}$ are $\geq 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $\geq 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively at 25 °C and $I = 0.10 \text{ mol dm}^{-3}$.

shows greater reactivity than the protonated species¹³ and this suggests that transfer of a single electron to $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ is the more sluggish process. This is confirmed by conventional kinetic studies where reductions of $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ by ascorbate ion and $[\text{Fe}(\text{CN})_6]^{4-}$ have second-order rate constants of $3.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 7) and $6.2 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 8) at 35°C whereas the corresponding rates for $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ are $1.5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 3)* and $\geq 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ † at 25°C . Detailed reasons for this are not obvious since the one-electron reduction potential of $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ is not known.¹⁶ The inability to detect $[\text{Ni}^{\text{III}}(\text{dmg})_3]^{3-}$ in conventional spectrophotometric studies¹⁷ may be the result of higher reactivity for this species than for $[\text{Ni}^{\text{IV}}(\text{dmg})_3]^{2-}$ although detection is difficult since $[\text{Ni}^{\text{II}}(\text{Hdmg})_2]$ is the ultimate, insoluble product in these reactions and turbid solutions of $[\text{Ni}^{\text{II}}(\text{Hdmg})_2]$ have a broad absorption centred around 555 nm.

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† See footnote on previous page.

* A. G. Lappin, M. C. M. Laranjeira, and L. Youde-Owei, *J. Chem. Soc., Dalton Trans.*, 1981, 721. Experiments at low pH indicate that reduction of $[\text{Ni}^{\text{IV}}\text{L}]^{2+}$ is comparable in rate with that of $[\text{Ni}^{\text{III}}(\text{HL})]^{2+}$.

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