Iron catalysis of the reduction of oxime-bound nickel(IV) by hydroxylamine†

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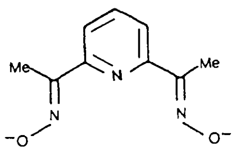
The nickel(IV) complex of the dianion of 2,6-diacetylpyridine dioxime was reduced very slowly by NH_3OH^+ at pH 1–3, but this reduction is catalysed dramatically by dissolved iron, with Fe^{II} being the active reductant. With NH_3OH^+ in excess, the products of the catalysed reaction are N_2 and Ni^{II}. Non-exponential kinetic profiles for this reaction are consistent with a sequence in which Fe^{II} is generated by $1e^-$ reduction of Fe^{III} by NH_2OH, after which Fe^{II} reduces Ni^{IV} to Ni^{III} *via* competing protonated and non-protonated paths. Subsequent reduction of Ni^{III} is taken to be rapid. Rate constants and equilibrium quotients calculated from 15 runs are in accord with literature values.

Since 1970 the roster of derivatives of the higher oxidation states of nickel has expanded markedly. In addition to over 300 co-ordination compounds of Ni^{III}, there has been reported a less impressive, but growing, collection of nickel(IV) complexes.[2] Intensification of interest in these hypervalent states is due, in large part, to evidence that the operation of several enzymes, among them CO dehydrogenases and (NiFe)hydrogenase involves nickel(III) centres.[3]

Reflecting the greater availability of such complexes, there has been a remarkable burst of mechanistic investigations pertaining to their reductions to the dominant state Ni^{II}.[4] With Ni^{IV}, as in the case of other reagents which partake in net two-unit redox transactions,[5] it has not yet been established whether the $Ni^{IV} \rightarrow Ni^{II}$ change invariably requires transition through a nickel(III) species or whether a direct $2e^-$ change may, under suitable conditions, occur.

In an earlier contribution to this area[6] we considered the reactions of the bis(chelated) nickel(IV) complex of the dianion of 2,6-diacetylpyridine dioxime **I**, a $Ni^{IV}N_6$ derivative **1**[7] which is more robust at high acidities than are nearly all related complexes in this class. Complex **1** was found to be reduced quickly by the $1e^-$ reductants Fe^{2+} and I^-, but was virtually inert to the $2e^-$ reagents H_3AsO_3 and H_3PO_2. Evidence was also presented that reaction with U^{IV} proceeds through the odd-electron species U^V, whereas doubt remained as to the path for the slow reduction by Sn^{2+}.

This report deals with the reaction of this nickel(IV) chelate with hydroxylamine, which is present preponderantly as the NH_3OH^+ cation in the media employed. The reduction is unusually slow but is catalysed strikingly by dissolved Fe^{III}.



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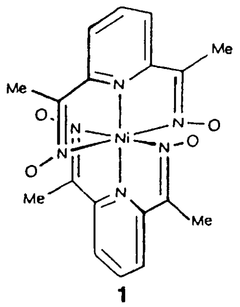

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Experimental

Materials

Hydroxylamine hydrochloride (Aldrich Chemicals), iron(III) perchlorate (Alfa) and perchloric acid (Fisher) were used as received. Solutions for kinetic experiments were made from Millipore water which was treated with zinc amalgam as described,[8] filtered, boiled for 2 h, and then sparged with N_2 for 2 h more to remove dissolved O_2. Bis(2,6-diacetylpyridine dioximato)nickel(IV) **1** was prepared as described,[6] using an adaptation of the procedure of Baucom and Drago.[7a] This complex is very nearly insoluble in water, but very dilute (supersaturated) solutions for redox runs could be prepared by dissolving the powdered crystalline product in water–methanol (1 : 1) under reflux for 2 h with stirring and kept at 50 °C (to minimize precipitation of the complex) until use, at which time aliquots were cooled, filtered, and diluted with distilled water. Solutions in kinetic studies contained 2–3% MeOH, but kinetic profiles were found to be independent of the methanol content within this range. Such solutions, which deteriorated slowly on standing, were prepared fresh for each set of experiments. The low-energy maximum at 615 nm in dimethylformamide[3b] is shifted[7a] to 572 nm ($\varepsilon = 1.28 \times 10^4\ dm^3\ mol^{-1}\ cm^{-1}$) in water–methanol (49:1).

Stoichiometric experiments

Stoichiometric determinations were carried out under N_2. Measured deficient amounts of hydroxylamine hydrochloride were added to a known excess of the nickel(IV) complex. To insure complete reaction within a convenient time interval under these conditions, reactions were carried out at pH 3.5–5.0 in the presence of $2 \times 10^{-5}\ mol\ dm^{-3}\ Fe^{III}$, rather than at the higher acidities (pH 1–2) used in the kinetic runs. After reaction had ceased (0.5–2.2 h), decreases in absorbance at 572 nm were compared with those resulting from addition of an excess of reductant. Corrections were applied for the slow deterioration of Ni^{IV} under the conditions used. Results appear in Table 1.

Kinetic studies

Reactions, which were run under N_2, were monitored at 572 nm using a Beckman model 5260 recording spectrophotometer. Ionic strength was maintained at 0.10 mol dm^{-3} ($HClO_4$–$NaClO_4$), and [H^+] was allowed to vary between 0.005 and 0.1 mol dm^{-3}. All runs were made with a large excess of reductant. Temperatures were kept at 25.0 ± 0.2 °C during all rate measurements. Reactions carried out at pH values near 1.0 in the absence of transition-metal ions were so slow that profiles were seriously complicated by the decomposition of the nickel(IV) chelate in this medium.[6] Conversions were, however,

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† Electron transfer. Part 131.[1]

Table 1 Stoichiometry of the reduction of oxime-bound nickel(IV) with hydroxylamine*

$10^5[Ni^{IV}]$/mol dm^{-3}	$10^5[NH_2OH]$/mol dm^{-3}	$10^5\Delta[Ni^{IV}]$/mol dm^{-3}	$\Delta[Ni^{IV}]/\Delta[NH_2OH]$
11.8	8.0	7.1	0.89
10.1	8.0	6.7	0.84
7.4	7.0	5.4	0.77
9.8	10.0	6.5	0.65
12.7	13.0	7.7	0.59
12.0	15.0	8.7	0.58
12.7	20.0	10.9	0.55

* Reductions of the bis-chelated nickel(IV) complex **1** were carried out with hydroxylamine hydrochloride under N_2 in methanol–water (1:4). Reactions were catalysed by 2.0×10^{-5} mol dm^{-3} Fe^{III}; λ = 572 nm; pH 3.5–5.0. Waiting periods were 0.50–2.10 h.

markedly catalysed by Fe^{III} (added as the hydrated perchlorate salt) and modestly by Cu^{II}; added Ni^{II} was without effect. Logarithmic curves were never observed. Instead, initial portions of decay profiles were nearly linear, but an approach toward exponential behaviour was apparent near the end of each reaction (Fig. 1). Based upon estimates of initial rates, reactions were inhibited by increases in $[H^+]$, but the dependency was less marked than that corresponding to a $[H^+]^{-1}$ proportionality. Initial rates were very nearly proportional to $[Fe^{III}]$ and to $[NH_3OH^+]$. No irregularities in profiles attributable to the growth or destruction of an intermediate on a time-scale comparable to that of the principal redox transformation were observed.

Results and Discussion

The stoichiometry of the Ni^{IV}–NH_3OH^+ reaction, as catalysed by Fe^{III}, is seen to fall in the range $[Ni^{IV}]/[NH_3OH^+] = 0.55$–$0.89$ when the oxidant is in excess. The value drops steadily and approaches 0.50 as the ratio $[NH_3OH^+]/[Ni^{IV}]$ is increased. Since no spectral distortions indicating the accumulation of the intermediate state Ni^{III} were noted, all Ni^{IV} may be taken to be converted into Ni^{II}, as is the case for reductions by metal centres and by iodide.[6]

Stoichiometries analogous to the observed range (0.50–1.0 equivalent of oxidant per hydroxylamine) have been reported for oxidations by V^V,[9] Ce^{IV},[10] $IrCl_6^{2-}$,[11] and $[Ni^{IV}(dmg)_3]^{2-}$ (dmg = dimethylglyoximate)[12] (the latter in basic media), and have been shown to reflect the formation of mixtures of N_2 and N_2O. The consumption of Ni^{IV} in the present system may thus be represented as a competition between reactions (1) and (2)

$$Ni^{IV} + 2\,NH_3OH^+ \longrightarrow Ni^{II} + N_2 + 2\,H_2O + 4\,H^+ \quad (1)$$

$$2\,Ni^{IV} + 2\,NH_3OH^+ \longrightarrow 2\,Ni^{II} + N_2O + H_2O + 6\,H^+ \quad (2)$$

with (2) becoming relatively less important at high concentrations of the reductant. Under kinetic conditions, with NH_3OH^+ in large excess, only reaction (1) contributes significantly.

The reported ease with which Fe^{2+} reduces Ni^{IV} in acidic media[6] strongly suggests that the active reductant in these solutions is Fe^{II}. The observed retardation of the reaction with increasing acidity points to a preequilibrium involving release of H^+, and since reducing agents generally become more effective upon deprotonation we may assume that proton loss from NH_3OH^+ (pK_a 6.0)[13] is part of the picture.

The progressive changes in the nature of the decay profiles as each reaction proceeds imply a gradual change in the rate-limiting step in the catalytic sequence. In the early stages of reaction, rates are determined principally by formation of the active catalytic species, which then reacts rapidly with Ni^{IV}, relegating the oxidant to the role of a scavenger. As Ni^{IV} becomes depleted it is consumed more slowly, and its loss becomes rate-determining, leading to an approach to exponential behaviour as the reaction draws near to completion.

Data for all runs are consistent with the sequence (3)–(9), in

$$NH_3OH^+ \overset{K_3}{\rightleftharpoons} NH_2OH + H^+ \quad (3)$$

$$Fe^{III} + NH_2OH \xrightarrow{k_4} Fe^{II} + NH_2O^{\bullet} + H^+ \quad (4)$$

$$Ni^{IV} + H^+ \overset{K_5}{\rightleftharpoons} Ni^{IV}(H^+) \quad (5)$$

$$Ni^{IV} + Fe^{II} \xrightarrow{k_6} Fe^{III} + Ni^{III} \quad (6)$$

$$Fe^{II} + Ni^{III} \xrightarrow{k_7} Ni^{II} + Fe^{III} \quad (7)$$

$$Fe^{II} + Ni^{IV}(H^+) \xrightarrow{k_8} Ni^{III} + Fe^{III} + H^+ \quad (8)$$

$$2\,NH_2O^{\bullet} \xrightarrow{k_9} N_2 + 2\,H_2O \quad (9)$$

which the net rate shortly after mixing is determined by the generation of Fe^{II} [step (4)], whereas that near the end of the reaction depends also on steps (6) and (8), both of which involve Ni^{IV}. The reduction of Ni^{IV} by Fe^{II} is taken to proceed by a combination of a protonated path [steps (5) and (8)] and a non-protonated route (6), in keeping with the two-term rate law reported[6] for this reaction in the absence of NH_3OH^+. The proposed intervention of the $NH_2O^{\bullet}$ radical [step (4)] is in accord with the recognized[11,14] generation of this species by the action of 1e$^-$ oxidants on NH_2OH.

Expression of this sequence as a series of differential equations and numerical integration using an adaptation of the program KINSIM[15] yields concentrations of participating species at appropriate time intervals during the course of each reaction, and incorporation of the absorption coefficient of the nickel(IV) chelate (the only species absorbing appreciably at 572 nm) yields calculated values for the absorbance of the reaction mixture at each point.

Rate constants and equilibrium constants leading to optimum agreement between calculated and observed absorbances for all curves are listed in Table 2. The parameters describing this sequence are not wholly independent; the present experiments allow us to estimate the products K_3k_4 and K_5k_8, but not the individual constants. The reduction of the proposed nickel(III) intermediate [step (7)] is assumed to be much more rapid than that of the nickel(IV) oxidant (and therefore kinetically silent) in accord with previous comparisons[6] of the reactions of these two hypervalent states with 1e$^-$ metal-centre reductants. The bimolecular rate constant (k_9) for reaction of two $NH_2O^{\bullet}$ radicals, which is taken to be near the

Table 2 Rate constants and equilibrium quotients contributing to the reaction of complex **1** with hydroxylamine catalysed by Fe^{III} *

K_3k_4	8×10^{-2} s^{-1}	k_7	1×10^7 dm^3 mol^{-1} s^{-1}
K_5k_8	8.4×10^4 dm^6 mol^{-2} s^{-1}	k_9	1×10^9 dm^3 mol^{-1} s^{-1}
k_6	8×10^2 dm^3 mol^{-1} s^{-1}		

* Parameters pertain to the sequence (3)–(9). Reactions were run in water–methanol (49 : 1) at 25 °C, $I = 0.10$ mol dm^{-3} (ClO_4^-), $[H^+] = 0.005$–0.10 mol dm^{-3}, $\lambda = 572$ nm, $[Ni^{IV}] = (0.95$–$1.20) \times 10^{-5}$ mol dm^{-3}, $[NH_3OH^+] = 0.0010$–0.032 mol dm^{-3}, $[Fe^{III}] = (1.0$–$16.0) \times 10^{-5}$ mol dm^{-3}. Values listed are those giving optimum agreement between calculated and observed absorbances for 15 runs in which the concentrations of reagents, catalyst, and acidity were systematically varied.

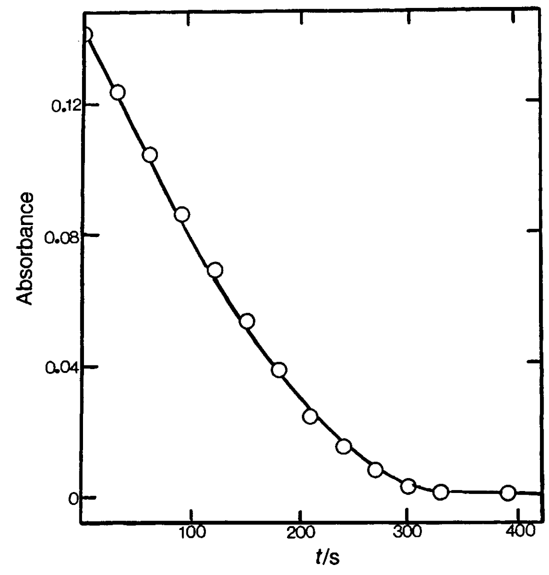

Fig. 1 Kinetic profile at 572 nm for reduction of the nickel(IV) chelate **1** (1.10×10^{-5} mol dm^{-3}) with NH_3OH^+ (2.0×10^{-3} mol dm^{-3}) catalysed by Fe^{III} (2.0×10^{-5} mol dm^{-3}) in water–methanol (49 : 1) at 25 °C; $[H^+] = 0.04$ mol dm^{-3}, $I = 0.10$ mol dm^{-3} (ClO_4^-). The solid line is the experimental curve whereas the circles are absorbances calculated from numerical integration of differential equations based on the sequence (3)–(9), taking parameters from Table 2. The absorption coefficient used for the nickel(IV) oxidant is 1.28×10^4 dm^3 mol^{-1} cm^{-1}, and the other species were taken to be negligibly absorbent. Optical path length = 1.00 cm

diffusion-controlled limit, likewise does not affect the quality of fit. Absorbances calculated from the parameters in Table 2 are compared to a representative experimental curve in Fig. 1.

Although k_4, pertaining to the Fe^{III}–NH_2OH reaction, cannot be directly evaluated from our data, division of K_3k_4 by the recorded[13] acidity constant of NH_3OH^+ yields the bimolecular rate constant 8×10^4 dm^3 mol^{-1} s^{-1}. Values of k_6 and K_5k_8, associated with the two components of the Ni^{IV}–Fe^{II} reaction, are in agreement with the acid-independent (7.5×10^2 dm^3 mol^{-1} s^{-1}) and $[H^+]$-proportional [7.4×10^4 dm^6 mol^{-2} s^{-1}] contributions reported earlier[6] for this redox couple in hydroxylamine-free systems.

The observed shifts toward 1 : 1 reaction stoichiometry as the ratio $[Ni^{IV}]/[NH_3OH^+]$ is increased (Table 1) may, as in related systems,[9–12] be attributed to a competition for the $NH_2O^•$ intermediate between its bimolecular destruction [reaction (9)] and its reaction with the primary oxidant. The latter, (10), has been reasonably considered to lead to formation of N_2O (11).[11,12]

$$NH_2O^• + Ni^{IV} \longrightarrow HNO + Ni^{III} + H^+ \qquad (10)$$

$$2\,HNO \longrightarrow N_2O + H_2O \qquad (11)$$

Stanbury and co-workers[11] have linked a very low calculated electron self-exchange rate (5×10^{-13} dm^3 mol^{-1} s^{-1}) for the NH_2OH^+–NH_2OH couple to the marked reluctance of hydroxylamine to undergo uncatalysed outer-sphere oxidations with any but the most powerful acceptors. Accordingly, oxidation by Fe^{III} [step (4) in the proposed reaction sequence] may be taken to proceed by an inner-sphere path. Moreover, Ghosh and Gould[16] have presented evidence that an iron(III)–hydroxylamine complex (K_{ass} 1×10^3 dm^3 mol^{-1}) is involved when the same combination of reductant and catalyst (although under quite different conditions) reacts with the diethylenetriamine derivative of Cr^{IV}, $[Cr^{IV}(dien)(O_2)_2]$, a reduction which is likewise exceedingly slow in the absence of catalyst.

The present study serves to remind us why iron (and to a lesser extent) copper are active catalysts for a number of additional oxidations of hydroxylamine.[11,17] The suggested sequence (3)–(9) implies that the catalytic metal must exist in accessible oxidation states a single unit apart, that the higher state must co-ordinate quickly and effectively with the reductant, and that its potential should be sufficiently positive to allow electron transfer from the bound reductant to proceed. Catalytic action becomes compromised when ligand substitution at the higher state is disfavoured, either thermodynamically or kinetically.

Acknowledgements

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