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Coordination Chemistry Reviews
170 (1998) 47–74

COORDINATION
CHEMISTRY
REVIEWS

Electron transfer reactions of nickel(III) and nickel(IV) complexes

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Received 30 May 1997; received in revised form 24 October 1997; accepted 30 November 1997

Contents

Abstract

This review narrates the electron transfer reactions of various nickel(III) and nickel(IV) complexes reported during the period 1981 until today. The reactions have been categorized mainly with respect to the type of nickel complexes. The reactivity of nickel(III) complexes of macrocycles, 2,2′-bipyridyl and 1,10-phenanthroline, peptides and oxime–imine, and of nickel(IV) complexes derived from oxime–imine, oxime and miscellaneous ligands with various organic and inorganic electron donors have been included. Kinetic and mechanistic features associated with such interactions have been duly analyzed. The relevance of Marcus cross-relation equations in the delineation of the electron transfer paths has also been critically discussed. © 1998 Elsevier Science S.A.

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PII S0010-8545(98)00065-4

Keywords: Electron transfer reactions; Kinetics and mechanism; Nickel(III) and nickel(IV) complexes

1. Introduction

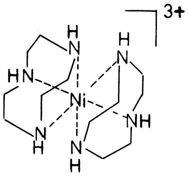
Nickel in oxidation states +3 and +4 is considered comparatively rare, but during the last two decades the roster of complexes of hypervalent nickel has expanded impressively [1]. In general, these oxidation states are highly reactive and can bring about oxidation of a number of organic and inorganic substrates. A detailed account of the chemistry of nickel oxidation states (+1, +3 and +4) has been presented by Nag and Chakravorty [2] in 1980. Just after that, another article by Haines and McAuley [3] entitled "synthesis and reactions of nickel(III) complexes" appeared in 1981. The present review aims to summarize the results of recent studies on the electron transfer reactions of nickel(III) and nickel(IV) complexes. It focuses on work published during the period 1981–1997.

We attempt to categorize the reactions with respect to the type of nickel(III) and nickel(IV) complexes. A chronological arrangement is mostly followed.

2. Electron transfer reactions of nickel(III) complexes

2.1. Reactions of macrocyclic complexes

The thermodynamic and kinetic stability imparted by triaza- and tetraaza-macrocyclic ligands to transition metal ions in uncommon oxidation states, have led to extensive studies of their properties in last two decades [4]. This property in nickel complexes is fairly well explored, and a number of reports involving the nickel(III) complexes have appeared during the period 1981 until today. The complex with 1,4,7-triazacyclononane, $[Ni(tacn)_2]^{3+}$ (**1**) has received much attention.



(1)

McAuley et al. have reported the electron transfer reactions of this nickel(III) complex by $[Co(phen)_3]^{2+}$ and iodide [5] (phen = 1,10-phenanthroline). The octahedral NiN_6 configuration is retained on electron transfer, and the reaction proceeds through outer-sphere path. A self-exchange rate for the $Ni^{III/II}$ couple of $6.0\times10^3\ dm^3\ mol^{-1}\ s^{-1}$ has been evaluated by using the Marcus correlation. The system represents one of the few examples where the outer-sphere reaction pathways of Co^{3+} and $CoOH^{2+}$ have been assigned. The origin of pH dependence could, however, arise from an intramolecular $[Ni(tacn)_2^{3+}]$&[ndash];Co^{II} hydrogen-bonding interaction or from a proton transfer coupled to the electron-transfer step.

McAuley et al. have further extended [6] the studies with new synthesis of the rac- and (-)-(*R*)-2-methyl-1,4,7-triazacyclononane (or (-)-(*R*)-Me-9-ane N_3) ligands and of the nickel(II) and nickel(III) complexes. The nickel(III) ion shows slight decomposition at pH 3.0, but is indefinitely stable in acetonitrile. A series of outer-sphere electron transfer reactions have been followed with $[Co(phen)_3]^{2+}$ and I^- reducing $[Ni((-)R\text{-}Me\text{-}9\text{-}ane\ N_3)_2]^{3+}$ and with $[Ni(cyclam)]^{3+}$,$[Ni(tacn)_2]^{3+}$, $[Ni^{IV}(L^1)]^{2+}$ (H_2L^1=3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) and $Co^{3+}(aq)$ oxidizing $[Ni((-)R\text{-}Me\text{-}9\text{-}ane\ N_3)_2]^{2+}$. Application of Marcus cross-correlation yields a self-exchange rate constant for the $[Ni((-)R\text{-}Me\text{-}9\text{-}ane\ N_3)_2]^{3+/2+}$ couple of $(1.2 \pm 0.5) \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$ which indicates that the methyl groups in the nickel(III) complex do not pose any structural impediment in the self-exchange reaction.

Outer-sphere electron transfer reactions involving some of the components of nitrous acid (e.g. NO_2^- and NO) with the substitutionally inert $[Ni(tacn)_2]^{3+}$ in the range pH 2.0–6.0 at 25 °C suggest a rate law [7]

$$-d/dt\,[Ni(tacn)_2^{3+}] = \frac{k[Ni(tacn)_2^{3+}][NO_2^-]}{1+[H^+]/K_a}, \qquad (1)$$

where K_a denotes the acid dissociation constant of nitrous acid. In the reaction with NO an inverse dependence of rate on $[H^+]$, coupled with the small systematic deviations from linearity (specially at low pH) suggests the presence of a small term in the rate law that is independent of pH and represented as

$$k_{obs} = k' + k''[H^+]^{-1}. \qquad (2)$$

An explanation has been offered for the k″ path which takes into account the formation of nitrosoamine through the N-deprotonated conjugate base form of the Ni^{III} oxidant. The k′ pathway corresponds to an outer-sphere electron transfer between NO and $[Ni(tacn)_2]^{3+}$ and is justified by application of cross-reaction relations. It appears to be the first report of outer-sphere electron transfer from nitric oxide in a homogeneous solution.

The oxidation of thiosulfate by $[Ni(tacn)_2]^{3+}$ [8] follows a mechanism

$$[Ni(tacn)_2]^{3+} + S_2O_3^{2-} \Leftrightarrow [Ni(tacn)_2]^{2+} + S_2O_3^- \quad k_1, k_{-1}, \qquad (3)$$

$$S_2O_3^{2-} + S_2O_3^- \Leftrightarrow S_4O_6^{3-} \quad k_2, \qquad (4)$$

$$[Ni(tacn)_2]^{3+} + S_4O_6^{3-} \rightarrow [Ni(tacn)_2]^{2+} + S_4O_6^{2-} \quad k_3. \qquad (5)$$

The value of k_2 is large enough, $> 10^6\ dm^3\ mol^{-1}\ s^{-1}$ [9] to maintain a substantial fraction of the radicals as $S_4O_6^{3-}$, and k_3 is also expected to be large. There is no evidence for the reverse electron transfer (k_{-1}) to occur, and application of steady-state approximation to the two radicals enables one to derive a rate law

$$-d/dt\,[Ni(tacn)_2^{3+}] = 2k_1[Ni(tacn)_2^{3+}][S_2O_3^{2-}], \qquad (6)$$

which is established experimentally. It is catalysed by trace levels of Cu^{II} ion, but can be eliminated by using $C_2O_4^{2-}$ as scavenger. Analysis of a plot of log k_1 as a function of E° for all known reactions where $S_2O_3^{2-}$ is oxidized by substitutionally inert oxidant, indicates that the oxidation by $[Ni(tacn)_2]^{3+}$ is activation-controlled and outer-sphere in nature. An effective self-exchange rate constant for the $S_2O_3^-/S_2O_3^{2-}$ couple of 2.3×10^5 $dm^3\,mol^{-1}\,s^{-1}$ has been evaluated. Since the structural differences between $S_2O_3^{2-}$ and $S_2O_3^-$ are minimal, such a rapid exchange seems reasonable.

The kinetics of oxidation of excess thiocyanate by $[Ni(tacn)_2]^{3+}$[10] shows kinetic inhibition by the product, $[Ni(tacn)_2]^{2+}$, and with a large excess of the nickel(II) complex, a pseudo-second-order behaviour is noted which is accommodated by a reaction scheme,

$$Ni^{III}+SCN^- \Leftrightarrow Ni^{II}+SCN \quad k_1, k_{-1}, \qquad (7)$$

$$Ni^{III}+2SCN^- \Leftrightarrow Ni^{II}+(SCN)_2^- \quad k_2, k_{-2}, \qquad (8)$$

$$Ni^{III}+(SCN)_2^- \rightarrow Ni^{II}+(SCN)_2 \quad k_3, \qquad (9)$$

$$SCN+SCN^- \Leftrightarrow (SCN)_2^- \quad k_4, k_{-4}, K_{rad}, \qquad (10)$$

$$3(SCN)_2+4H_2O \rightarrow 5SCN^- +HCN+SO_4^{2-}+7H^+ \ \text{(fast)}. \qquad (11)$$

At high $[Ni^{II}]$,

$$k_{obs}=\frac{2(k_1[SCN^-]+k_2[SCN^-]^2)k_3K_{rad}[SCN^-]}{(k_{-1}+k_{-2}K_{rad}[SCN^-])[Ni^{II}]}. \qquad (12)$$

In the presence of the spin trap DMPO (5,5-dimethyl-1-pyrroline N-oxide) the rate law is pseudo-first-order with $k_{obs}=(2k_1[SCN^-]+2K_2\,[SCN^-]^2)$ having rate constants, $k_1=(0.046\pm0.003)$ $dm^3\,mol^{-1}\,s^{-1}$ and $k_2=(2.04\pm0.012)$ $dm^6\,mol^{-2}\,s^{-1}$ at 25 °C, $I=0.1$ $mol\,dm^{-3}$. Under these conditions, inhibition by nickel(II) is significant only at relatively high nickel(II) concentrations. On the basis of a LFER, it is shown that the rate-limiting step for the forward process (k_1) is diffusive separation of the products rather than the electron transfer within the encounter complex, and owing to the effect of diffusion the calculated self-exchange rate constant ($k_{11}=5\times10^4$ $dm^3\,mol^{-1}\,s^{-1}$) for the SCN/SCN^- couple should be treated as the lower limit. It may be mentioned here that though the LFER approach enables moderate empirical success in correlating the values of k_2 and k_{-2}, it does not provide any rationale for the deviations noted for the reactions following the same mechanism.

The electrochemical oxidation of $[Ni^{II}L^2]^{2+}$(L^2=Me$_6$cyclam=meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) in aqueous solution in the presence of sulfate, phosphate, chloride and phthalate yields $Ni^{III}L^2X_2$ [11]. The results reported indicate that simple anions stabilize $[NiL^2]^{3+}$ by axial coordination. Kinetic studies show that the complexes $[Ni^{III}L^2(SO_4)_2]^-$ and $[Ni^{III}L^2(H_2PO_4)_2]^+$ decompose via $[Ni^{III}L^2]^{3+}$ and perhaps also partially via $[Ni^{III}L^2SO_4]^+$ and

$[Ni^{III}L^2(H_2PO_4)]^{2+}$. A very important aspect which emerges from here, is that the ligation of anions to the nickel decreases the inductive effect of the nickel on the N–H bond, thereby decreasing the acidity of these protons. This is of major importance in the stabilization of the +3 oxidation state.

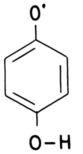
A kinetic study on the oxidation of hydroquinone (1,4-dihydroxy-benzene) and catechol (1,2-dihydroxybenzene) by $[Ni^{III}L^3]^{3+}$(L^3 = cyclam = 1,4,8,11-tetraaza-cyclotetradecane) over the range pH 0–2.9 has been reported [12]. Two regions are examined separately, namely $0.1 < [H^+] < 1.0$ mol dm^{-3} and $[H^+] < 0.05$ mol dm^{-3}. A small retardation of the reaction at pH < 1.0 indicates the involvement of a protonation equilibrium of quinol (H_2Q) rather than the existence of the protonated form of $[Ni^{III}L^3]^{3+}$ which could lead

$$H_3Q^+ \overset{K}{\Leftrightarrow} H^+ + H_2Q, \tag{13}$$

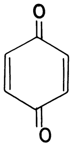
to dissociation of the complex. The kinetic sequence has been interpreted as

$$[Ni^{III}L^3]^{3+} + H_2Q \xrightarrow{k_1} [Ni^{II}L^3]^{2+} + S\dot{Q} + H^+. \tag{14}$$

$$[Ni^{III}L^3]^{3+} + S\dot{Q} \xrightarrow{\text{fast}} [Ni^{II}L^3]^{2+} + Q + H^+. \tag{15}$$



(Semiquinone)
SQ•



(Quinone)
Q

with a reasonable fit of the experimental data which yield $K = 4.5 \pm 1.2$ and 3.3 ± 0.9 mol dm^{-3} for hydroquinone and catechol, respectively. Comparison of the equilibrium constants with the previously reported values [13–15] shows reasonable agreement. Since the pK_a for formation of hydroquinone anion is 10.35, in the pH range 1.5–3.2 studied, the increase in rate with decreasing $[H^+]$ has been attributed to a reaction of a second nickel(III) species as

$$[Ni^{III}L^3(OH_2)_2]^{3+} \overset{K_h}{\Leftrightarrow} [Ni^{III}L^3(OH)(OH_2)]^{2+} + H^+. \tag{16}$$

From pulse radiolysis studies on $[Ni^{III}L^2]^{3+}$,a pK_h value of 3.7 has been reported, and the value of 3.1 obtained from kinetic results here is in good agreement. Further evidence for the monohydroxy complex comes from ESR measurements. A more marked increase in rate at higher pH for the hydroquinone system where the pK_h for Hcat$^-$ formation is lower (9.85) may be due to a reaction pathway involving $[Ni^{III}L^3(OH)(OH_2)]^{2+}$ with Hcat$^-$. The sulfate ion has a marked effect on the rates, showing pronounced retardation owing to the formation of sulfate complexes with lower redox potentials. The kinetic data have been interpreted with Marcus cross-correlation and are considered outer-sphere in character showing fairly good agreement of electron transfer rates with those reported in the literature.

McAuley et al. [16] have reported the kinetic results of reduction of several nickel(III) macrocycles [e.g. cyclam(L^3); dimethylcyclam (Me_2L^3); c-rac-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane(tet-c), 1,4,7-triazacyclononane(tacn)] by titanium(III) in aqueous trifluoromethane sulfonate or chloride media. The variation of E° values for these oxidants ($\sim$0.6–1.2 V) provides a range of driving force for the reactions. The kinetic data have been combined to provide a Marcus correlation, and the outer-sphere character of these reactions has been established. In the case of the reaction with $[Ni(tacn)_2]^{3+}$, a chloride promoted pathway arising from the reaction of the ion-pair $Ni(tacn)_2^{3+},Cl^-$ with the reductant is observed.

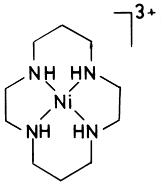
$$Ni(tacn)_2^{3+} + Cl^- \overset{K}{\Leftrightarrow} Ni(tacn)_2^{3+}, Cl^-, \tag{17}$$

$$Ti(OH)^{2+} + Ni(tacn)_2^{3+} \xrightarrow{K_1} Ti(IV) + Ni(II), \tag{18}$$

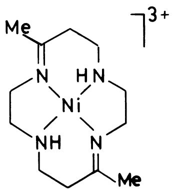
$$Ti(OH)^{2+} + Ni(tacn)_2^{3+} \cdot Cl^- \xrightarrow{k_2} Ti(IV) + Ni(II), \tag{19}$$

$$Ti_{aq}^{3+} + Ni(tacn)_2^{3+} \cdot Cl^- \xrightarrow{k_3} Ti(IV) + Ni(II). \tag{20}$$

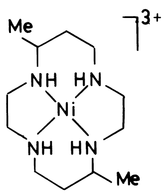
The aqueous redox chemistry of a number of nickel(III) macrocycles [(**1**)–(**8**)], both tetraaza and triaza, has been studied in detail by Macartney et al. [17].



$[Ni (cyclam)]^{3+}$
(2)

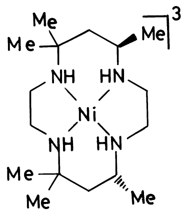


$[Ni (Me_2diene)]^{3+}$
(3)



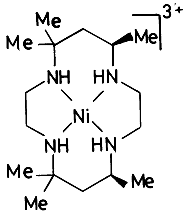
$[Ni (Me_2cyclam)]^{3+}$
(4)

In the reduction of nickel(III) macrocycles by Fe^{2+} in acidic perchlorate media, the rate constants are found to be independent on $[H^+]$. For Ni(III)-cyclam complex having labile axial coordination sites the increased rate constant with increasing $[SO_4^{2-}]$ may involve a sulfate-bridged species though an alternative route via anion bridging may also accelerate the reaction in a small way. A dominant pathway involving $VO(OH)^+$ is apparent from an inverse dependence of rate on $[H^+]$. Applications of the Marcus theory relationship to the cross-reactions yield estimated self-exchange rate constants of 10^{-3}–10^{-2} $dm^3\ mol^{-1}\ s^{-1}$ for $Fe(H_2O)_6^{2+/3+}$ and



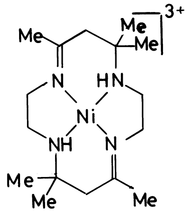
$[\mathrm{Ni(tet\text{-}c)}]^{3+}$

(5)



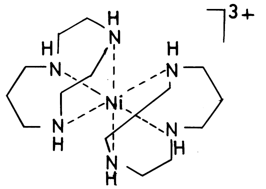
$[\mathrm{Ni(tet\text{-}d)}]^{3+}$

(6)



$[\mathrm{Ni(Me_6diene)}]^{3+}$

(7)



$[\mathrm{Ni(decane)_2}]^{3+}$

(8)

10–10^3 dm^3 mol^{-1} s^{-1} for $VO(OH)^{+/2+}$. These values are larger than those derived from metal polypyridine cross-reactions, where electron exchange in the oxidant couples takes place via a ligand π*–π* pathway, resulting from the stacked overlap of π* lobes of the pyridines. For the low-spin d^7 nickel(III) complex containing saturated nitrogen macrocycles, electron self-exchange occurs by overlap of metal-centred dσ* orbitals causing lesser steric interference and greater ligand–ligand compatibility in the approach of the metal aqua-ion for electron transfer by d–d overlap. The behaviour of $VO(OH)^+$ showing an enhanced reactivity toward the nickel(III) macrocycles may reflect the formation of a uniquely oriented outer-sphere activated complex that enhances electron transfer.

The kinetics of substitution reactions of a series of diaquanickel(III) macrocyclic complexes, $[NiL^4(H_2O)_2]^{3+}$ (where L^4=[α]-c-meso-5,12-dimethylcyclam; c-rac-5,12-dimethylcyclam and c-meso-5,12-diethylcyclam) with Cl^- and Br^- ions have been reported by Fairbank and McAuley [18]. In aqueous perchloric acid reactions proceed as,

$$[NiL^4(H_2O)_2]^{3+} + X^- \Leftrightarrow [NiL^4X(H_2O)]^{2+} + H_2O \quad k_1, k_{-1}. \qquad (21)$$

Steric crowding of the axial site of the complexes by a methyl substituent substantially increases the rate consistent with a dissociative mechanism. The presence of a second step subsequent to the formation of a monohalo complex is considered as a rearrangement in the complex from an octahedral to a more stable pentacoordinated configuration. Such propositions are adequately supported by kinetic, spectral and ESR measurements [19]. The above observations are relevant to the redox study of the same nickel(III) macrocycles with iodide ion [20]. The mechanism of such interaction follows as

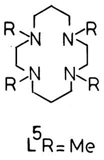
$$[NiL^4(H_2O)_2]^{3+} + I^- \Leftrightarrow [NiL^4(H_2O)I]^{2+} + H_2O \quad k_1, k_{-1}, \tag{22}$$

$$[NiL^4(H_2O)I]^{2+} + I^- \rightarrow [NiL^4]^{2+} + I_2^- + H_2O \quad k_2, \tag{23}$$

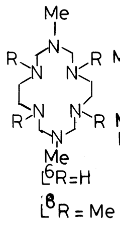
$$I_2^- + [NiL^4(H_2O)_2]^{3+} \xrightarrow{\text{rapid}} [NiL^4]^{2+} + I_2 + 2H_2O. \tag{24}$$

The evaluated rate parameters indicate that the complex formation step is higher than the redox step. The thermodynamic stability of the iodonickel(III) complex is greater than that with Cl^- or Br^- owing to an increased nephelauxetic effect of I^- that can produce a more covalent Ni–I bond. Comparison with other outer-sphere reactions of iodide, supports the operation of an inner-sphere mechanism.

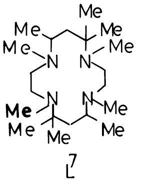
Meyerstein et al. [21] have very recently reported the stability and redox properties of a series of nickel(III) complexes with polyaza macrocycles (L^5–L^9) formed upon electrochemical oxidation of the nickel(II) analogue.



(9)



(10)



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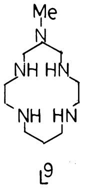


(12)

The kinetics of decomposition of the nickel(III) complexes of L^5 and L^7 ligands measured from UV-VIS spectral change shows a first-order decay though the oxidation of both the ligands or water are $2e^-$ processes. We note that since these complexes of L^5 and L^7 ligands do not possess any secondary nitrogen atom, the decomposition via the generation of a free radical species by proton abstraction is unlikely. The authors have not indicated clearly in this short communication about the actual process of decomposition, though they mentioned that the rate determining step involves some type of intramolecular rearrangement/isomerization followed by a fast reaction with a second molecule of nickel(III) complex. Nickel(III) species of this type having secondary nitrogen atom (e.g. L^6 and L^9) show faster rates of decomposition owing to proton abstraction and simultaneous intramolecular electron transfer. The ion $[NiL^7]^{3+}$ does not oxidize N_3^- or Br^- and is precipitated when SCN^- is added to the solution. The mechanisms of these oxidations are believed to follow

$$[NiL^i]^{3+}_{aq} + X^- \Leftrightarrow [NiL^i]^{2+}_{aq} + \dot{X}, \tag{25}$$

$$\dot{X} + X^- \rightarrow \dot{X}_2^-, \tag{26}$$

or alternately by the sequence

$$[\mathrm{NiL}^{i}]^{3+}_{\mathrm{aq}} + \mathrm{X}^{-} \Leftrightarrow [\mathrm{NiXL}^{i}]^{2+}_{\mathrm{aq}}, \tag{27}$$

$$[\mathrm{Ni}^{\mathrm{III}}\mathrm{XL}^{i}]^{2+}_{\mathrm{aq}} + \mathrm{X}^{-} \Leftrightarrow [\mathrm{NiL}^{i}]^{2+}_{\mathrm{aq}} + \mathrm{X}_2^{\dot{-}}, \tag{28}$$

$$2\dot{\mathrm{X}} \rightarrow \text{products}, \tag{29}$$

$$2\mathrm{X}_2^{\dot{-}} \rightarrow \text{products}, \tag{30}$$

or

$$[\mathrm{NiL}^{i}]^{3+}_{\mathrm{aq}} + \mathrm{X}_2^{\dot{-}} \rightarrow [\mathrm{NiL}^{i}]^{2+}_{\mathrm{aq}} + \mathrm{X}_2. \tag{31}$$

The redox properties of the couple $[\mathrm{NiL}^8]^{2+/+}$ are shown to be very similar to those of the couple $[\mathrm{NiL}^5]^{2+/+}$. The E° for the former couple is low (450 mV versus SCE) which is even somewhat lower than that of the couple $[\mathrm{NiL}^6]^{3+/2+}$. This result is very surprising as the ligand field induced by L^8 is relatively low [22]. The complex $[\mathrm{NiL}^8]^{3+}$oxidizes I^- and ascorbate. It is quite surprising again that the product of reduction of $[\mathrm{NiL}^8]^{3+}_{\mathrm{aq}}$ by ascorbate is $[\mathrm{NiL}^8]^{2+}_{\mathrm{aq}}$ in its planar trans III isomeric form. One tentative explanation may be that this complex is stabilized via hydrogen bonding of the aqua ligands to the 1,8-nitrogens which gets support from the observation [23] laid down to explain the effect of the nature of substituents R on the redox potential of the couples $[\mathrm{NiL}^9]^{3+/2+}$ where $\mathrm{L}^9 =$ 1-R-1,3,5, 8,12-pentaazacyclotetradecane.

A recent EPR and ^{2}H NMR study [24] shows that inverted porphyrins, 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin and 2-methyl-5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin do stabilize the rare organonickel(III) derivatives. The EPR patterns indicate that the spectral parameters markedly depend on the axial ligand introduced by oxidants (e.g. Br_2, $(\mathrm{CH}_3\mathrm{COO})_4\mathrm{Pb}^{\mathrm{IV}}$ etc.) or in methathesis. A metal-centered oxidation rather than a cation radical formation is suggested.

2.2. Reactions of 2,2′-bipyridyl and 1,10-phenanthroline complexes

Macartney and Sutin [25] have reported the kinetics of the oxidation of $[\mathrm{Ni}\{4,4'\text{-}(\mathrm{CH}_3)_2\mathrm{bpy}\}_3]^{2+}$ and $[\mathrm{Ni(phen)}_3]^{2+}$ by $[\mathrm{Ni(bpy)}_3]^{3+}$ and the reduction of $[\mathrm{Ni}\{4,4'\text{-}(\mathrm{CH}_3)_2\mathrm{bpy}\}_3]^{3+}$ and $[\mathrm{Ni(bpy)}_3]^{3+}$ by $[\mathrm{Ni(H}_2\mathrm{L}^1)]^{2+}$ (bpy = 2,2′-bipyridyl and $\mathrm{H}_2\mathrm{L}^1 =$ 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime), $[\mathrm{RuL}^{10}_3]^{2+}$ ($\mathrm{L}^{10} =$ 5-nitro-1,10-phenanthroline) and $[\mathrm{Fe(H}_2\mathrm{O)}_6]^{2+}$ in acidic aqueous media. The self-exchange rate constants (k_{11}) for the $[\mathrm{Ni(bpy)}_3]^{2+/3+}$ and $[\mathrm{Ni}\{4,4'\text{-}(\mathrm{CH}_3)_2\,\mathrm{bpy}\}_3]^{2+/3+}$ couples have been estimated to be 1.5×10^3 dm^3 mol^{-1} s^{-1} at 25 °C by employing modified Marcus cross-relations. The $[\mathrm{Fe(H}_2\mathrm{O)}_6]^{2+}$ reduction of both $[\mathrm{Ni}\{4,4'\text{-}(\mathrm{CH}_3)_2\,\mathrm{bpy}\}_3]^{3+}$ and $[\mathrm{Ni(bpy)}_3]^{3+}$ does not show good agreement to above calculations. Using an effective $[\mathrm{Fe(H}_2\mathrm{O)}_6]^{2+/3+}$ exchange rate constant that corresponds to 5×10^{-4} dm^3 mol^{-1} s^{-1} would yield a value 2×10^3 dm^3 mol^{-1} s^{-1} as the average rate constant for the $[\mathrm{Ni(bpy)}_3]^{2+/3+}$ and $[\mathrm{Ni}\{4,4'\text{-}(\mathrm{CH}_3)_2\,\mathrm{bpy}\}_3]^{2+/3+}$ exchanges, in excellent agreement with those estimated from other tris(polypyridine)nickel(III) reactions. The significance of this effective rate constant is debatable since $Fe(H_2O)_6^{2+/3+}$ exchange may involve a water bridging pathway or be associated with certain elements of nonadiabaticity. An excellent account of the rate variations in terms of inner-shell reorganization barriers and electronic factors for the reactions is presented.

The nickel(III) complexes of 2,2′-bipyridine (bpy) and 4,4′-dimethyl-2,2′-bipyridine (dmbpy) is synthesized electrochemically [26] in anhydrous acetonitrile containing 0.1 mol dm^{-3} tetraethyl ammonium perchlorate. The dark green nickel(III) complexes are obtained by slow evaporation of the solvent to near dryness. The kinetics of oxidation of L-ascorbic acid (H_2A) by $[Ni(dmbpy)_3]^{3+}$ in acidic aqueous media in the range temperature 9–25 °C showing an inverse dependence of rate on [acid] suggest a mechanism involving H_2A and HA^- pathways, for which the specific rate and activation parameters have been determined. Application of Marcus relationships provides estimates of the self-exchange parameters for the $1e^-$ couples: $H_2A/HA^{\dot{+}}$, $k_{11}=2\times10^3$ dm^3 mol^{-1} s^{-1}; HA^-/HA, $k_{11}=1\times10^5$ dm^3 mol^{-1} s^{-1}; $A^{2-}/A^{\dot{-}}$, $k_{11}=2\times10^5$ dm^3 mol^{-1} s^{-1}. It appears that the small dependence of k_{11} on the extent of protonation in these species likely results from the effects of protonation on the inner-sphere reorganization barriers which could be further resolved by structural characterization of the various ascorbate and ascorbate radical species.

2.3. Reactions of peptide complexes

Coordination of deprotonated nitrogens stabilizes the trivalent oxidation state of nickel. Studies of the temperature dependence [27] of the electrode potentials indicate that the nickel(II) peptide complexes are not axially solvated in contrast to the nickel(III) forms. The substitution by monodentate nitrogen ligands (imidazole, SCN^- etc.) is too fast to observe by stopped-flow methods, and a lower limit for the axial water exchange rate is estimated, $k_{H2O}>4\times10^6 s^{-1}$ [28].

The protonation of tetraglycline and tetraglycinamide complexes of nickel(III) has been kinetically investigated by Margerum et al. [29] over a wide range of $[H^+]$, 4.3×10^{-3}–0.2 mol dm^{-3}. The data are consistent with the interpretation that one of the equatorial positions of the complex is relatively labile and carboxylate or peptide nitrogen group coordinated to the fourth equatorial position undergo substitution and protonation rapidly with ultimate cleavage from the coordination sphere. Evidence from EPR spectral measurements establishes the involvement of peptide oxygen as the exact protonation site. A related study [30] on the acid dissociation of $[Ni^{III}(H_{-1}Aib_2)_2]^-$ (where Aib_2 = dipeptide of α-aminoisobutyric acid) and its cross-reaction electron transfer with excess $[Cu^{II}(H_{-3}Aib_3a)]^-$ (where Aib_3a = tripeptideamide of α-aminoisobutyric acid) in the range pH 12–13 has been reported. A self-exchange rate constant (=48 dm^3 mol^{-1} s^{-1}) for the $Ni^{III/II}$ couple of Aib_2 is evaluated on the basis of Marcus equation. A three-step process for the reaction of $[Ni^{III}(H_{-1}Aib_2)_2]^-$ which likely generates two other nickel(III) complex species is postulated; the reactivity of such intermediates is, however, less focussed.

Lappin et al. [31] have undertaken the kinetics of oxidation of $[Co(edta)]^{2-}$ ($edta^{4-}$ = 1,2-diaminoethane-*N*,*N*,*N*′,*N*′-tetraacetate(4-)) by four bis(dipeptide) nickel(III) complexes, $[Ni(H_{-1}GG)_2]^-$, $[Ni(H_{-1}AG)_2]^-$ and $[Ni(H_{-1}AA)_2]^-$ (GH = glycine, AH = (*S*)-alanine). The reactions show a complex dependence on pH. The dominant pathway over the range pH 4–10 is proposed to involve the acid-catalysed formation of a precursor complex between N-terminal amine hydrogen atom and carboxylato oxygen atom of $[Co(edta)]^{2-}$ through which electron transfer occurs:

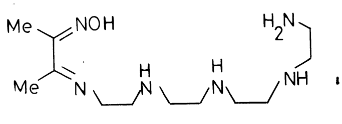
$$[Ni(H_{-1}GG)_2]^- + [Co(edta)]^{2-} + H^+ \Leftrightarrow \{[Ni(H_{-1}GG)_2^-] \cdot [Co(edta)^{2-}]\} + H^+ \quad k_1, k_{-1}, \tag{32}$$

$$\{[Ni(H_{-1}GG)_2^-] \cdot [Co(edta)^{2-}]\} \rightarrow [Ni(H_{-1}GG)_2]^{2-} + [Co(edta)]^- \quad k_2. \tag{33}$$

Reaction pathways involving $[Co(Hedta)]^-$ and $[Co(edta)(OH)]^{3-}$ are not well explored.

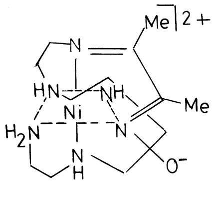
2.4. Reactions of oxime–imine complex

The ligand HL^{11} [(**13**) = 15-amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oxime] yields cationic nickel(II) and nickel(III) complexes which are quite stable and have pseudo-octahedral geometry [32,33]. This ligand with one oximato group is capable of stabilizing nickel upto +3 oxidation state. The negative charge on the oximato oxygen plays an important role in stabilizing the higher oxidation states of nickel through σ donation and inductive transmission.



HL^{11}

(13)



$[Ni^{III}(L^{11})]^{2+}$

(14)

Rate studies on the reduction of $[Ni^{III}L^{11}]^{2+}$ (**14**) with $[Co(phen)_3]^{2+}$ and hydroquinone (H_2Q) in the pH range 4–8 have been reported by McAuley et al. [34]. The lack of proton dependence on rate associated with the Co^{II} reduction has been noted and treatment of the kinetic data permits calculation of the self-exchange rate constant of the $[Ni^{III}L^{11}]^{2+}$–$[Ni^{II}L^{11}]^+$ couple of $k_{ex} = (6 \pm 1) \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$. In the reaction of hydroquinone, the observed hydrogen ion dependence may be attributed to equilibria involving the organic substrate.

$$H_2Q \overset{K}{\Leftrightarrow} HQ^- + H^+, \tag{34}$$

$$H_2Q + [Ni^{III}L^{11}]^{2+} \xrightarrow{k_1} [Ni^{II}(HL^{11})]^{2+} + S\dot{Q}, \tag{35}$$

$$HQ^- + [Ni^{III}L^{11}]^{2+} \xrightarrow{k_2} [Ni^{II}(L^{11})]^+ + S\dot{Q}, \tag{36}$$

$$S\dot{Q} + [Ni^{III}L^{11}]^{2+} \xrightarrow{\text{fast}} [Ni^{II}(HL^{11})]^{2+} + Q. \tag{37}$$

Deprotonated Ni^{II} species exists at higher pH. The large difference in reactivity (ca. 10^5) between the protonated and dissociated forms of H_2Q may be rationalized in terms of the redox potentials and self-exchange parameters. The exchange rate for the $[Ni^{III}L^{11}]^{2+}$–$[Ni^{II}L^{11}]^+$ couple is $3 \times 10^2\ dm^3\ mol^{-1}\ s^{-1}$, in excellent agreement with the value obtained using $[Co(phen)_3]^{2+}$. It is noteworthy that the exchange parameter calculated similarly from data for the cross reaction ($[Ni^{III}L^{11}]^{2+}/H_2Q$) turns out as $4 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$. This deviation can be caused from a substantial negative driving force ($\Delta E^\circ = -0.60$ V) for $[Ni^{III}L^{11}]^{2+}/H_2Q$ making it outside the range where the Marcus relationship generally applies.

The kinetics of oxidation of ascorbic acid (H_2A) by the nickel(III) oxime–imine complex, $[Ni^{III}L^{11}]^{2+}$ has been investigated in the range pH 2.5–8.0 at 30 °C by Saha et al.[35]. The second-order rate constant for electron transfer is very much influenced by acidity of the medium, and the rate contributions by H_2A, HA^- and A^{2-} have been evaluated by detailed analysis of rate-pH profile. The formation of hydrogen-bonded adduct between the hydrogen atom of H_2A or HA^- and oximato oxygen atom could lead to a low energy electron transfer pathway. The analysis of kinetic data by Marcus cross-reaction relations suggests an outer-sphere route for A^{2-} species and it indeed does not pose any dilema by its degree of protonation. In the reactions of $[Ni^{III}L^{11}]^{2+}$ by sulfur(IV) [36], almost identical mechanistic model follows and the reactivity order of sulfur(IV) species is $SO_2 \cdot H_2O > HSO_3^- < SO_3^{2-}$ dominated by the extent of hydrogen-bond formation. For a less adequately constituted reaction partner (SO_3^{2-}), an outer-sphere route is the only accessible pathway supported by Marcus cross-relation calculations. The reactivity of $HSeO_3^-$ is ca. 10^3 times slower than that of HSO_3^- owing to the large difference in reduction potentials ($\Delta E^\circ = 0.75$ V) of the SO_4^{2-}/SO_3^{2-} over SeO_4^{2-}/SeO_3^{2-} couples.

The kinetics of oxidation of thiosulfate ion by $[Ni^{III}L^{11}]^{2+}$ [37] has been investigated in the range pH 3.5–5.5 over the temperature range 20–40 °C. A reaction scheme has been postulated taking into consideration the reactivity of $S_2O_3^{2-}$ and $HS_2O_3^-$ supported by pH-variation rate data. The calculated electron transfer rate constants for the $S_2O_3^{2-}$ path by using a Marcus format is ca. 10^4 times lower than that obtained experimentally. Such deviation from an outer-sphere route has been justified by the formation of an inner-sphere adduct formed through ring opening via one of the nitrogen atoms of the ligand or by donation of electrons from oximato oxygen to the vacant d-orbital of sulfur atom of $S_2O_3^{2-}$. Judging from the lability of the complex ($<10^2\ s^{-1}$) and the magnitude of the electron transfer rate constant (ca. $10^{-1}\ dm^3\ mol^{-1}\ s^{-1}$), the former process may become more important. However, no experimental evidence has been accumulated for such process. The oxidation of several thiourea derivatives (e.g. thiourea, allyl thiourea, methyl thiourea and phenyl thiourea) by $[Ni^{III}L^{11}]^{2+}$ [38] has been considered to follow an inner-sphere route following the same analogy. The validity of Marcus correlation has not been tested owing to the non-availability of requisite exchange parameters.

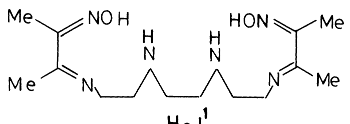
Oxidation of formate, oxalate and malonate by the $[Ni^{III}L^{11}]^{2+}$ [39] over the range pH 2.5–7.6 indicates a parallel auto decomposition path of the nickel(III) complex on the time scale of the slow reactions. The reactivity order for the carboxylates is $k_{HCOOH} > k_{HCOO^-}, k_{H2Ox} > k_{HOx^-} > k_{Ox^{2-}}$ and $k_{H2mal} > k_{Hmal^-} < k_{mal^{2-}}$. The observed trend contrary to that obtained in the reactions with other metal complex oxidants illustrates the significant hydrogen bonding interactions between the carboxylato hydrogen and oximato oxygen of the coordinated ligand.

In the reaction of thioglycolic acid (H_2T) with $[Ni^{III}L^{11}]^{2+}$, the formation of a hydrogen bonded adduct is justified from the observation of a wide shift in the pK_1 value of H_2T obtained kinetically [40,41]. A large association constant ($418\ dm^3\ mol^{-1}$) calculated from the rate saturation profile of thiomalate species ($Htmal^{2-}$) is in keeping with an inner-sphere path. However, the preferred path for the ($tmal^{3-}$) interaction is outer-sphere apparent from its higher reactivity ($\sim 10^5\ dm^3\ mol^{-1}\ s^{-1}$) compared with the lower substitution lability of the nickel(III) species.

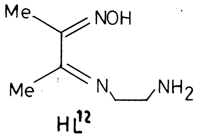
3. Electron transfer reactions of nickel(IV) complexes

3.1. Reactions of oxime–imine complexes

The most widely acclaimed chelates to stabilize nickel(IV) are the oxime–imine ligand [H_2L^1 = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime (**15**) and HL^{12} = 6-amino-3-methyl-4-azahex-3-en-2-one oxime (**16**)] through the strong L→M (σ) donation.



H_2L^1
(15)



HL^{12}
(16)

Several kinetic investigations have appeared on the reduction of $[Ni^{IV}L^1]^{2+}$ and $[Ni^{IV}L^{12}_2]^{2+}$ by organic molecules, metal ions and complexes and inorganic substrates. The oxidation of L-ascorbic acid (H_2A) with $[Ni^{IV}L^1](ClO_4)_2$ over the range pH 1.0–6.0 at 25 °C and $0.1\ mol\ dm^{-3}$ ionic strength is reported by Lappin et al. [42]. The reaction is first-order in both oxidant and reductant. The second-order rate constants for electron transfer show a bell-shaped dependence on pH. To explain it, an "outside-protonated" $\mathrm{Ni^{IV}}$ species is considered with $\mathrm{p}K_\mathrm{h}=3.70$ for nickel(IV) complex. The proposed reaction scheme is

$$\mathrm{H_2A \Leftrightarrow H^+ + HA^-}, \tag{38}$$

$$\mathrm{[Ni(H\cdots L^1)]^{3+}} \overset{K_h}{\Leftrightarrow} \mathrm{[NiL^1]^{2+} + H^+}, \tag{39}$$

$$\mathrm{[Ni(H\cdots L^1)]^{3+} + HA^- \rightarrow [Ni(HL^1)]^{2+} + H\dot{A}}, \tag{40}$$

$$\mathrm{[NiL^1]^{2+} + HA^- \rightarrow [NiL^1]^+ + H\dot{A}}, \tag{41}$$

$$\mathrm{[Ni(HL^1)]^{2+} \Leftrightarrow [NiL^1]^+ + H^+}, \tag{42}$$

$$\mathrm{[Ni(HL^1)]^{2+} + HA\cdot} \overset{\text{fast}}{\rightarrow} \mathrm{[Ni(H_2L^1)]^{2+} + A}, \tag{43}$$

where A = dehydroascorbic acid. The process involves two discrete one-electron transfer steps with formation of a nickel(III) oxime–imine intermediate. This work has been reinterpreted by the same group of workers [43]. The characterization of $\mathrm{[Ni^{III}L^1]^+}$ intermediate allows to consider the data of ascorbate ion oxidation as to involve the protonation of $\mathrm{Ni^{III}}$ species instead of "outside-protonated" $\mathrm{Ni^{IV}}$ species.

The kinetics of reduction of $\mathrm{[Ni^{IV}L^1]^{2+}}$ by one-electron reagent, $\mathrm{[Co(phen)_3]^{2+}}$ [43] is biphasic over the whole range of pH 3.5–9.0 at 25 °C. An initial rapid pH independent reaction between $\mathrm{[Ni^{IV}L^1]^{2+}}$ and $\mathrm{[Co(phen)_3]^{2+}}$ is proposed leading to the formation of a nickel(III) intermediate. Subsequent reduction of this species and its protonated form, $\mathrm{[Ni^{III}(HL^1)]^{2+}}$ by $\mathrm{[Co(phen)_3]^{2+}}$ gives the nickel(II) product.

$$\mathrm{[Ni^{IV}L^1]^{2+} + [Co(phen)_3]^{2+} \rightarrow [Ni^{III}L^1]^+ + [Co(phen)_3]^{3+}}, \tag{44}$$

$$\mathrm{[Ni^{III}(HL^1)]^{2+} \Leftrightarrow [Ni^{III}L^1]^+ + H^+}, \tag{45}$$

$$\mathrm{[Ni^{III}L^1]^+ + [Co(phen)_3]^{2+} \rightarrow [Ni^{II}L^1] + [Co(phen)_3]^{3+}}, \tag{46}$$

$$\mathrm{[Ni^{III}(HL^1)]^{2+} + [Co(phen)_3]^{2+} \rightarrow [Ni^{II}(HL^1)]^+ + [Co(phen)_3]^{3+}}. \tag{47}$$

Application of Marcus cross-reaction relation to these outer-sphere processes enables to estimate the self-exchange rate constants of $\mathrm{[Ni^{IV/III}L^1]^{2+/+}} = 1\times10^5\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$, and those for $\mathrm{[Ni^{III/II}L^1]^{+/0}}$ and $\mathrm{[Ni^{III/II}(HL^1)]^{2+/+}}$ as 2×10^3 and $1\times10^3\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$, respectively. The kinetics of the reduction of $\mathrm{[Ni^{IV}L^1]^{2+}}$ by $\mathrm{[Co(edta)]^{2-}}$ investigated by Lappin et al. [44] also shows biphasic absorbance changes over the whole pH range 3.5–8.0, and the sequence of reactions has been rationalized in an indentical way. The application of Marcus cross-reaction relations for the calculated rate constants of $\mathrm{Ni^{IV}}$ species shows a reasonable agreement to the experimental values but those for the nickel(III) complexes exhibit considerable deviations. This may be a consequence of strong hydrogen-bonded precursor complex formation between $[Ni^{III}(HL^1)]^{2+}$ and $[Co(edta)]^{2-}$.

The stereospecific synthesis of a nickel(IV) derivative, $[Ni^{IV}((s)\text{-}Me_2L^{13})]^{2+}$ where (s)-$Me_2H_2L^{13}$ = (5*S*, 12*S*)-4,7,10,13-tetraaza-3,5,12,14-tetramethylhexadeca-3,13-diene-2,15-dione dioxime and its comparison with those of the partially resolved $[Ni^{IV}L^1]^{2+}$ complex suggest the same amount of stereospecificity in the reduction of nickel(IV) and nickel(III). This shows that the stereoselectivity is determined mainly by the chirality of the participating reagents and not by the strength of precursor complex formation.

Macartney and McAuley [45] have reported the redox interaction of $[Ni^{IV}L^1]^{2+}$ by Fe^{2+}, VO^{2+} and $[Ni(cyclam)]^{2+}$. The reduction by Fe^{2+} shows no hydrogen ion dependence in the acidity range, $[H^+] = 0.2\text{–}1.0\ \text{mol dm}^{-3}$ but in the region pH 2.0–5.1, the rate constant shows an increasing trend with pH, and has been rationalized with the equilibrium

$$[Fe(H_2O)_6]^{2+} \Leftrightarrow [Fe(H_2O)_5(OH)]^+ + H^+. \tag{48}$$

Addition of SO_4^{2-} ion has a positive effect on the observed rate constant owing to the possible formation of a reactive $FeSO_4$ species. The oxidations of VO^{2+} and $[Ni^{II}(cyclam)]^{2+}$ by $[Ni^{IV}L^1]^{2+}$ produce vanadium(V) and nickel(III) intermediates, respectively, and the observed second-order rate constants increase with increase in pH. A general mechanism has been proposed:

$$[Ni^{IV}L^1]^{2+} + M^{n+} \rightarrow [Ni^{III}L^1]^+ + M^{(n+1)+}, \tag{49}$$

$$[Ni^{III}L^1]^+ + M^{n+} + 2H^+ \rightarrow [Ni^{II}(H_2L^1)]^{2+} + M^{(n+1)+}. \tag{50}$$

Assuming an outer-sphere path the calculated self-exchange rate constant turns out to be $6 \times 10^4\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ for the $[Ni^{IV/III}]^{2+/+}$ couple.

A kinetic and mechanistic investigation on the oxidation of catechol, hydroquinone and 2-methyl hydroquinone by $[Ni^{IV}L^1]^{2+}$ in the range pH 3.5–6.0 at 25 °C has been carried out by Macartney and McAuley [46]. Below pH 4.5 the reaction is monophasic with $Ni^{IV} \rightarrow Ni^{III}$ reduction followed by a slower reduction of the nickel(III) intermediate. The following scheme of mechanistic route is suggested in the range pH 3.5–6.0.

$$H_2Q \Leftrightarrow H^+ + HQ^-, \tag{51}$$

$$[Ni^{IV}L^1]^{2+} + H_2Q \rightarrow [Ni^{III}L^1]^+ + H_2\dot{Q}^+, \tag{52}$$

$$[Ni^{IV}L^1]^{2+} + HQ^- \rightarrow [Ni^{III}L^1]^+ + H\dot{Q}. \tag{53}$$

H_2Q is the abbreviated form of the reductants. The reduction of the Ni^{III} species (at pH > 4.5) follows the sequence

$$[\mathrm{Ni^{III}(HL^1)}]^{2+} \Leftrightarrow [\mathrm{Ni^{III}L^1}]^{+} + \mathrm{H^+}, \tag{54}$$

$$[\mathrm{Ni^{III}(HL^1)}]^{2+} + \mathrm{H_2Q} \rightarrow [\mathrm{Ni^{II}(HL^1)}]^{+} + \mathrm{H_2\dot{Q}^+}, \tag{55}$$

$$[\mathrm{Ni^{III}(HL^1)}]^{2+} + \mathrm{HQ^-} \rightarrow [\mathrm{Ni^{II}(HL^1)}]^{+} + \mathrm{S\dot{Q}}, \tag{56}$$

$$[\mathrm{Ni^{III}L^1}]^{+} + \mathrm{H_2Q} \rightarrow [\mathrm{Ni^{II}L^1}] + \mathrm{H_2\dot{Q}^+}, \tag{57}$$

$$[\mathrm{Ni^{III}L^1}]^{+} + \mathrm{HQ^-} \rightarrow [\mathrm{Ni^{II}L^1}] + \mathrm{S\dot{Q}} \tag{58}$$

From calculations involving the Marcus cross-reaction relation, a prediction for outer-sphere route has been made observing a reasonable agreement within an order of magnitude in most cases between the experimental and calculated values of rate constants. The discrepancies may be due to uncertainities in the reduction potentials and self-exchange parameters of the species involved. The same study reported by Lappin et al. [47] in the range pH 3.5–6.5 concludes the nickel(IV) reactions to be outer-sphere whereas those of nickel(III) seem to follow the inner-sphere path. It is proposed that a Ni–N (oxime) bond is broken to facilitate electron transfer specially in the case of $[\mathrm{Ni^{III}(HL^1)}]^{2+}$ species. Deviations of the self-exchange parameters from those calculated theoretically from the cross-reactions with $[\mathrm{Co(phen)_3}]^{2+}$ and other outer-sphere reagents is an additional support to justify the inner-sphere route. The kinetic studies of the reduction of $[\mathrm{Ni^{IV}L^1}]^{2+}$ by $[\mathrm{Cu^I(dpsmp)_2}]^{3-}$, where $\mathrm{dpsmp^{2-}}$ is diphenyl-sulfonated derivative of 2,9-dimethyl-1,10-phenanthroline, over the range pH 3.0–7.3 by Lappin et al. [48] show a monophasic absorbance change throughout, and the rate-determining step is attributed to the reduction of nickel(III) complex. The strong pH dependence owes its origin to the protic equilibrium Eq. (54). Previous indications that a structural barrier to electron transfer might reduce the self-exchange efficiency of the copper(II) species compared with copper(I) are shown to be invalid from the results.

The kinetics of the reduction of $[\mathrm{Ni^{IV}L^1}]^{2+}$ by organic radicals, $\mathrm{H_2\dot{C}OH}$, $\mathrm{\dot{C}O_2^-}$, $\mathrm{(CH_3)H\dot{C}OH}$, $\mathrm{(CH_3)_2\dot{C}OH}$, in aqueous solution have been measured by Baral and Lappin [49] using pulse radiolysis technique. The overall second-order rate constants are independent of pH in the range 2.2–4.1. Spectral evidence has been accumulated to show that the electron is transferred to the metal centre producing a nickel(III) intermediate.

The kinetics of the reduction of $[\mathrm{Ni^{IV}L^1}]^{2+}$ by $[\mathrm{Ni^{II}(H_2L^1)}]^{2+}$ over the range pH 4.0–10.0, and the disproportionation of nickel(III) complex in the range pH 1.0–4.0 have been undertaken [50]. The nickel(III) intermediates are thermodynamically stable above pH 5.0. When $[\mathrm{Ni^{III}L^1}]^{+}$ is acidified (pH < 4.0), the visible spectrum changes to that of $[\mathrm{Ni^{III}(HL^1)}]^{2+}$ and disproportionation to $[\mathrm{Ni^{IV}L^1}]^{2+}$ and $[\mathrm{Ni^{II}(H_2L^1)}]^{2+}$ takes place. At a very low pH, where the concentration of $[\mathrm{Ni^{III}L^1}]^{+}$ is very small, disproportionation of $[\mathrm{Ni^{III}(HL^1)}]^{2+}$ though thermodynamically favored, is slow. The reduction of $[\mathrm{Ni^{IV}L^1}]^{2+}$ by $[\mathrm{Ni^{II}L^1}]$ follows the equation

$$\mathrm{Ni^{IV}} + \mathrm{Ni^{II}} \Leftrightarrow 2\mathrm{Ni^{III}}. \tag{59}$$

From Marcus cross-reaction treatment of kinetic data it can be predicted that the ratio of reaction rates of these two complexes k$[Ni^{IV}L^1]^{2+}$ / k$[Ni^{III}(HL^1)]^{2+}$ by a common reductant should be independent of the reductant and equal to the square root of the ratio of the respective self-exchange rates, $\sqrt{(4\times10^4/4\times10^2)}=10$. In this work the ratio varies between 7.8 and 10.1 showing a good evidence for the outer-sphere route.

A careful strategy in preventing racemization by a self-exchange electron transfer pathway involves the use of chiral ligands which complex with metal ions in a stereospecific fashion. This has been utilized [51] in the reduction of $[Ni^{IV}L^1]^{2+}$ and a chiral analogue of it i.e. $[\Lambda\text{-}Ni^{IV}((S)\text{-}Me_2L^{13})]^{2+}$ [where (S)-$Me_2(H_2L^{13})$ = (5*S*,12*S*)-4,7,10,13-tetraaza-3,5,12,14-tetramethylhexadeca-3,13,-diene-2,15-dione dioxime] by $[Co(pdta)]^{2-}$ and $[Co(cdta)]^{2-}$ [where H_2pdta^{2-} = 1,2-diaminopropane-*N*,*N*,*N′*,*N′* tetraacetate and H_2cdta^{2-} = 1,2-diaminocyclo hexane-*N*,*N*,*N′*,*N′*-tetraacetate]. A detailed picture of the electron transfer which involves the formation of a precursor complex has been drawn. These studies reflect that orientation restrictions in outer-sphere electron transfer reactions can be significant. Lappin et al. [52] have reported the oxidation reactions of $[Co(phen)_3]^{2+}$, $[Co(bpy)_3]^{2+}$, $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ by $[Ni^{IV}L^1]^{2+}$ and its substituted methyl and benzyl derivatives. Consideration of the reaction rates and comparison with those calculated from Marcus theory lead to the conclusion that the electron transfers are outer sphere in nature. Stereoselectivity experiments involving the optically active nickel(IV) complexes with $[Co(phen)_3]^{2+}$ show the formation of $[\Lambda\text{-}Co(phen)_3]^{3+}$ having optical purities 19–36%. The magnitude of stereoselectivity indicates an intimate interaction between the reactants which are both cationic species. The dependence on structure, however, owes its origin to hydrophobic interactions and to the multiplicity of orientations of the complexes.

Rate studies on the reduction of $[Ni^{IV}L^{12}_2]^{2+}$ by $[Co(phen)_3]^{2+}$, hydroquinone and catechol in the range pH 4–7.2 have been measured by McAuley et al. [34]. Both monophasic and biphasic reaction traces depending on pH have been noted and the kinetic parameters evaluated as done earlier [43]. Applications of Marcus theory shows the outer-sphere nature of the reactions with $[Co(phen)_3]^{2+}$ allowing the determination of self-exchange rate constants for the different oxidant species as

Couples	Self-exchange rate constants ($dm^3\ mol^{-1}\ s^{-1}$)
$[Ni^{IV}L^{12}_2]^{2+}-[Ni^{III}L^{12}_2]^{+}$	$(8\pm3)\times10^4$
$[Ni^{III}L^{12}_2]^{+}-[Ni^{II}L^{12}_2]^{0}$	$(8\pm4)\times10^3$
$[Ni^{III}(L^{12})(HL^{12})]^{2+}-[Ni^{II}(L^{12})(HL^{12})]^{+}$	5×10^2

For hydroquinone and catechol these calculations show that although the $Ni^{IV}\rightarrow Ni^{III}$ reduction is outer-sphere in nature, the corresponding $Ni^{III}\rightarrow Ni^{II}$ process involves an inner-sphere route which might be substitution controlled. An important piece of work involves the determination of the self-exchange rate for the couple $[Ni^{IV/III}L^1]^{2+/+}$ ($k_{ex}=2.4\times10^4\ dm^3\ mol^{-1}\ s^{-1}$) by Lappin et al. [53] making use of ^1H NMR line broadening method.

The oxidation of ascorbic acid (H_2A) by $[Ni^{IV}L_2^{12}]^{2+}$ in the range pH 2.5–8.2 at 30 °C has been reported [35]. The monophasic reaction trace throughout the whole region of pH is ascribed to the reduction of $[Ni^{III}L_2^{12}]^{+}$ to nickel(II); the reduction of $[Ni^{IV}L_2^{12}]^{2+}$ is too fast to measure within the time scale of the stopped-flow. Marcus cross-relation calculations show that although the reduction with bivalent ascorbate anion (A^{2-}) occurs through an outer-sphere route, the protonated species,H_2A and HA^- follow mainly the inner-sphere pathway.

The reactions of $[Ni^{IV}L_2^{12}]^{2+}$ and $[Ni^{IV}L^1]^{2+}$ with sulfite have been investigated thoroughly by Banerjee et al. [54] over the range pH 2.0–8.0. Single-step two-electron transfer reactions are encountered in the regions $2.0 \leqslant pH \leqslant 5.5$ for $[Ni^{IV}L_2^{12}]^{2+}$ and $2.0 \leqslant pH \leqslant 4.25$ for $[Ni^{IV}L^1]^{2+}$ reductions. A distinct biphasic process with faster initial one-electron reduction of Ni^{IV} to Ni^{III} followed by a slower conversion of Ni^{III} into Ni^{II} was observed above pH 5.75 and 4.50 for the respective complexes. With an excess of sulfite over the complex, the product of oxidation is dithionate. The reactivity of the different sulfur(IV) species towards a particular nickel(IV) and nickel(III) complexes have been extracted from appropriate rate equations. For the $[Ni^{IV}L_x] \rightarrow [Ni^{III}L_x]$ reduction(where $x = 1,2$ for H_2L^1 and HL^{12}, respectively), the reactivity order follows the general trend, $SO_2 \cdot H_2O < HSO_3^- < SO_3^{2-}$, and this is also valid for $[Ni^{III}L^1]^+ \rightarrow [Ni^{II}L^1]$ and $[Ni^{III}(HL^1)]^{2+} \rightarrow [Ni^{II}(HL^1)]^+$. However, the trend $HSO_3^- > SO_3^{2-}$ is at variance with the general picture of reactivity in the case of $[Ni^{III}L_2^{12}]^{2+}$ and $[Ni^{III}L^{12}(HL^{12})]^{2+}$. A logical interpretation is that the reactions proceed through the initial formation of a hydrogen-bonded adduct (Eq. (60)). This hydrogen bonded adduct is likely to be formed through the oximato oxygen of the ligand and the proton of HSO_3^-.

The intermediate(II) (Eq. (61)) may be of the outer-sphere type formed through strong electrostatic attraction between the two oppositely charged species, as there is no possibility of hydrogen bonding. Application of Marcus cross-reaction relationship shows that the calculated rate constants for the oxidation of SO_3^{2-} by various nickel(IV) and nickel(III) species are one or two orders of magnitude lower than the corresponding experimental values. It seems that differences of this order of magnitude are not unusual for the simplified cross-relation adopted here.

$$[Ni^{III}L_2^{12}]^+ + HSO_3^- \Leftrightarrow I \rightarrow \text{products}, \tag{60}$$

$$[Ni^{III}L_2^{12}]^+ + SO_3^{2-} \Leftrightarrow II \rightarrow \text{products}, \tag{61}$$

The oxidation of thiosulfate [55] and azide [56] by $[Ni^{IV}L_2^{12}]^{2+}$ and $[Ni^{IV}L^1]^{2+}$ reported by the same group also shows identical pH dependent phase separation of the reactions. An "outside" protonation is revealed from the pH-rate profile [pK_H $[Ni^{IV}L_2^{12} \cdots H]^{3+}$, 6.0 ± 0.6 and pK_H $[Ni^{IV}L^1 \cdots H]^{3+}$, 5.2 ± 0.5]. The kinetically extracted constants agree reasonably with those obtained by pH-metric titrations. Marcus cross-relation calculations indicate that the reduction of $[Ni^{IV}L_x]^{2+} \rightarrow [Ni^{III}L_x]^+$ follows an outer-sphere route whereas $[Ni^{III}L_x]^+$ and $[Ni^{III}(HL_x)]^{2+}$ complexes may follow inner-sphere paths.These "outside" protonated nickel(IV) species need not ensue any adjustment in the inner coordination sphere.

A partial unwrapping of one of the N_6-coordinated atoms and the relatively labile axial site in nickel(III) could facilitate the transient inner-sphere coordination. There is, however, no such experimental evidence for delineation of the two paths.

A very recent study concerns the oxidation of thiourea and its N-substituted derivatives by $[Ni^{IV}L_2^{12}]^{2+}$ [57]. Reactions conducted at $2.0 \leqslant pH \leqslant 5.0$ do not correspond to a pseudo-first-order monophasic $2e^-$ transfer path as observed with other reductants. Rather the semilog plots of absorbance versus time indicate an autocatalytic phenomenon showing an induction phase (slowing down during this period) and then picks up speed (a rapid change in absorbance with time). The following two-component processes Eqs. (62) and (63) are considered to explain the autocatalysis, a special feature [58,59] of the thiourea reagents:

$$\mathrm{CSSC} + 2\mathrm{H_2O} \rightarrow 2\mathrm{CSOH} + 2\mathrm{H^+} + 2\mathrm{e^-}, \tag{62}$$

$$\mathrm{CSOH} + \mathrm{TU} \rightarrow \mathrm{CSSC} + \mathrm{H_2O}. \tag{63}$$

where CSSC is $HN{=}C(NH_2)\text{-}S\text{-}S\text{-}(NH_2)C{=}NH$, CSOH is $NH{=}C(NH_2)\text{-}S\text{-}OH$, and TU is thiourea. Making the combination Eqs. (62) and (63) the overall process is now autocatalytic in CSSC.

$$CSSC + 2TU \rightarrow 2CSSC + 2H^+ + 2\mathrm{e}^- \tag{64}$$

Of course, the important intermediate in this scheme is CSOH which is yet to be identified in the Ni^{IV}-thiourea reaction and need to be addressed in detail separately. A distinct biphasic $1e^-$ transfer reduction of the Ni^{IV} complex is observed at $pH \geqslant 6.0$, of which the Ni^{IV}–Ni^{III} reduction step is faster, followed by a slower reduction for the Ni^{III}–Ni^{II} step. In combination with previously determined [55] "outside" protonation constant of the $[NI^{IV}L_2^{12}]^{2+}$ complex, the rate parameters have been computed. The proposition of an inner-sphere process, specially for the Ni^{III} species, gains support from a comparison of the electron transfer rate and the lability of the metal centre of Ni^{III} complexes.

3.2. Reactions of oxime complexes

The synthesis, characterization as well as a number of kinetic studies on tris(dimethylglyoximato)nickelate(IV) have been reported by Panda et al. during 1982–84. The potassium salt of the complex, $K_2[Ni(dmg)_3]$ has been prepared [60] by a modification of the procedure laid down by Simek [61]. Electronic, IR and ^1H NMR spectra are in conformity with an octahedral geometry of this compound with dmg^{2-} units bonded through nitrogen donors. The formation of $[Ni(dmg)_3]^{2-}$ from Ni^{II} and dmg^{2-} in the presence of hypoiodite generated in situ from tri-iodide and hydroxide ions, exhibits pseudo-first order kinetics. The rate constants of formation (k_{obs}) exhibit a linear dependence on the [oxidant] and at $[OH^-] = 4.8 \times 10^{-2}\,mol\,dm^{-3}$, but attain a saturation in rate at relatively higher $[dmg^{2-}]$. The k_{obs} values remain constant in the range $[OH^-]$, 0.105–$1.1 \times 10^{-2}\,mol\,dm^{-3}$ showing, however, a decreasing tendency at further lowering of [OH$^-$]. Since no [Ni(dmg)$_2$] is formed under the conditions employed, an alternative mechanism of formation which differs from that proposed by Simek [61] has been suggested. This takes into account: (1) the above kinetic behaviours; (2) the formation of [Ni(dmg)$_3$]$^{2-}$ from Ni$^{\text{II}}$ involving two basically different processes of ligation of the dmg^{2-} units to the central nickel; and (3) the oxidation of Ni$^{\text{II}}$ to Ni$^{\text{IV}}$.

An investigation [62] on the proton-assisted decomposition of the [Ni(dmg)$_3$]$^{2-}$, with concerted intramolecular electron transfer forming bis(dimethylglyoximato)nickel(II) and /or hexaaquanickel(II), was reported. The pseudo-first-order rate constants (k_{ad}) are given by

$$k_{\text{ad}}=\frac{k_{0\text{d}}+k_{1\text{d}}K_{1\text{H}}[\text{H}^+]+k_{2\text{d}}K_{1\text{H}}K_{2\text{H}}[\text{H}^+]^2}{1+K_{1\text{H}}[\text{H}^+]+K_{1\text{H}}K_{2\text{H}}[\text{H}^+]^2},$$

where, $k_{0\text{d}}$, $k_{1\text{d}}$ and $k_{2\text{d}}$ denote the solvent-assisted, first proton-assisted and second proton-assisted paths of decomposition, and $K_{1\text{H}}$ and $K_{2\text{H}}$ are the first and second proton equilibrium constants of [Ni(dmg)$_3$]$^{2-}$, respectively. In devising the reaction scheme, it has been assumed that the first (outside) protonation occurs at dioximato oxygens of two ligands, and that rupture of a metal–nitrogen (ligand) bond is not involved. The cleavage of a Ni–N bond is considered as the rate-determining step which may lead to ring-opening with a simultaneous intramolecular or a subsequent very rapid electron transfer from the ligand to the central Ni$^{\text{IV}}$ and dissociation. It may be mentioned here that this type of outside protonation to form an intramolecular hydrogen bond has also been considered by Banerjee et al. [55] in the case of nickel(IV) oxime–imine complexes, and demonstrated by both kinetic and pH-metric studies.

The proton-assisted decomposition of this complex [63] is significantly influenced by the presence of added metal ions (e.g. Cu$^{\text{II}}$, Zn$^{\text{II}}$ and Ni$^{\text{II}}$). The reactions proceed via equilibrium formation of 1:1 adducts involving the protonated Ni$^{\text{IV}}$ complex and the aqua metal ions which may be ligated to the ring-opened or the dioximato oxygen end. While the rate-determining steps in the reactions with Cu$^{\text{II}}$ are envisaged to involve acid decomposition of the adduct in addition to the proton-assisted decomposition of the Ni$^{\text{IV}}$ complex, those in the reactions with Zn$^{\text{II}}$ and Ni$^{\text{II}}$ proceed essentially by routes parallel to the proton-assisted path. The mechanistic picture gets support from kinetic and spectrophotometric titration data. But the unambiguous assignment of the protonation or initial M$^{\text{II}}$ coordination site is difficult to resolve since repeated attempts to record the ^{13}C NMR spectra of the Ni$^{\text{IV}}$ complex at various pH were not successful.

The kinetics of electron transfer from L-ascorbic acid (H$_2$A) to [Ni(dmg)$_3$]$^-$ [64] follows a pseudo-first-order decay of the Ni$^{\text{IV}}$ complex conforming to a rate law, $k_{\text{obs}}=k_{\text{d}}+k_{\text{r}}$ where k_{d} is the pseudo-first-order rate constant for the independently determined proton-assisted decomposition of the complex and k_{r}, that for the reduction of Ni$^{\text{IV}}$ by H$_2$A. In the range pH 1.6–12.3, the decomposition rate is ca. 10^{-7} s^{-1} but those for the redox reaction it varies from 510–8 dm^3 mol^{-1} s^{-1} (pH range 1.6–11.1). The reaction scheme takes into account the probable interactions of the acid ascorbate anion (HA^-) and ascorbic acid (H_2A) with the different protonated and deprotonated nickel(IV) species. The reactivity of A^{2-} has been assumed to be negligible. The rate-determining step is considered to be an outer-sphere one-electron transfer from the reducing substrate to the oxidizing Ni^{IV} species followed by a kinetically indistinguishable rapid reduction of the Ni^{III} intermediate, the presence of which has been established through EPR measurement. This also discounts the possibility of a single-step $2e^-$ redox process. The pH dependent redox potentials of the various nickel couples derived from $[Ni(dmg)_3]^{2-}$ could not be determined owing to decomposition and no test for the validity of Marcus relation has been attempted.Data on the proton-assisted decomposition of the nickel(IV) complex suggested [62] that the first (outside) protonation of the complex occurs at a dioximate oxygen forming an intramolecular hydrogen-bonding network between dioximate oxygen of two ligands and during this process there is a little change in the pseudo-octahedral structure. Thus a contribution from an inner-sphere path is unlikely.

The kinetics of the oxidation of hydrazine and *t*-butylhydrazine [65] using $[Ni(dmg)_3]^{2-}$ in the presence of added Cu^{II} and in the range pH 5.0–7.0 follow pseudo-first-order and pseudo-zero-order dependence on the Ni^{IV} complex, respectively. The Cu^{II} promoted oxidation is governed by pH dependent equilibrium interactions of various species of Ni^{IV} with 1:1 intermediate complex of Cu^{II} and hydrazine to form adducts. A proton-coupled electron transfer from the reductant species to the latter may constitute the rate-controlling step(s). An intermediate 1:1 complex between the Cu^{II} and *t*-butylhydrazine is involved in the corresponding oxidation of *t*-butylhydrazine. The data for the oxidation of phenylhydrazine [66,67] by $[Ni(dmg)_3]^{2-}$ are insufficient to unequivocally establish whether electron transfer in the rate-determining step(s) proceeds by formation and decomposition of a precursor intermediate or by two successive $1e^-$ steps. An outer-sphere direct electron transfer from the phenylhydrazine and phenylhydrazinium cation to the deprotonated and monoprotonated nickel(IV) species is postulated. In the presence of catalytic amounts of added Cu^{II}, the kinetics exhibit a pseudo-zero-order disappearance of Ni^{IV} with an excess of phenylhydrazine. The oxidation of hydroxylamine [68] by this Ni^{IV} complex also shows a pseudo-zero-order dependence on the [oxidant] both in the presence and absence of Cu^{II}. A qualitative explanation for the differential behaviour of the observed kinetics and envisaged mechanistic routes in the above oxidations of hydrazine and related substrates is sought. It takes into account the significant Cu^I character of the $Cu^{II}Y_n$ ($Y=NH_2OH$, $n=1$, 2 or 4) which decomposes readily in aqueous solutions to Cu^I and oxidation products of hydroxylamine. On the other hand $[Cu^{II}(N_2H_4)_n]$($n=1, 2$) complexes do not have the successor character, and also decompose with accompanying electron transfer so easily to the Cu^I species. The first-order decay of the oxidant (Ni^{IV}) is thereby exhibited in the related oxidation process. This view gets support from the fact that the stability of the metal-ion complexes of hydrazine derivatives decreases [69] in general with steric crowding and particularly with substituents having electron-releasing property. This could make the oxidation of the reduced metal ion (Cu^I)

species or the intermediate products of oxidation of Y by $[Ni(dmg)_3]^{2-}$ facile, ultimately leading to a zero-order dependence on $[Ni^{IV}]$.

The kinetics of electron transfer between hexacyanoferrate(II) and $[Ni(dmg)_3]^{2-}$ to produce $[Fe(CN)_6]^{3-}$ and $[Ni(dmgH)_2]$ follows a pseudo-first-order disappearance of Ni^{IV} [70]. The results are interpreted in terms of a probable mechanism involving rate-determining outer-sphere electron transfer steps:

$$[Ni(dmg)_3]^{2-} + H^+ \Leftrightarrow [Ni(dmg)_3(H)]^-, \tag{66}$$

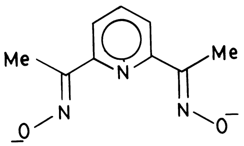
$$[Fe(CN)_6]^{4-} + H^+ \Leftrightarrow [HFe(CN)_6]^{3-}, \tag{67}$$

$$[Ni(dmg)_3]^{2-} + [Fe(CN)_6]^{4-} \rightarrow \text{products}, \tag{68}$$

$$[Ni(dmg)_3(H)]^- + [Fe(CN)_6]^{4-} \rightarrow \text{products}, \tag{69}$$

$$[Ni(dmg)_3(H)]^- + [HFe(CN)_6]^{3-} \rightarrow \text{products}. \tag{70}$$

The protonated reductant species apparently reacts ca. five orders of magnitude faster than the unprotonated one, and is explained on the basis of an enhanced electrophilicity of $[HFe(CN)_6]^{3-}$ over that of $[Fe(CN)_6]^{4-}$. The reaction of an intermediate nickel(III) species with the reductant has been considered to be faster than the outer-sphere route involving the nickel(IV) complex which seems reasonable from a comparison of redox potential magnitudes of the corresponding nickel oxime–imine couples reported elsewhere [2]. Reduction of the complex $[Ni^{IV}(dmg)_3]^{2-}$ by the radical $(CH_3)_2\dot{C}O^-$ has been studied by Baral and Lappin [71] in the pH range 12.5–13.0. The reaction monitored at a variety of wavelengths, is rapid, substantially pH independent and first-order in both $(CH_3)_2\dot{C}O^-$ and $[Ni^{IV}(dmg)_3]^{2-}$ concentrations with a second-order rate constant of $(2.39 \pm 0.15) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ at the high pH limit. It is worthy to note a previously undetected species, presumably $[Ni^{III}(dmg)_3]^{3-}$, in the reaction with absorption maxima at 280 ($\epsilon_{280} = 29\,500\ dm^3\ mol^{-1}\ cm^{-1}$) and 520 nm ($\epsilon_{520} = 3700\ dm^3\ mol^{-1}\ cm^{-1}$). This species is stable on the millisecond time-scale.



(17)

Nickel(IV) complex of the dianion of 2,6-diacetylpyridine dioxime (**17**) is substantially more stable in solution at low pH values than the corresponding chelates of this type and its detailed structure [72] has been reported. The nickel(III) analogue although preparable [73] with special care, has been found to be much less accessible than the nickel(II) and nickel(IV) complexes [74,73]. The nickel(IV) complex is reduced clearly to nickel(II) by aqueous solutions of Fe^{II}, Sn^{II}, I^- and U^{IV}, but reacts unusually slowly with $2e^-$ reductants like H_3PO_2 and H_3AsO_3 [75]. No evidence for the accumulation of intermediate Ni^{III} has been obtained even with the oxidant in large excess. Rate laws for the reductions by Fe^{II}, Sn^{II} and I^- involve prominent $[H^+]$ dependent terms which indicate the involvement of an unusually reactive chloro-substituted reductant. In the reactions with U^{IV} at $H^+ < 0.002$ mol dm^{-3}, catalysis by $[UO_2]^{2+}$ is noted. A sequence of reactions have been proposed whereby the reactive intermediate, a U^V species, may follow one of the two competing pathways. (1) reduction of Ni^{IV}; or (2) reversible disproportionation to U^{VI} and U^{IV}. These results point to the view that the conversions of Ni^{IV} to Ni^{II}, a net $2e^-$ process, must involve pairs of $1e^-$ steps. The relatively slow reduction by Sn^{II} appears to be initiated by the formation of a stable chloride bridged Sn^{III} species supporting the above view. It is noteworthy that although Sn(II) stands out to be a $2e^-$ donor, evidence has been gathered that even strong oxidants having Co(III) and Cr(VI) centers can remove a single electron. Such transactions should be favoured by the absence of bridging functions, since transfer of two oxidation units cannot proceed by a simple outer-sphere path. The presence of a chloride bridging here leads to a net single $2e^-$ transfer step without the involvement of any nickel(III) intermediate. The protonation equilibrium associated with the $[H^+]$ dependent paths has been proposed to involve the monoprotonated and diprotonated forms of the complex; the $[H^+]^2$ term originates from the contribution of a highly reactive triprotonated cation. No evidence for such protonation equilibria or proton dependent redox potential measurements have been gathered.

The reduction of this nickel(IV) complex by hydroxylamine [76] is catalysed by dissolved Fe^{III}, and in a modest way by Cu^{II}. The consumption of Ni^{IV} may be represented as a competition between Eqs. (71) and (72):

$$Ni^{IV} + 2NH_3OH^+ \rightarrow Ni^{II} + N_2 + 2H_2O + 4H^+, \tag{71}$$

$$2Ni^{IV} + 2NH_3OH^+ \rightarrow 2Ni^{II} + N_2O + H_2O + 6H^+, \tag{72}$$

with Eq. (72) showing relatively less predominance at high concentration of the reductant. Under the kinetic conditions, with large excess of NH_3OH^+, reaction Eq. (71) is relevant. The mechanistic sequence has been framed by noting the progressive changes in the nature of the decay profiles. During the early stages of reactions, rates are determined principally by formation of the active catalytic species (Fe^{II}), which then reacts rapidly with Ni^{IV} converting 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 approaches near to completion. The present study reminds us why iron and copper function as active catalysts for a number of additional oxidations of hydroxylamine [77,78]. For a $1e^-$ reductant (e.g. hydroxylamine) any nickel(III) intermediate formed is reduced much more rapidly than that of the nickel(IV) oxidant and therefore remains kinetically silent.

3.3. Reactions of miscellaneous species

A hydrated oxohydroxonickel(IV) species of the composition $NiO(OH)_2.3H_2O$ has been reported [79]. This is prepared by the persulfate oxidation of a mixture of hexamminenickel(II) sulfate and ammonia. The resulting black mass on treatment with aqueous hydrochloric acid shows oxidizing property but slowly decomposes to a greenish solution of hexaaquanickel(II) and oxygen. The kinetics of this decomposition process have been measured as also the intermolecular electron transfer from dimethyl sulfoxide to the Ni^{IV} producing $[Ni(H_2O)_6]^{2+}$ and dimethyl sulfone as products. We note that this is a poorly characterized oxide of nickel since the ratios of the sample dissolved to the liberated iodine for measuring oxidation equivalence are 64±2% and 43±3% for the granular and powdery samples, respectively. No authentic kinetic results could emerge from this oxidant.

Reports of the use of diperiodatonickelate(IV) (DPN) as an oxidant in alkaline medium are limited primarily to the oxidation of organic substrates. The complex is synthesized following the method of Ray [80]. The formula of DPN is suggested by Kandlikar et al. [81] as $[Ni(OH)_2(H_3IO_6)_2]^{2-}$ but Anzou et al. [82] considers it as $[Ni(OH)_2(H_2IO_6)]^-$. The latter gains considerable support owing to its similarity with the formulation of Mukherjee et al. [83] established through powder X-ray data and other measurements. The oxidations of a number of aliphatic amines to the corresponding aldehydes by DPN have been followed kinetically in the range pH 8–14 [81]. Taking the active form of the complex as $[Ni(OH)_2(H_2IO_6)]^-$ resulting from the loss of a periodate ion at high pH, an electron transfer route has been proposed:

$$[Ni(OH)_2(H_3IO_6)_2]^{2-} + OH^- \overset{K_1}{\Leftrightarrow} [Ni(OH)_2(H_2IO_6)(H_3IO_6)]^{3-} + H_2O, \quad (73)$$

$$[Ni(OH)_2(H_2IO_6)(H_3IO_6)]^{3-} \overset{K_2}{\Leftrightarrow} [Ni(OH)_2(H_2IO_6)]^- + H_3IO_6^{2-}, \quad (74)$$

$$RCH_2NH_2 + [Ni(OH)_2(H_2IO_6)]^- \xrightarrow{\text{slow}} RCH{=}NH + H_2O + Ni(II)$$
$$+ H_3IO_6^{2-} + OH^-, \quad (75)$$

$$RCH{=}NH \xrightarrow[\text{fast}]{H_2O} R{-}CHO + NH_3. \quad (76)$$

Since there is no rate saturation at higher substrate concentrations, it is concluded that the electron transfer follows an outer-sphere path. Other evidences ought to be sought for such generalization. As an extension to this work oxidation reactions of several aliphatic aldehydes and cyclic ketones have been reported [84,85].

A single report [86] on the oxidation of an inorganic substrate is that of the phosphite ion (HPO_3^{2-}) by DPN in alkaline medium. A reactive dihydroxymonoperiodatonickelate(IV) complex of lower steric hindrance is considered as:

$$[Ni(OH)_2(H_2IO_6)_2]^{4-} + OH^- \Leftrightarrow [Ni(OH)_2(HIO_6)]^{2-} + H_2IO_6^{3-} + H_2O. \quad (77)$$

The dissociative equilibrium is supported by the observation that the electron transfer rate increases with increasing alkalinity and decreases with increase in [periodate]. The intermediate formation of $DPN{-}HPO_3^{2-}$ adduct has been postulated which assumes significance by way of axial substitution at the metal centre in the square plane.

The electron transfer reactions of nonamolybdonickelate(IV), $[NiMo_9O_{32}]^{6-}$ have been included in an earlier review [87]. This heteropoly ion can oxidize aromatic hydrocarbons and arylacetic acids in acetic acid and acetic acid–water media yielding acetates and alcohols [88].

4. Concluding remarks

This review highlights the kinetics and mechanism of electron transfer reactions involving nickel(III) and nickel(IV) complexes. Such results have often been tested with theoretical equations of electron transfer developed by Marcus, Hush and Sutin, and this insight is most valuable in the evaluation of various self-exchange rate parameters of oxidizing and reducing species. It is hoped that this article will stimulate further research on the variable oxidation states of nickel chemistry since this metal had a role in the hydrogen world and would be more important than it is today in multicellular organisms [89].

Acknowledgements

Both SB and BS thank the Council of Scientific and Industrial Research (New Delhi) for the award of research fellowships. PB thanks the said Council for a research project.

Appendix

Note added in proof

In the time period since submission of this article, there have been three more studies on this aspect of electron transfer chemistry. The oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$ (**1**) has been studied in acidic aqueous solution under the conditions $2 \leq -\log[H^+] \leq 5.5$ at ionic strength = 0.1 mol dm^{-3} [90]. The stoichiometry is determined iodometrically as 2:1 ($[Ni^{III}]:[H_2O_2]$). Kinetic measurements with an excess of hydrogen peroxide reveal that HO_2^- is the only redox-active species, the second-order rate-constant for which is $(6.15 \pm 0.06) \times 10^6$ dm^3 mol^{-1} s^{-1} at 25°C. This is ca.10^3 times faster than the predicted rate-constant for other outer-sphere reactions. The kinetic isotope effect ($k_H/k_D = 2.28$) indicates that the reaction of HO_2^- with the metal complex proceeds via a transition state structure in which a specific interaction between HO_2^- and the amino proton on the tacn ligand is operative. This gets support from the fact that the oxidation of HO_2^- by $[Fe(ttcn)_2]^{3+}$ where ttcn = 1,4,7-trithiacyclononane which has a similar structure to that of $[Ni(tacn)_2]^{3+}$ with no labile hydrogen atom occurs via the outer-sphere route. Since the proton exchange on the amino nitrogen atom of tacn is reported to be very fast, it is likely that a proton-coupled electron transfer occurs first followed by a rapid protonation of the amino nitrogen atom of the N-deprotonated conjugate base of $[Ni(tacn)_2]^{2+}$. However, the possibility of other proton-mediated phenomena, i.e., the double exchange or superexchange-type mechanism may not be completely ruled out.

The reductions of $[Ni^{IV}L^{12}{}_2]^{2+}$ and $[Ni^{IV}L^1]^{2+}$ with nitrite have been reported [91] in the range pH 4.5–7.0. At low pH($\leq$4.25), the presence of kinetically active oxy-nitrogen species renders complicacy and erroneous pH dependency on rate is noted. The reduction of $[Ni^{IV}L^{12}{}_2]^{2+}$ involves 2e− transfer single-step path at $4.5 \leq pH \leq 6.0$ and above this, it shows biphasic reduction steps involving Ni^{III} intermediate. On the other hand, the reduction of $[Ni^{IV}L^1]^{2+}$ is biphasic in nature throughout the whole range of pH studied. At a constant pH, the reactions show an overall third-order rate – first-order on $[Ni^{IV}]$ complex and second-order on $[NO_2^-]$, and exhibits a notable dependence on the final Ni^{II}-product complex added externally. The overall order of the reaction then turns to four. The outer-sphere electron transfer route is supported from the predicted ion-pair mechanism whereby a low value of the ion-pair constant is obtained.

The reactions of $[Ni^{IV}L^{12}{}_2]^{2+}$ and $[Ni^{IV}L^1]^{2+}$ with thioglycolic acid have been investigated thoroughly [92] over the range pH 3.0–8.0 using stopped-flow technique. Both the reactions have been proposed to follow the inner-sphere mechanism through the formation of an associated species involving the sulfur atom of the thiol and the metal centre of the oxidants. The observed shift in pK_2 value of thioglycolic acid, the formation of disulfide as the sole oxidation product of thioglycolic acid as well as the rate saturation kinetics found at higher concentrations of thiol support the above view.

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