Kinetic Studies on the Electron Transfer between Azide and Nickel(IV) Oxime Imine Complexes in Aqueous Solution

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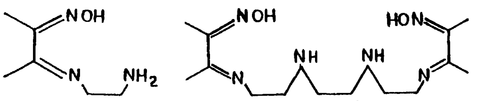
In aqueous solution at 30 °C, azide is oxidized to N_2 by $[Ni^{IV}(L^1)_2]^{2+}$ and $[Ni^{IV}(L^2)]^{2+}$ (where HL^1 = 6-amino-3-methyl-4-azahex-3-en-2-one oxime and H_2L^2 = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime). The reaction is of overall second order, first order in both $[N_3^-]$ and $[Ni^{IV}]$ and exhibits a strong dependence on $[H^+]$ of the medium. In the range $2.0 \leqslant pH < 6.0$ for $[Ni^{IV}(L^1)_2]^{2+}$ and $2.0 \leqslant pH < 4.5$ for $[Ni^{IV}(L^2)]^{2+}$ single step two-electron transfer reactions are encountered, whereas a distinct biphasic process with initial faster step of $Ni^{IV} \rightarrow Ni^{III}$ conversion followed by a second slower step of $Ni^{III} \rightarrow Ni^{II}$ reduction was observed in the range $6.0 \leqslant pH \leqslant 8.0$ and $4.50 \leqslant pH \leqslant 8.0$ for the respective oxidants. The bell-shaped pH-rate profile for the reduction of Ni(IV) → Ni(III) step confirms the involvement of an 'outside' protonated Ni(IV)-complex as a kinetic intermediate. All the kinetic parameters have been evaluated and the mechanism of the reaction is discussed. Application of Marcus cross-reaction relations shows that the reaction of $[Ni^{IV}(L_x)]^{2+}$ and N_3^- follows an outer-sphere mechanism, but the reduction of $[Ni^{III}(L_x)]^+$ may differ from this path.

Prior reports have developed an understanding of the oxidation reactions of azide with simple inorganic substrates like nitrite,[1] permanganate,[2] bromate,[3] HSO_5^-,[4] ozone,[5] or chromium(II)[6] where N_2 was one of the main products. Also a number of substitution reactions of azide with copper–zinc superoxide dismutase,[7] $[Ru(edta)H_2O]^-$,[8] $Fe^{III}(aq)$,[9] $[Ru^{III}(hedtra)H_2O]$[10] are known, despite the high thermodynamic instability of hydrazoic acid and azide ion ($E^\circ = -3.4$ and -3.1 V vs. NHE for the N_2/N_3^- and N_2/HN_3 couples respectively).[11] The chemistry of azide has been reviewed extensively[12—15] and the oxidation of azide by Co(III),[16] Mn(III),[17] Ce(IV),[18] Ag(III),[19,20] Cu(III),[20] $[Ni(bpy)_3]^{3+}$,[21] $[IrCl_6]^{2-}$,[22] $[IrBr_6]^{2-}$,[22] $[Fe(bpy)_3]^{3+}$,[22] and ClO_2[23] have been examined thoroughly. In the cases of aquametal cations of Co(III), Mn(III), Ce(IV), and Ag(III), the kinetic and spectral evidence clearly indicate the substitution in the coordination spheres of the metal ions leading to the formation of azido (or hydrazido) complexes as intermediates. This is the situation with Cu(III) and Ag(III)–tellurate complexes[20] as well. On the other hand, the reactions of $[Ni(bpy)_3]^{3+}$, $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, $[Fe(bpy)_3]^{3+}$, and ClO_2 with azide are clearly outer-sphere in nature, assuring the fact that, although N_3^- has its unpaired electrons in a nonbonding orbital, it reacts with activation controlled 'Marcusian' kinetics.

In an attempt to investigate the kinetic behavior of tetravalent nickel towards simple nonmetallic inorganic reagents, redox studies on the interaction of two nickel(IV) complexes derived from ligands : HL^1(I) and H_2L^2(II) (where HL^1 and H_2L^2 are 6-amino-3-methyl-4-azahex-3-en-2-one oxime and 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) with azide have been carried out. These nickel(IV) complexes, $[Ni^{IV}(L^1)_2](ClO_4)_2$ and $[Ni^{IV}(L^2)](ClO_4)_2$ have been found to be moderate oxidizing agents in aqueous solution. Based on the cyclic voltammetric studies[24] at different pH values, the following redox couples are appropriate :



HL^1 (I) H_2L^2 (II)

Chart 1.

$$[Ni^{IV}(L_x)]^{2+} + e^- \rightleftharpoons [Ni^{III}(L_x)]^+ \tag{1}$$

$$E^\circ([Ni^{IV}(L^1)_2]^{2+}) = 0.63 \text{ V (vs. NHE)}$$

$$\text{and} \quad E^\circ([Ni^{IV}(L^2)]^{2+}) = 0.654 \text{ V (vs. NHE)}.$$

$$[Ni^{III}(HL_x)]^{2+} \rightleftharpoons [Ni^{III}(L_x)]^+ + H^+ \tag{2}$$

$$pK_H([Ni^{III}(HL^1)(L^1)]^{2+}) = 4.43^{24)}$$

$$\text{and} \quad pK_H([Ni^{III}(HL^2)]^{2+}) = 4.05.^{25)}$$

$$[Ni^{III}(HL_x)]^{2+} + e^- \rightleftharpoons [Ni^{II}(HL_x)]^+ \tag{3}$$

$$E^\circ([Ni^{III}(HL^1)(L^1)]^{2+}) = 0.63 \text{ V (vs. NHE)}$$

$$\text{and} \quad E^\circ([Ni^{III}(HL^2)]^{2+}) = 0.64 \text{ V (vs. NHE)}.$$

$$[Ni^{III}(L_x)]^+ + e^- \rightleftharpoons [Ni^{II}(L_x)] \tag{4}$$

$$E^\circ([Ni^{III}(L^1)_2]^+) = 0.30 \text{ V (vs. NHE)}$$

$$\text{and} \quad E^\circ([Ni^{III}(L^2)]^+) = 0.42 \text{ V (vs. NHE)}.$$

At pH<6.0 for $[Ni^{IV}(L^1)_2]^{2+}$ and pH<5.0 for $[Ni^{IV}(L^2)]^{2+}$, the $[Ni^{III}(L_x)]^+$ is converted to the corresponding nickel(II) complexes in a very fast proton coupled electron transfer step as

$$[\mathrm{Ni}^{\mathrm{III}}(\mathrm{L}_x)] + y[\mathrm{H}^+] + \mathrm{e}^- \rightleftharpoons [\mathrm{Ni}^{\mathrm{II}}(\mathrm{H}_y\mathrm{L}_x)]. \tag{5}$$

For convenience, the charges on the complexes are omitted. When $y=2$, $E°$ are 1.23 and 1.25 V, and with $y=1$, $E°$ are 0.86 and 0.89 V for $[\mathrm{Ni^{III}(L^1)_2}]^+$ and $[\mathrm{Ni^{III}(L^2)}]^+$ complexes respectively. This interesting electrochemical behavior of these complexes has prompted us to investigate their redox behavior towards azide, and to explore the intrinsic mechanism of the reaction in relation to Marcus cross reaction parameters.

Experimental

Reagents and Solutions. The nickel(IV) oxime–imine complexes $[\mathrm{Ni^{IV}(L^1)_2}]^{2+}$ and $[\mathrm{Ni^{IV}(L^2)}]^{2+}$ (hereafter designated in general as $\mathrm{Ni^{IV}}$ or $[\mathrm{Ni^{IV}(L_x)}]^{2+}$ with x=2 for $\mathrm{HL^1}$ and =1 for $\mathrm{H_2L^2}$ unless mentioned otherwise) were prepared, characterized and standardized as reported earlier.[26] Sodium azide of analytical reagent grade was obtained from Aldrich and used without further purification. Solutions of $\mathrm{NaN_3}$ were initially standardized by titration with Ce(IV) in 1.0 mol dm^{-3} $\mathrm{H_2SO_4}$ using Ferroin as indicator. As the azide was found to be 100±2% pure and the concentration of the solutions did not change over several days, for later experiments stock solutions of $\mathrm{NaN_3}$ were prepared according to the weight of $\mathrm{NaN_3}$. Doubly recrystallized sodium perchlorate (Fluka) was used to maintain the ionic strength of the reaction medium. The pH of the reaction solution was adjusted by using AnalaR $\mathrm{HClO_4}$, $\mathrm{CH_3COOH}$–$\mathrm{CH_3COONa}$ and $\mathrm{Na_2HPO_4}$–NaOH buffer as required. All solutions were prepared with doubly distilled water and were purged with argon to minimize formation of nitrogen bubbles.

Analytical Methods. Kinetic experiements were carried out with a Shimadzu UV-vis recording spectrophotometer (UV-2100) equipped with thermostatted cell compartments under conditions at which $[\mathrm{N_3^-}] \gg [\mathrm{Ni^{IV}}]$. The reactions were monitored at 30 °C and I=0.2 mol dm^{-3} through the disappearance of oxidants at 505 nm for $[\mathrm{Ni^{IV}(L^1)_2}]^{2+}$ (ϵ=6100 dm^3 mol^{-1} cm^{-1}) and 500 nm for $[\mathrm{Ni^{IV}(L^2)}]^{2+}$ (ϵ=6300 dm^3 mol^{-1} cm^{-1}). The pH of the solutions was measured at room temperature (ca. 25 °C) with the help of a Systronics digital pH-meter (μ-pH system-361, India) equipped with a salt-bridge and calibrated with standard pH solutions. The measured pH is usually defined in terms of the activity of hydrogen ions and the hydrogen ion concentration was calculated by using the following experimental relationship:[27]

$$[\mathrm{H}^+] = 10^{-[(\mathrm{pH}-0.131)/0.982]}. \tag{6}$$

The reaction temperature was controlled (±0.1 °C) by circulating water from a Haake F3 thermostat around the reservoir of the reaction solutions.

Polymerization Study. The oxidation of azide by both the nickel(IV) complexes proceeds through intermediate radical formation and was tested by the polymerization of acrylonitrile. Two separate solutions of $[\mathrm{Ni^{IV}(L^1)_2}]^{2+}$ and $[\mathrm{Ni^{IV}L^2}]^{2+}$ complexes [ca. 2.0×10^{-3} mol dm^{-3}] were taken, and the pH of these solutions were adjusted to 4.50. The solutions were then degassed with dinitrogen and acrylonitrile (5 ml 20% v/v) was added to both of these solutions at room temperature. Degassed solutions of sodium azide (ca. 0.01 mol dm^{-3}, pH=4.50) were then added separately to the above mixtures. In both the cases, a heavy white precipitate appeared almost immediately. No polymerisation of acrylonitrile was encountered when the complex and the azide solutions were treated separately with acrylonitrile. This observation indicates that the oxidation of azide by nickel(IV) proceeds via the generation of free radicals.

Stoichiometry and Reaction Products. Stoichiometries for the oxidation of azide by the two nickel(IV) complexes were studied by reacting excess amounts of the complexes, $[\mathrm{Ni^{IV}(L_x)^{2+}}]$= (1.0—8.0)$\times10^{-4}$mol dm^{-3} with the fixed concentration of azide, $[\mathrm{N_3^-}]_\mathrm{T}=2.0\times10^{-4}$ mol dm^{-3} at pH 5.0. The unreacted complexes were estimated spectrophotometrically. All these studies (Table 1) reveal a 1 : 2 stoichiometry with respect to both the nickel(IV) complexes. The oxidation product of azide was found to be nitrogen gas and this was confirmed by the method reported earlier.[20] A closed reaction cell containing the reactants and kept at constant temperature (30 °C) was continuously purged with pure and dry argon. The outgoing gas was passed for several hours through a solution of $[\mathrm{Ru(NH_3)_5(H_2O)}]^{2+}$. A red complex was isolated and characterized as $[\mathrm{(NH_3)_5Ru(N_2)Ru(NH_3)_5}]^{4+}$. This indicates that the coordinated $\mathrm{N_2}$ must have been generated by the oxidation of azide ion by $\mathrm{Ni^{IV}}$ complexes. Thus the stoichiometric reaction would in general be given by

$$[\mathrm{Ni^{IV}(L_x)}]^{2+} + 2\mathrm{N_3^-} \rightarrow [\mathrm{Ni^{II}(L_x)}] + 3\mathrm{N_2}. \tag{7}$$

Results

Preliminary kinetic studies showed no indication of the formation of an appreciable amount of thermodynamically stable intermediate for the oxidation of azide by $[\mathrm{Ni^{IV}(L^1)_2}]^{2+}$

Table 1. Stoichiometric Results for the Reaction of Nickel(IV) with $\mathrm{N_3^-}$ at pH=5.0, I=0.20 mol dm^{-3}, and at 25 °C[a)]

Oxidant	$10^4[\mathrm{Ni^{IV}}]_\mathrm{t}$ / mol dm^{-3}	$10^4[\mathrm{N_3^-}]_\mathrm{t}$ / mol dm^{-3}	$10^4[\mathrm{Ni^{IV}}]_\mathrm{c}$ / mol dm^{-3}	$10^4[\mathrm{N_3^-}]_\mathrm{c}$ / mol dm^{-3}	$[\mathrm{Ni^{IV}}]_\mathrm{c}$: $[\mathrm{N_3^-}]_\mathrm{c}$
$[\mathrm{Ni^{IV}(L^1)_2{}^{2+}}]$	2.04	2.0	0.96	2.0	1 : 2.08
	3.78	2.0	1.02	2.0	1 : 1.96
	5.10	2.0	1.04	2.0	1 : 1.98
	8.00	2.0	1.10	2.0	1 : 1.82
$[\mathrm{Ni^{IV}(L^2)^{2+}}]$	2.00	2.0	1.00	2.0	1 : 2.00
	3.50	2.0	1.03	2.0	1 : 1.94
	6.00	2.0	1.07	2.0	1 : 1.87
	8.00	2.0	1.12	2.0	1 : 1.79

a) The suffixes t-stands for 'taken' and c-stands for 'consumed'.

and $[Ni^{IV}(L^2)]^{2+}$. All the kinetic runs were performed under pseudo-first-order conditions with excess of azide over Ni^{IV}. Oxidation of azide (or hydrazoic acid) was found to follow a single step $2e^-$ transfer process in the pH region $2.0 \leqslant pH \leqslant 6.0$ for the reduction of $[Ni^{IV}(L^1)_2]^{2+}$ [Fig. 1(a)] and $2.0 \leqslant pH \leqslant 4.5$ for the reduction of $[Ni^{IV}(L^2)]^{2+}$.

A distinct biphasic one electron transfer reaction appeared at $pH \geqslant 6.0$ [Fig. 1(b)] and $\geqslant 4.5$ for the respective complexes. In the biphasic reactions at higher pH-region, the initial faster step corresponds to the conversion $Ni^{IV} \rightarrow Ni^{III}$ and the relatively slower decay to the $Ni^{III} \rightarrow Ni^{II}$. In the lower pH region, $Ni^{IV} \rightarrow Ni^{III}$ conversion is rate-determining, followed by a very fast reduction of $Ni^{III} \rightarrow Ni^{II}$ showing an overall single step $2e^-$ transfer process.

Semilog plots for the disappearance of Ni^{IV} species [i.e., $\log(A_t - A_\infty)$ vs. time] (Fig. 2) by single step two-electron transfer process were linear up to ca. 85% of the total reaction, and this confirmed the first-order dependence of reaction rate on the concentration of oxidant. From the slopes of such plots, the pseudo-first-order rate constants (k_{obs}) were calculated. In the case of biphasic reaction traces, the first phase accounted for 30—40% of the observed absorbance change and the reaction proceeded to 95—100% yield of the product. For this, following the reported method of Weyh and Hamm,[28] the absorbance time curves were successfully treated in terms of two first-order reactions yielding observed rate constants (k^{I}_{obs} and k^{II}_{obs}) for the consecutive steps.

Dependence on $[N_3^-]$. The dependence of observed rates (k_{obs}) on reductant concentration was investigated at pH 3.0, 6.0, and 6.5 for the reduction of $[Ni^{IV}(L^1)_2]^{2+}$ and at pH 4.5, 5.0, and 5.5 for the reduction of $[Ni^{IV}(L^2)]^{2+}$. Conditions adopted are : $[N_3^-]_T = (1.0-15.0) \times 10^{-2}$ mol dm^{-3}, $[Ni^{IV}(L_x)^{2+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $I = 0.20$ mol dm^{-3}($NaClO_4$) at temperature 30 °C. Plots of k_{obs} vs. $[N_3^-]_T$ (Fig. 3) at all pH were straight lines with a positive intercept. Hence under pseudo-first-order conditions using excess of azide ion over the metal complexes, the rate law is :

$$-d[Ni^{IV}(L_x)^{2+}]/dt = k_{obs}[Ni^{IV}(L_x)^{2+}] \tag{8}$$
$$= 2nk_{ox}[N_3^-]_T[Ni^{IV}(L_x)^{2+}] + k'[Ni^{IV}(L_x)^{2+}],$$

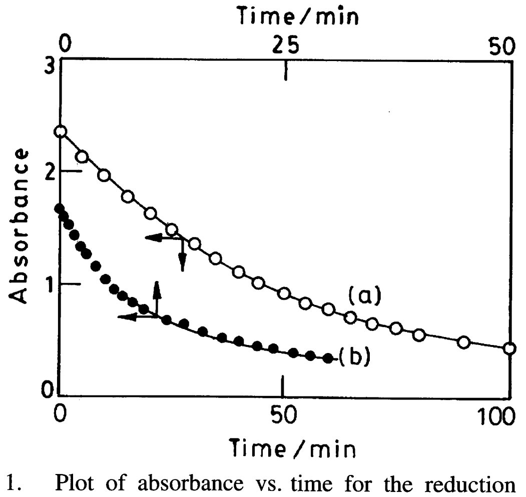


Fig. 1. Plot of absorbance vs. time for the reduction of $[Ni^{IV}(L^1)_2]^{2+}$ by azide at $[Ni^{IV}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[N_3^-] = 1.0 \times 10^{-3}$ mol dm^{-3}, temp=30°C, and $I = 0.20$ mol dm^{-3}, (a) pH=3.0, (b) pH=7.0.

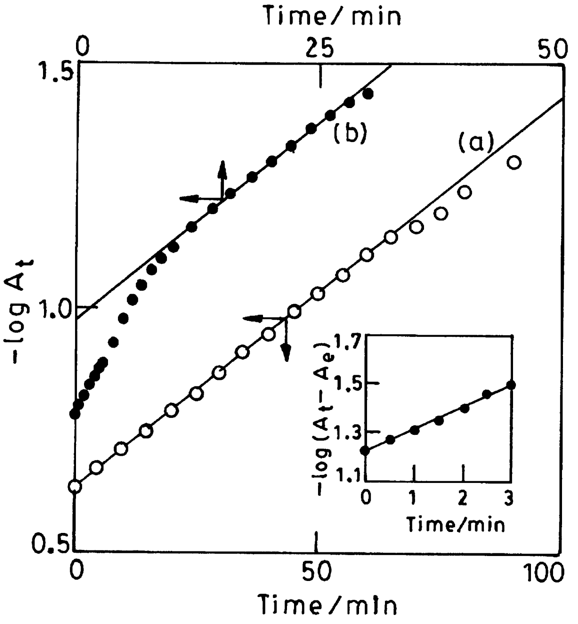


Fig. 2. Plot of $-\log A_t$ vs. time for the reduction of $[Ni^{IV}(L^1)_2]^{2+}$ by azide at (a) pH=3.0 and (b) pH=7.0, other details are same as in Fig. 1. The inset Figure shows the plot of $-\log(A_t - A_e)$ vs. time for the first step of the biphasic reduction of Ni(IV) at pH 7.0 where the A_e values were calculated by the extrapolation of straight line for the second phase to zero time.

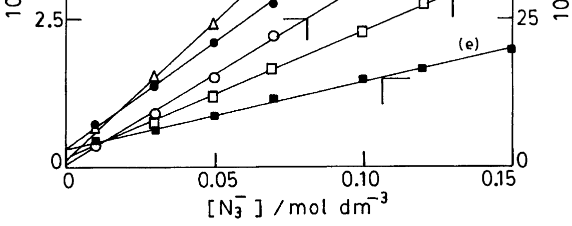


Fig. 3. Plot of k_{obs} vs. [reductant] for the oxidation of azide by $[Ni^{IV}(L^1)_2]^{2+}$. Conditions are : $[Ni^{IV}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $I = 0.20$ mol dm^{-3} ($NaClO_4$), [buffer] = 0.02 mol dm^{-3} (acetate or phosphate), temp=30°C. $[N_3^-] =$ (0.01—0.15) mol dm^{-3}; (a) at pH=3.0, (b) at pH=6.0, corresponding to $Ni^{IV} \rightarrow Ni^{III}$ conversion, (c) at pH=6.0, corresponding to $Ni^{III} \rightarrow Ni^{II}$ conversion, (d) at pH=6.50, corresponding to $Ni^{IV} \rightarrow Ni^{III}$ conversion, and (e) at pH=6.50 corresponding to $Ni^{III} \rightarrow Ni^{II}$ conversion.

where n is the stoichiometric factor due to oxidant and has got the value 0.5 for $2e^-$ transfer process and 1 for single electron transfer step, k' is the auto-decomposition rate of the complex. This autodecomposition to Ni^{2+} complex may occur by the withdrawl of imino H-atom by OH^- of the medium, thereby causing transference of the e^- from $N^- \rightarrow Ni^{IV}$. Corresponding results are summarized in Table 2.

Dependence on $[H^+]$. The effect of acidity on the rate of reaction was performed in the range pH 2.0—8.0 in order to ascertain the contributions of the various reacting species. Figure 4 describes the plots of k_{ox} vs. $-\log[H^+]$ of $Ni^{IV} \rightarrow Ni^{III}$ conversion for both the complexes. This shows that the rate of reaction increases, reaches a maximum and then decreases steadily with $-\log[H^+]$ from 1.90 to 8.01. On the other hand, there is a steady decrease of reaction rate with $-\log[H^+]$ for $Ni^{III} \rightarrow Ni^{II}$ reduction and this is depicted in Fig. 5.

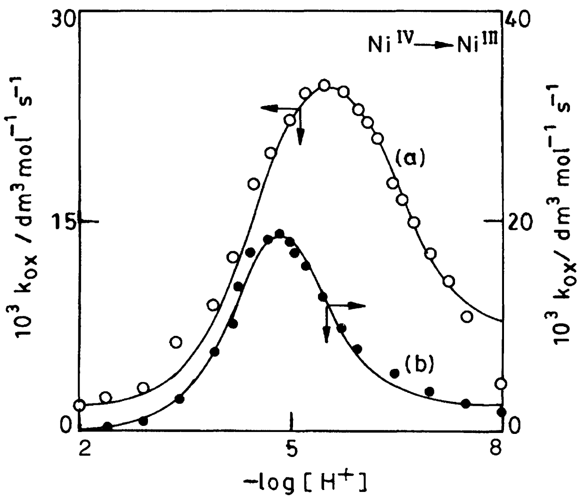


Fig. 4. Plot of k_{ox} vs. $-\log[H^+]$ for the reduction of nickel(IV) to nickel(III) by azide: (a) $[Ni^{IV}(L^1)_2]^{2+}$ and (b) $[Ni^{IV}(L^2)]^{2+}$. Other details are same as in Fig. 1. Solid line represents the calculated and the experimental values are shown in by points.

Discussion

Based on the poor substitution lability of the nickel(IV)/(III) complexes a general outer-sphere mechanism, consistent with the kinetic observations could be framed as Scheme 1. The existence of the proposed intermediates $\dot{N}_3$,

$$Ox + N_3^- \rightleftharpoons Red + \dot{N}_3 \quad k_1/k_{-1} \tag{9}$$

$$Ox + \dot{N}_3 \rightarrow Red + N_3^+ \quad k_2 \tag{10}$$

$$N_3^+ + N_3^- \xrightarrow{\text{fast}} N_6 \tag{11}$$

$$N_6 \xrightarrow{\text{fast}} 3N_2 \tag{12}$$

Scheme 1.

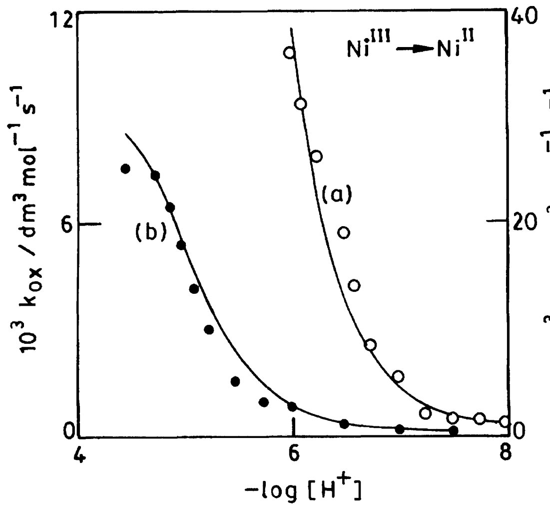


Fig. 5. Plot of k_{ox} vs. $-\log[H^+]$ for the reduction of (a) Ni^{III}–L^1, (b) Ni^{III}–L^2 by azide, other details as in Fig. 1.

Table 2. Pseudo-First-Order Rate Constants for the Oxidation of Azide by $[Ni^{IV}(L^1)_2]^{2+}$ and $[Ni^{IV}(L^2)]^{2+}$ at Different pH[a)]

Oxidant	$[N_3^-]$ / mol dm^{-3}		10^4k_{obs} / s^{-1}				
$[Ni^{IV}(L^1)_2]^{2+}$		pH	3.0	6.0		6.5	
	0.02		0.66	10.8[b)]	5.60[c)]	10.0[b)]	5.20[c)]
	0.05		1.50	24.0[b)]	12.0[c)]	21.0[b)]	8.80[c)]
	0.07		2.22	33.6[b)]	16.4[c)]	27.6[b)]	11.6[c)]
	0.10		3.07	47.6[b)]	22.8[c)]	38.9[b)]	14.6[c)]
	0.15		4.56	69.6[b)]	33.2[c)]	57.0[b)]	20.0[c)]
$[Ni^{IV}(L^2)]^{2+}$		pH	3.5	5.0		5.5	
	0.03		1.0	10.4[b)]	3.60[c)]	7.6[b)]	1.24[c)]
	0.04		1.32	14.4[b)]	4.40[c)]	10.0[b)]	1.60[c)]
	0.06		1.92	21.2[b)]	6.40[c)]	15.6[b)]	2.12[c)]
	0.10		3.22	36.0[b)]	10.8[c)]	26.0[b)]	3.37[c)]
	0.12		3.76	42.8[b)]	12.8[c)]	30.8[b)]	3.92[c)]

a) At 30 °C, I=0.20 mol dm^{-3}($NaClO_4$), $[Ni^{IV}]=5.0\times10^{-5}$ mol dm^{-3}, [buffer]=0.02 mol dm^{-3} (phosphate or acetate), b) k_{obs} for $Ni^{IV} \rightarrow Ni^{III}$ conversion, c) k_{obs} for $Ni^{III} \rightarrow Ni^{II}$ conversion.

N_3^+, and N_6 is well supported in the literature.[20,22,29] Applying the steady-state approximation to the radicals, the derived rate law was found to be:

$$-\mathrm{d[Ox]}/\mathrm{d}t = \frac{2nk_1k_2[\mathrm{Ox}]^2[\mathrm{N_3}^-]}{k_{-1}[\mathrm{Red}]+k_2[\mathrm{Ox}]}, \tag{13}$$

with $n=0.5$ for two electron transfer monophasic process and $n=1$ for single electron transfer biphasic reduction. If we consider $k_{-1}[\mathrm{Red}] \ll k_2[\mathrm{Ox}]$, the general rate law simplifies to

$$-\mathrm{d[Ox]}/\mathrm{d}t = 2nk_1[\mathrm{Ox}][\mathrm{N_3}^-]. \tag{14}$$

The equation is very similar to the equation experimentally established, Eq. 8, only differing by an additional term. This term can be explained by considering the auto-redox-decomposition of the nickel(IV) complexes that depends to some extent on the pH of the medium. At 30 °C and $I=0.2$ mol dm^{-3} ($\mathrm{NaClO_4}$) and $[\mathrm{Ni^{IV}}]=5.0\times10^{-5}$ mol dm^{-3}, k' varies from 4.0×10^{-6} s^{-1} to 18.9×10^{-4} s^{-1} in the range pH 2.0—8.0. When extracting the k_{ox} from Eq. 8, the auto-decomposition of the complex at each pH was taken into account.

Reduction of Nickel(IV). Reduction of $\mathrm{Ni^{IV}}$ complexes by azide is overall second-order at a particular pH, first order in both $[\mathrm{Ni^{IV}}]$ and $[\mathrm{N_3}^-]$, but is greatly influenced by the acidity of the medium.

From cyclic voltammetric and spectrophotometric studies it has been reported earlier that the $\mathrm{p}K_{\mathrm{H}}$s for $[\mathrm{Ni^{IV}}(\mathrm{L}_x)]^{2+}$ complexes are less than 1.0. Hence the deprotonated species, $[\mathrm{Ni^{IV}}(\mathrm{L}_x)]^{2+}$, would be expected to exist in the pH range 2.0—8.0. Again $\mathrm{p}K_1$ for the dissociation of hydrazoic acid, defined by Eq. 15, is in the range 4.19—4.74[8,18,20]

$$\mathrm{HN_3} \overset{K_1}{\rightleftharpoons} \mathrm{H^+} + \mathrm{N_3}^- . \tag{15}$$

But the observed bell-shaped dependence of rate on [H$^+$] cannot be explained by considering only three species—deprotonated $\mathrm{Ni^{IV}}$, $\mathrm{HN_3}$, and $\mathrm{N_3}^-$. A more realistic representation would be to consider a protic equilibrium Eq. 16 involving the 'outside' protonation of nickel(IV) complexes where Ni–N bond is not substantially weakened.

$$[\mathrm{Ni^{IV}}(\mathrm{L}_x)]^{2+} + \mathrm{H^+} \underset{K_\mathrm{a}}{\rightleftharpoons} [\mathrm{Ni^{IV}}(\mathrm{L}_x)\cdots\mathrm{H}]^{3+}. \tag{16}$$

This has been further confirmed from potentiometric titration of $\mathrm{Ni^{IV}}$ complexes and reported earlier.[30] Thus the pH-rate profile leads us to frame the following sequence in the range pH 2.0—8.0:

$$[\mathrm{Ni^{IV}}(\mathrm{L}_x)\cdots\mathrm{H}]^{3+} + \mathrm{HN_3} \xrightarrow{k_0} [\mathrm{Ni^{III}}(\mathrm{L}_x)\cdots\mathrm{H}]^{2+} + \mathrm{H^+} + \dot{\mathrm{N}}_3 \tag{17}$$

$$[\mathrm{Ni^{IV}}(\mathrm{L}_x)\cdots\mathrm{H}]^{3+} + \mathrm{N_3}^- \xrightarrow{k_1} [\mathrm{Ni^{III}}(\mathrm{L}_x)\cdots\mathrm{H}]^{2+} + \dot{\mathrm{N}}_3 \tag{18}$$

$$[\mathrm{Ni^{IV}}(\mathrm{L}_x)]^{2+} + \mathrm{HN_3} \xrightarrow{k_2} [\mathrm{Ni^{III}}(\mathrm{L}_x)]^{+} + \mathrm{H^+} + \dot{\mathrm{N}}_3 \tag{19}$$

$$[\mathrm{Ni^{IV}}(\mathrm{L}_x)]^{2+} + \mathrm{N_3}^- \xrightarrow{k_3} [\mathrm{Ni^{III}}(\mathrm{L}_x)]^{+} + \dot{\mathrm{N}}_3 \tag{20}$$

Scheme 2.

The fate of $\dot{\mathrm{N}}_3$ radical is the same as described earlier in Scheme 1.

The rate law is derived as:

$$k_{\mathrm{ox}} = \frac{k_0[\mathrm{H^+}]^2 + (k_1K_1 + k_2K_\mathrm{a})[\mathrm{H^+}] + k_3K_1K_\mathrm{a}}{(K_\mathrm{a} + [\mathrm{H^+}])(K_1 + [\mathrm{H^+}])} \tag{21}$$

This was solved with the help of a Simplex optimization program by allowing the equilibrium constants to vary. The best fit data were again fitted by a nonlinear least-squares program involving six variables to evaluate the standard deviations. The evaluated parameters are:

$$k_0 = (1.70 \pm 0.05)\times10^{-3}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_1 = (2.83 \pm 0.08)\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_2 = (4.58 \pm 0.14)\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_3 = (7.20 \pm 0.22)\times10^{-3}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$K_1 = (3.48 \pm 0.10)\times10^{-5}\,\mathrm{mol^{-1}\,dm^3}\ (\mathrm{p}K_1 = 4.46),$$
$$K_\mathrm{a} = (3.10 \pm 0.09)\times10^{-7}\,\mathrm{mol^{-1}\,dm^3}\ (\mathrm{p}K_\mathrm{a} = 6.51)$$

for $[\mathrm{Ni^{IV}}(\mathrm{L}^1)_2]^{2+}$ reduction and

$$k_0 = (8.00 \pm 0.24)\times10^{-5}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_1 = (3.31 \pm 0.01)\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_2 = (3.72 \pm 0.11)\times10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_3 = (2.50 \pm 0.06)\times10^{-3}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$K_1 = (2.49 \pm 0.07)\times10^{-5}\,\mathrm{mol^{-1}\,dm^3}\ (\mathrm{p}K_1 = 4.60),$$
$$K_\mathrm{a} = (8.91 \pm 0.27)\times10^{-6}\,\mathrm{mol^{-1}\,dm^3}\ (\mathrm{p}K_\mathrm{a} = 5.05)$$

for $[\mathrm{Ni^{IV}}(\mathrm{L}^2)]^{2+}$ reduction.

The validity of the proposed mechanism originates from the fact that acid-dissociation constant (K_1) values for hydrazoic acid obtained here are in excellent agreement with each other (4.46, 4.60) and also with the reported values.[20] Further the $\mathrm{p}K_\mathrm{a}$ for $[\mathrm{Ni^{IV}}(\mathrm{L}^1)_2\cdots\mathrm{H}]^{3+}$ and $[\mathrm{Ni^{IV}}(\mathrm{L}^2)\cdots\mathrm{H}]^{3+}$ are found to be 6.51 and 5.05 here, and these are also in good agreement with the respective $\mathrm{p}K_\mathrm{a}$ values (6.10 for $[\mathrm{Ni^{IV}}(\mathrm{L}^1)_2\cdots\mathrm{H}]^{3+}$ and 5.20 for $[\mathrm{Ni^{IV}}(\mathrm{L}^2)\cdots\mathrm{H}]^{3+}$) obtained from the analysis of the pH titration curve[30] by the conventional Bjerrum $(\bar{n})_{1/2}$ method.

Reduction of Nickel(III). The second slower phase at higher pH ($\geqslant 6.0$ for $[\mathrm{Ni^{IV}}(\mathrm{L}^1)_2]^{2+}$ and $\geqslant 4.50$ for $[\mathrm{Ni^{IV}}(\mathrm{L}^2)]^{2+}$) was identified with the reduction of $[\mathrm{Ni^{III}}(\mathrm{L}_x)]^+$. This was confirmed by using electrochemically generated $[\mathrm{Ni^{III}}(\mathrm{L}^2)]^+$ as reductant at pH 5.0. Plots of k_{ox} vs. $-\log[\mathrm{H^+}]$ for these steps (Fig. 5) show a descending trend. This can be explained by considering the protic equilibria of

$$[\mathrm{Ni^{III}}(\mathrm{L}_x\mathrm{H})]^{2+} + \mathrm{HN_3} \xrightarrow{k_4} [\mathrm{Ni^{II}}(\mathrm{L}_x\mathrm{H})]^{+} + \mathrm{H^+} + \dot{\mathrm{N}}_3 \tag{22}$$

$$[\mathrm{Ni^{III}}(\mathrm{L}_x\mathrm{H})]^{2+} + \mathrm{N_3}^- \xrightarrow{k_5} [\mathrm{Ni^{II}}(\mathrm{L}_x\mathrm{H})]^{+} + \dot{\mathrm{N}}_3 \tag{23}$$

$$[\mathrm{Ni^{III}}(\mathrm{L}_x)]^{+} + \mathrm{HN_3} \xrightarrow{k_6} [\mathrm{Ni^{II}}(\mathrm{L}_x)] + \mathrm{H^+} + \dot{\mathrm{N}}_3 \tag{24}$$

$$[\mathrm{Ni^{III}}(\mathrm{L}_x)]^{+} + \mathrm{N_3}^- \xrightarrow{k_7} [\mathrm{Ni^{II}}(\mathrm{L}_x)] + \dot{\mathrm{N}}_3 \tag{25}$$

Scheme 3.

$[Ni^{III}(L_xH)]^{2+}$ (Eq. 2) and hydrazoic acid (Eq. 15) as well. We suggest following Scheme 3 (Eqs. 22, 23, 24, and 25) :

The reduced species of the complexes would be protonated or deprotonated ones depending upon the pH of the medium. The extent of protonation (two or one) also depends upon the pH governed by the pK values of the nickel(II) complexes pK_1 and pK_2 values of Ni(II) complexes are 7.80±0.05 and 10.00±0.05 for $[Ni^{II}(HL^1)_2]^{2+}$ and 5.90±0.05 and 7.80±0.05 for $[Ni^{II}(H_2L^2)]^{2+}$ complex.[24] The rate Eq. 26 can be derived from the above scheme.

$$k_{ox} = \frac{k_4[H^+]^2 + (k_5K_1 + k_6K_H)[H^+] + k_7K_1K_H}{(K_1 + [H^+])(K_H + [H^+])}. \tag{26}$$

The evaluated parameters obtained in an analogous manner to that described earlier are as follows :

$$k_4 = (5.00 \pm 0.15) \times 10^{-5}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_5 = (3.40 \pm 0.10) \times 10^{-1}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_6 = (6.50 \pm 0.20) \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_7 = (2.50 \pm 0.08) \times 10^{-4}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$K_1 = (3.66 \pm 0.10) \times 10^{-5}\,\mathrm{mol^{-1}\,dm^3}\ (\mathrm{p}K_1 = 4.43),$$
$$K_H = (3.60 \pm 0.11) \times 10^{-5}\,\mathrm{mol^{-1}\,dm^3}\ (\mathrm{p}K_H = 4.44)$$

for $[Ni^{III}(L^1)_2]^+$ reduction and

$$k_4 = (3.13 \pm 0.08) \times 10^{-4}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_5 = (1.10 \pm 0.03) \times 10^{-3}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_6 = (2.01 \pm 0.06) \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$k_7 = (1.40 \pm 0.04) \times 10^{-4}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},$$
$$K_1 = (2.57 \pm 0.08) \times 10^{-5}\,\mathrm{mol^{-1}\,dm^3}\ (\mathrm{p}K_1 = 4.59),$$
$$K_H = (8.67 \pm 0.26) \times 10^{-5}\,\mathrm{mol^{-1}\,dm^3}\ (\mathrm{p}K_H = 4.06)$$

for $[Ni^{III}(L^2)]^+$ reduction.

Here also an excellent agreement between the kinetically evaluated and reported pK_H values of the Ni^{III} complexes is noted. This supports strongly the proposed mechanism.

These nickel(IV)/(III) complexes possessing pseudo-octahedral geometry and moderate reduction potential values are expected to show low substitution labilities (<10^2 s^{-1}). The electron transfer is thus more likely to be operative through outer-sphere routes. The pre-equilibrium formation of hydrogen-bonded adducts is also encountered in some reactions[26] of these complexes. Unfortunately we could not gather any direct spectral evidence to support the inner-sphere route. The reactivities of hydrazoic acid and azide ion towards different Ni(IV) and Ni(III) complexes are listed in Table 3 and follow the order :

$$[Ni^{IV}(L_x)\cdots H]^{3+} \ :\ HN_3 < N_3^-;$$
$$[Ni^{IV}(L_x)]^{2+} \ :\ HN_3 > N_3^-;$$
$$[Ni^{III}(L_xH)]^{2+} \ :\ HN_3 < N_3^-$$
$$\text{and}\quad [Ni^{III}(L_x)]^{+} \ :\ HN_3 > N_3^-.$$

This reactivity can be explained as due to the formation of an H-bond between the free oximato oxygen atom and the hydrogen atom of the reductant. Some electrostatic interactions and thermodynamic considerations may come into play as well.

Table 3. Reactivity of Different Azide Species

Oxidants	k_{12}/dm^3 mol^{-1} s^{-1}	
	HN_3	N_3^-
$[Ni^{IV}(L^1)_2\cdots H]^{3+}$	$(1.70\pm 0.05)\times 10^{-3}$	$(2.83\pm 0.08)\times 10^{-2}$
$[Ni^{IV}(L^1)_2]^{2+}$	$(4.58\pm 0.14)\times 10^{-2}$	$(7.20\pm 0.22)\times 10^{-3}$
$[Ni^{III}(L^1)(L^1H)]^{2+}$	$(5.00\pm 0.15)\times 10^{-5}$	$(3.40\pm 0.10)\times 10^{-1}$
$[Ni^{III}(L^1)_2]^{+}$	$(6.50\pm 0.20)\times 10^{-2}$	$(2.50\pm 0.08)\times 10^{-4}$
$[Ni^{IV}(L^2)\cdots H]^{3+}$	$(8.00\pm 0.24)\times 10^{-5}$	$(3.31\pm 0.10)\times 10^{-2}$
$[Ni^{IV}(L^2)]^{2+}$	$(3.72\pm 0.11)\times 10^{-2}$	$(2.50\pm 0.06)\times 10^{-3}$
$[Ni^{III}(L^2H)]^{2+}$	$(3.13\pm 0.08)\times 10^{-4}$	$(1.10\pm 0.03)\times 10^{-3}$
$[Ni^{III}(L^2)]^{2+}$	$(2.01\pm 0.06)\times 10^{-2}$	$(1.40\pm 0.04)\times 10^{-4}$

As these reactions may proceed without substitution at the metal center, it is helpful to apply the Marcus cross-relation equation for outer-sphere reactions[31] expressed in Eqs. 27, 28, 29, and 30 where k_{12} is the rate constant for electron transfer from N_3^- to the oxidant,

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}\, W_{12}, \tag{27}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{12})/RT]^2}{4[\ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]}, \tag{28}$$

$$W_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT], \tag{29}$$

$$w_{ij} = \frac{4.23Z_iZ_j}{a[1 + 0.328a\sqrt{I}]}. \tag{30}$$

k_{11} is the self-exchange rate constant for the $\dot{N}_3/N_3^-$ couple, k_{22} is the self-exchange rate constant for the various complexes (used as oxidants), K_{12} is the equilibrium constant for the electron transfer reaction, calculated by Eq. 31 :

$$\log K_{12} = (n\Delta E^\circ)/(0.06023) \qquad \text{at } 30\,^\circ\mathrm{C}. \tag{31}$$

W_{12} is the electrostatic work term, w_{ij} is the work required to bring ions i and j (charges Z_i and Z_j) to the separation distance a (equal to the sum of the radii of the ions in Å) : Z is the collision rate, a value 1×10^{22} is used for Z^2, and R is the gas constant (kcal mol^{-1} K^{-1}). The radius and self-exchange rate constant for $\dot{N}_3/N_3^-$ couple are reported to be 2.0 Å and 4.0×10^4 dm^3 mol^{-1} s^{-1} respectively.[22] The radius of nickel(IV)/(III) complexes are taken as 5.1 Å.[26]

Assuming the adiabatic nature of the self-exchange reaction, Eq. 27 could be rearranged to Eq. 32 :

$$2\ln k_{12} - \ln f_{12} - 2\ln W_{12} - \ln k_{22} = \ln k_{11} + \ln K_{12}. \tag{32}$$

Thus the plots of $(2\ln k_{12} - \ln f_{12} - 2\ln W_{12} - \ln k_{12})$ vs. $\ln K_{12}$ for the data in Table 4 is linear, Fig. 6, though the points corresponding to $[Ni^{III}(L^1H)(L^1)]^{2+}$, $[Ni^{III}(L^1)_2]^+$, and $[Ni^{III}(L^2)]^+$ show considerable deviation. The deviated points could form a straight line (with slope=1) giving rise to a value of $k_{11} \approx 10^{10}$ dm^3 mol^{-1} s^{-1}. The least-squares value of the slope, excluding the deviated points, (1.09±0.15), is exactly equal to the expected value of unity. The intercept $[\ln k_{11} = (1.19\pm 0.34)\times 10^1]$ results in a value of k_{11} equal to

Table 4. Cross Reaction Kinetic Data for the Oxidation of N_3^- by Different Oxidants

No.	Oxidant	r/Å	E_f V vs. NHE	ln k_{22}	ln k_{12}	ln f_{12}	ln W_{12}	ln K_{12}	$2\ln k_{12}-\ln f_{12}-2\ln W_{12}-\ln k_{22}$
1.	$[IrCl_6]^{2-}$	4.4[a]	0.93[c]	12.2[c]	4.55[c]	−2.00	0.60	−15.6	−2.30
2.	$[IrBr_6]^{2-}$	4.7[a]	0.88[c]	19.1[c]	3.50[c]	−3.54	0.62	−17.5	−9.80
3.	$[Fe(bpy)_3]^{3+}$	6.0[a]	1.06[c]	20.0[c]	10.6[c]	−1.95	1.53	−10.5	0.09
4.	$[Ni^{IV}(L^1)_2]^{2+}$	5.1[b]	0.63[d]	11.3[d]	−4.93[f]	−6.83	0.76	−26.8	−15.85
5.	$[Ni^{IV}(L^2)]^{2+}$	5.1[b]	0.654[d]	11.5[e]	−5.99[f]	−6.44	0.76	−25.9	−18.56
6.	$[Ni^{III}(L^1)(L^1H)]^{2+}$	5.1[b]	0.63[d]	6.21[d]	−1.08[f]	−5.79	0.76	−26.8	−4.10
7.	$[Ni^{III}(L^2H)]^{2+}$	5.1[b]	0.64[d]	6.91[e]	−6.81[f]	−5.75	0.76	−26.4	−16.30
8.	$[Ni^{III}(L^1)_2]^+$	5.1[b]	0.30[d]	8.99[d]	−8.29[f]	−12.8	0.24	−39.4	−13.25
9.	$[Ni^{III}(L^2)]^+$	5.1[b]	0.42[d]	7.60[e]	−8.87[f]	−9.61	0.24	−34.8	−16.21

a) Ref. 12, b) Ref. 26, c) Ref. 22, d) Ref. 24, e) Ref. 25, f) This work, $E°(N_3^-/\dot{N}_3)=1.33$ V vs. NHE and k_{11} $(\dot{N}_3/N_3^-)=4\times10^4$ $dm^3\ mol^{-1}\ s^{-1}$ (Ref. 22). Reactions (1)—(3) have I=0.10 mol dm^{-3} ($NaClO_4$), temp=25°C, and reactions (4)—(9) have I=0.20 mol dm^{-3} ($NaClO_4$), temp=30°C.

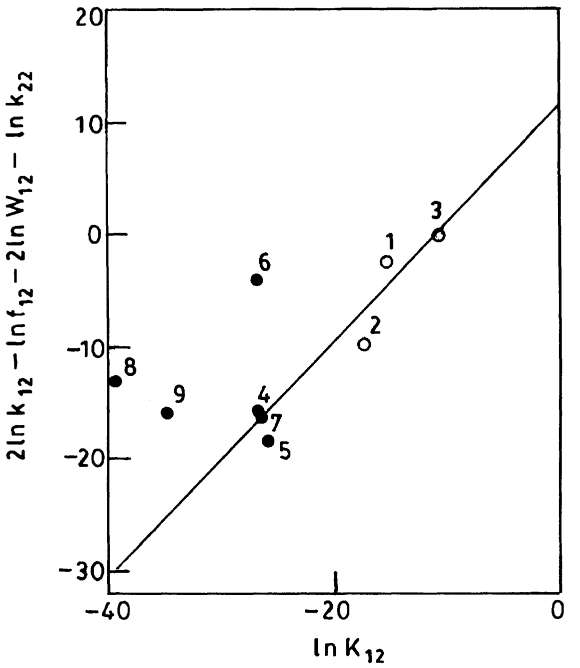


Fig. 6. Plot of $2\ln k_{12}-\ln f_{12}-2\ln W_{12}-\ln k_{12}$ against ln K_{12}. ● —Corresponds to the reaction involving nickel complexes and ○ —corresponds to other oxidants.

$(15.9\pm4.4)\times10^4$ $dm^3\ mol^{-1}\ s^{-1}$, which is in fair agreement with the estimated value 4.0×10^4 $dm^3\ mol^{-1}\ s^{-1}$.[22]

A close inspection of Fig. 6 reveals that $[Ni^{IV}(L_x)]^{2+}$, $[Ni^{III}(HL^2)]^{2+}$, $[IrCl_6]^{2-}$, $[IrBr_6]^{2-}$, and $[Fe(bpy)_3]^{3+}$ react by outer-sphere mechanism whereas the reaction of $[Ni^{III}(HL^1)(L^1)]^{2+}$, $[Ni^{III}(L^1)_2]^+$, and $[Ni^{III}(L^2)]^+$ may proceed through inner-sphere path. The inner-sphere mechanism of nickel(III) complexes may be supported by considering the partial unwrapping of one of the N_6-coordinated nitrogen atoms. This is because in nickel(III) complexes the axial positions are relatively labile, and there is an ease of rearrangement of tridentate bis(oxime) ligands having no continuity of the 'back bone' compared to the single-chain hexadentate (continuous) system.

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