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Studies in Nickel(IV) Chemistry. Kinetics of Electron Transfer from Hydrazine to Tris(dimethylglyoximato)nickelate(IV) in Aqueous Medium

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Kinetics of electron transfer from hydrazine(L) to tris(dimethylglyoximato)nickelate(IV), $[Ni(dmg)_3]^{2-}$, follow pseudo-first-order disappearance in the Ni(IV) in aqueous medium in the range $5.0 \leqslant pH \leqslant 7.0$. The pseudo-first-order rate constants (k_{obsd}) increase with increasing $[L]_0$ and attain limiting values at higher relative $[L]_0$. The k_{obsd}-pH profiles at various $[L]_0$ show that the k_{obsd} values register steep decrease with increasing pH till pH≈6.5 tending to level off at higher relative pH. Results are consistent with probable interactions of the one-protonated and two-protonated Ni(IV) species with the protonated substrate, or with the metal ion-substrate complex that might have been formed from trace metal ion and the substrate. The two-protonated Ni(IV) complex apparently reacts several orders of magnitude faster than the one-protonated species.

Several important reports are available on kinetics of electron transfer from hydrazine to various oxidants.[1-6] While two-electron transfer[7] from hydrazine resulted, almost exclusively and often quantitatively, in water and nitrogen as products, the products of one-electron change[4,8,9] were nitrogen and/or ammonia. We have been currently interested in the chemistry of tris(dimethylglyoximato)nickelate(IV), $[Ni(dmg)_3]^{2-}$ (dmg^{2-}=dimethylglyoximate dianion) and reported its preparation (in part) and reaction with 1-phenylhydrazine[10a] and with hydroxylamine.[10b] The details of the preparative methods and characterization studies were also described.[10c] An early qualitative report mentioned that hydroxylamine or hydrazine effectively reduced the Ni(IV) complex, prepared by Simek[11], by a two-electron transfer. In the kinetics of oxidation of hydroxylamine by $[Ni(dmg)_3]^{2-}$, we observed that the disappearance of the nickel(IV) was always pseudo-zero-order irrespective of the source of the samples employed and that the zero-order reactions were tremendously catalyzed by added aquacopper(II).[10b] in contrast, the disappearance kinetics of the Ni(IV) follow a pseudo-first-order pattern in the Ni(IV)-hydrazine reaction. The preliminary results on kinetics of this reaction are presented in this communication.

Experimental

Materials and Methods. Freshly prepared doubly distilled water (distilled from an all-glass apparatus containing *ca.* 1×10^{-4} M†† of EDTA) were used throughout. Characterization of $[Ni(dmg)_3]^{2-}$ and preparation of its aqueous solutions were performed as described earlier.[10] Hydrazinium chloride (BDH, AnalaR) reagent was recrystallized twice before use, its solutions were freshly prepared, and standardized by acid bromate method.[12a] The substrate solutions were appropriately diluted and their pH adjusted, as required, when they were employed for kinetic runs. Fresh stock solutions of a BDH(AnalaR) grade sample of $CuCl_2$ were prepared and standardized;[12b] requisite amounts from the stock were taken to prepare Cu(II) solutions for kinetic runs. Other reagents were of analytical grade. Standard buffer solutions were prepared in water using potassium salts. KCl was used to maintain the ionic strength (μ) of the medium.

The reactions were monitored for the disappearance of the Ni(IV) at 460 nm (ε_{460}=9 600 M^{-1} cm^{-1}). In a typical experiment, an aqueous solution of the freshly prepared Ni(IV) complex[10a] was rapidly mixed with an equal volume of the substrate solution at the desired pH, μ and temperature (±0.1 °C), and the progress of the reaction was monitored, continuously as a function of time, on a Pye Unicam SP 1800, a Zeiss VSU 2-P UV-visible spectrophotometer or on an Aminco stopped-flow assembly, as described earlier.[10] The pH values of the solutions were measured before and after the reactions and the mean value (which did not differ by more than ±0.01 units from the measured values) was taken into record after allowing due corrections for ionic strength effect. In experiments carried out in the presence of small amounts of added aquacopper(II), the Cu(II) was either taken along with the oxidant solution or with the substrate solution; in both the cases, the results obtained were practically the same. Pseudo-first-order rate constants were calculated from the usual expression and were found to remain practically constant for at least three half-lives of Ni(IV) disapperance in the 440—480 nm range or when the reactions were conducted in a nitrogen atmosphere in representative runs. Replicate runs (2 to 7) were reproducible to ±5%.

Stoichiometry and Products. The stoichiometry experiments were conducted at pH values of 5.3, 6.2, and 7.0. In a set of experiments at each of the pH and with $[Ni(IV)]_0 > [hydrazine]_0$ ($[Ni(IV)]_0 = 0.8\times10^{-4}-1.6\times10^{-4}$ M, $[hydrazine]_0 = 0.1\times10^{-4}-0.6\times10^{-4}$ M), the unreacted Ni(IV) was spectrophotometrically estimated at the end of the reaction. Keeping $[hydrazine]_0 > [Ni(IV)]_0$ ($[hydrazine]_0 = 1\times10^{-3}-4\times10^{-3}$ M, $[Ni(IV)]_0 = 0.4\times10^{-3}-1\times10^{-3}$ M), the left-over [hydrazine] was estimated by acid bromate method.[12a] One mol equivalent of the substrate was found to have reacted with 2±0.1 mol equivalents of Ni(IV) conforming to Eq. 1.

$$N_2H_5^+ + 2[Ni(dmg)_3]^{2-} + 3H^+ \longrightarrow N_2 + 2[Ni(dmgH)_2] + 2\,dmgH_2 \qquad (1)$$

The products were identified by a procedure similar to the one described earlier.[10b] Nitrogen was qualitatively identified by a gas chromatographic procedure. Tests for ammonia by Nessler's reagent method[13a] gave negative results.

Potentiometric Measurements. The first proton-dissociation constant (K_a) of hydrazinium ion (LH^+) was determined potentiometrically in an atmosphere of nitrogen gas with a Systronics 335 digital pH-meter equipped with glass and saturated calomel electrodes. The concentration of H^+ was calculated from the measured pH values after applying due corrections for ionic strength effect.[13b] The value of pK_a was

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†† 1 M=1 mol dm^{-3}.

Table 1. Average[a)] pseudo-first-order rate constants for the oxidation of hydrazine by Ni(IV) complex (Aqueous medium, $\mu=0.25$,[b)] 35 °C, $[\mathrm{N(IV)}]_0=(3—5)\times10^{-5}$ M)

pH[c)]	$10^3\,k_{\text{obsd}}/\text{s}^{-1}$ $10^3[\mathrm{N_2H_4}]_0$				
	1	4	10	20	40
5.0	27.0	40.5	46.0	47.5	48.6
5.0[b)]	48.3	129	257		
5.15	18.9	28.4	32.5	33.8	34.7
5.15[e)]	0.8		1.30		
5.3	13.6	20.3	23.5	24.2	24.8
5.3[d)]	24.3	65.0	130		
5.52	8.2	12.2	14.5	14.9	15.3
6.0	2.8	4.2	5.5	5.5	5.7
6.0[d)]	5.1	13.7	28.8		
6.15	2.0	3.0	4.5	4.5	4.5
6.15[e)]	0.1		0.2		
6.3	1.3	2.2	3.2	3.2	3.2
6.52	0.9	1.4	2.3	2.3	2.4
6.52[e)]		0.06	0.09		
7.0	0.4	0.6	1.4	1.4	1.4
7.0[d)]	0.8	2.2	6.0		

a) Deviations from the average value are within ±5%; $[\mathrm{N_2H_4}]_0$ refers to the initial analytical concentration of hydrazine. b) All concentration units are expressed in M (1 M=1 mol dm^{-3}). c) Corrected pH (±0.01 units). Buffer used (pH range): hydrogen phthalate-OH$^-$ (5.0—6.0); $\mathrm{H_2PO_4^-}$—$\mathrm{OH^-}$ (6.0—7.0). Potassium salts were used. d) In presence of 2×10^{-6} M of added aquacopper (II). e) In presence of 6×10^{-5} M of added EDTA.

Table 2. Average[a)] pseudo-first-order rate constants for the oxidation of hydrazine by Ni(IV) complex (Aqueous medium, 35 °C, $[\mathrm{Ni(IV)}]_0=(3—5)\times10^{-5}$ M, $[\text{hydrazine}]_0=4\times10^{-3}$ M)

pH	μ/M	$10^3k_{\text{obsd}}/\text{s}^{-1}$
5.62	0.25	9.9(9.7)[b)]
	0.50	10.1
	1.00	9.7
5.70	0.25	8.3(8.2)[b)]
	0.50	8.2
	1.00	8.4
6.23	0.25	2.6(2.4)[b)]
	0.50	2.5
	1.00	2.5
6.43	0.25	1.7(1.8)[b)]
	0.50	1.8
	1.00	1.7

a) Deviations from the average value are within ±5%. b) In the presence of 1×10^{-4} M of acrylonitrile ($\mathrm{N_2}$ atmosphere).

found to be 8.1±0.2 at 35 °C and $\mu=0.25$ M (KCl), which agreed with earlier reported values.[2,14)]

Results

In order to examine possible pathways for electron transfer from hydrazine to the Ni(IV), a series of experiments was designed maintaining pseudo-first-order excess of $[\mathrm{L}]_0$ over $[\mathrm{Ni(IV)}]_0$. The pseudo-first-order rate constants for the Ni(IV) disappearance (k_{obsd}) were found to remain almost constant in the range of $1\times10^{-5}\leq[\mathrm{Ni(IV)}]_0\leq1.4\times10^{-4}$ M at constant $[\mathrm{L}]_0$, temperature, μ and pH. In presence of added Cu(II)·aq, the pseudo-first-order disappearance of Ni(IV) was still maintained, but the pseudo-first-order rate constants were found to have enhanced values.

Table 3. Average[a)] pseudo-first-order rate constants and average values of the activation parameters for the oxidation of hydrazine by Ni(IV) complex (Aqueous medium, $\mu=0.25$,[b)] $[\mathrm{Ni(IV)}]_0=(3—5)\times10^{-5}$, $[\text{hydrazine}]_0=4\times10^{-3}$)

pH	$10^3\,k_{\text{obsd}}/\text{s}^{-1}$				
	30 °C	35 °C	40 °C	45 °C	50 °C
5.83	3.3	6.2	11.7	21.0	37.2
6.15	1.8	3.0	6.7	12.6	21.1
6.45	0.87	1.6	2.9	5.9	10.6
6.88	0.38	0.7	1.3	2.7	5.3
$10^{-3}\,k_{2z}K_{2\mathrm{H}}$	2.13	4.04	7.68	13.4	23.6
$10^{4}k_{2y}$	1.29	2.80	5.96	12.3	25.1

pH	$\Delta H^{\neq}/\text{kJ mol}^{-1}$ [c)]	$\Delta S^{\neq}/\text{J K}^{-1}\,\text{mol}^{-1}$ [c)]
5.83	96	29
6.10	113	71
6.45	100	33
6.88	105	33
$k_{2z}K_{2\mathrm{H}}$	95[d)]	133[d)]
k_{2y}	118[e)]	71[e)]

a) Deviations from the average value are within ±5%. b) All concentrations are in M. c) The net activation parameters. d, e) Respectively associated with the constants $k_{2z}K_{2\mathrm{H}}$ and k_{2y} (The temperature dependence of $K_{1\mathrm{H}}$ $K_{2\mathrm{H}}$, and K_{a} are assumed to be negligible).

Table 1 presents the values of the k_{obsd} for varying $[\mathrm{L}]_0$ and pH of the medium at 35 °C and $\mu=0.25$ M. The k_{obsd} values were found to increase with increasing $[\mathrm{L}]_0$, showing a tendency to attain limiting values at higher relative $[\mathrm{L}]_0$. The k_{obsd} values were found to decrease steeply with increasing pH, tending to level off at higher relative pH (Fig. 1). While the log k_{obsd} *vs.* pH plots were almost linear up to pH ≈6.5 with slopes of *ca.* −1, the corresponding slopes were nearly equal to zero beyond this pH. These observations pointed to probable involvement of different orders of $[\mathrm{H^+}]$.

The retarding effect of added EDTA (ethylenediaminetetraacetate added in the form of the disodium salt of the tetrabasic acid) on the k_{obsd}, shown in Table 1, suggested that the present reaction might be subject to influence of metal ions. It may be mentioned that the kinetics of the Ni(IV)-hydroxylamine reaction[10b)] was influenced in the presence of metal ions, significantly retarded by added EDTA and tremendously catalyzed by aquacopper(II).

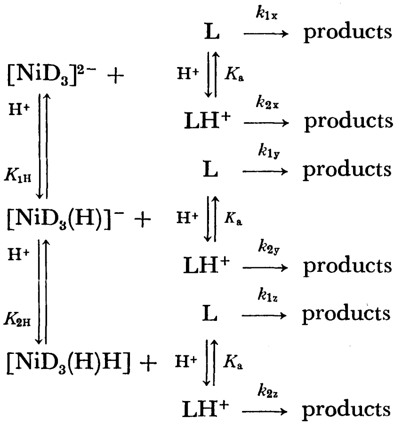
The values of the k_{obsd} were found to be almost insensitive to varying ionic strengths of the medium (Table 2). Added acrylonitrile also did not practically influence the values of the k_{obsd} (Table 2), nor was there any detectable polymerization (in a nitrogen atmosphere) observed, implying that radical-trapping agents might not have significant effect on the kinetics of the oxidation.

From the temperature dependence of the k_{obsd} in the range 30—50 °C and at different pH values (Table 3), the activation parameters were evaluated.

Discussion

It was shown earlier[10a,d] that in alkaline solutions (pH $\gtrsim$11.5) the Ni(IV) complex was in the form of pseudooctahedral $[\text{Ni(dmg)}_3]^{2-}$ which underwent two successive protonations; the subsequent protonations were much below pH 1.23 and were not detectable kinetically. The potentiometrically determined values (at 35 °C in aqueous medium) of the first and second protonation constants, $K_{1\text{H}}$ and $K_{2\text{H}}$, were 8.07×10^{10} M^{-1} and 2.24 M^{-1} at μ=0.57 M, and 7.08×10^{10} M^{-1} and 4.46 M^{-1} at μ=0.25 M; the $K_{1\text{H}}$ value as determined from spectrophotometric pH titrations was 8.33×10^{10} M^{-1} at 35 °C and μ=0.57 M. It was also shown earlier that protonations of the complex assisted its decomposition (with concomitant intramolecular electron transfer). The first (outside-) protonation was at a dioximate oxygen, forming a hydrogen bonded structure O—H···O between the dioximate oxygens, without much alteration of c.f.s.e. of the original pseudooctahedral $[\text{Ni(dmg)}_3]^{2-}$, and the second protonation most probably occurred *via* a direct proton-transfer to a ring-opened (ligand) nitrogen site. The values of the solvent-assisted, first proton-assisted and second proton-assisted rate constants ($k_{0\text{d}}$, $k_{1\text{d}}$, and $k_{2\text{d}}$) were respectively 2.6×10^{-7} s^{-1}, 1.2×10^{-5} s^{-1} and 44.3 s^{-1} at 35 °C and μ=0.25 M in aqueous medium. However, since the proton-assisted decomposition reaction was much too slow compared to the rates of the present redox system, it would not enter into the rate picture in the present investigation.

One general scheme which is consistent with the observed kinetic behaviour of the redox system can be presented as in Scheme 1.



$(\text{D}^{2-} = \text{dmg}^{2-}, \text{L} = \text{H}_2\text{NNH}_2)$

Scheme 1.

The rate law derivable from this scheme with all the possible reacting species is as in Eq. 2.

$$k_{\text{obsd}} = \frac{\{k_{1\text{x}}K_\text{a}+(k_{2\text{x}}k_{1\text{y}}K_{1\text{H}}K_\text{a})[\text{H}^+] + (k_{2\text{y}}K_{1\text{H}}+k_{1\text{z}}K_{1\text{H}}K_{2\text{H}}K_\text{a})[\text{H}^+]^2+k_{2\text{z}}K_{1\text{H}}K_{2\text{H}}[\text{H}^+]^3\}}{(1+K_{1\text{H}}[\text{H}^+]+K_{1\text{H}}K_{2\text{H}}[\text{H}^+]^2)([\text{H}^+]+K_\text{a})}, \tag{2}$$

where $k_{n\text{x}}$, $k_{n\text{y}}$, and k_{nz} are functions of $[\text{L}]_0$. Expressing the denominator terms as Y_1Y_2 and the coefficients of the $[\text{H}^+]$-independent, $[\text{H}^+]$, $[\text{H}^+]^2$, and $[\text{H}^+]^3$ terms in the numerator as a, b, p, and q respectively, Eq. 2 can be written in the form of Eq. 3 or 4.

$$k_{\text{obsd}}\,Y_1Y_2 = a + b[\text{H}^+] + p[\text{H}^+]^2 + q[\text{H}^+]^3 \tag{3}$$

$$\text{or}\ \frac{k_{\text{obsd}}\,Y_1Y_2}{[\text{H}^+]^2} = \frac{a}{[\text{H}^+]^2} + \frac{b}{[\text{H}^+]} + p + q[\text{H}^+] \tag{4}$$

It was seen that plots of $k_{\text{obsd}}\ Y_1Y_2/[\text{H}^+]^2$ *vs.* $[\text{H}^+]$ were linear (Fig. 2), implying that the terms containing the coefficients "*a*" and "*b*" were negligible in comparison with those containing the coefficients "*p*" and "*q*". In that event if the contributions of the $[\text{NiD}_3]^{2-}$ and the L species to the overall reactivity are assumed to be negligible under the conditions employed, Eq. 4 takes the form of Eq. 5.

$$\frac{k_{\text{obsd}}\,Y_1Y_2}{K_{1\text{H}}[\text{H}^+]^2} = k_{2\text{y}} + k_{2\text{z}}\,K_{2\text{H}}[\text{H}^+] \tag{5}$$

The values of $k_{2\text{y}}$ and $k_{2\text{z}}$ at varying $[\text{L}]_0$, as obtained from a least-squares fit of the data of Table 1 in accordance with Eq. 5, are listed in Table 4.

The limiting kinetics observed for varying $[\text{L}]_0$ can be explained in terms of Eqs. 6 and 7.

$$[\text{Ni D}_3(\text{H})]^- + \text{LH}^+ \overset{K_{2\text{C}}}{\rightleftarrows} \underset{(\text{C}_1)}{[\text{Ni D}_3(\text{H})\text{LH}]} \xrightarrow{k'_{2\text{y}}} \text{products} \tag{6}$$

$$[\text{Ni D}_3(\text{H})\text{H}] + \text{LH}^+ \overset{K_{2\text{D}}}{\rightleftarrows} \underset{(\text{C}_2)}{[\text{Ni D}_3(\text{H})\text{H LH}]^+} \xrightarrow{k'_{2\text{z}}} \text{products} \tag{7}$$

whence it follows that

$$k_{2\text{y}} = \frac{k'_{2\text{y}}K_{2\text{C}}[\text{L}]_0}{1+K_{2\text{C}}[\text{L}]_0}, \tag{8}$$

$$\text{and}\qquad k_{2\text{z}} = \frac{k'_{2\text{z}}K_{2\text{D}}[\text{L}]_0}{1+K_{2\text{D}}[\text{L}]_0}. \tag{9}$$

From plots of $1/k_{2\text{y}}$ *vs.* $1/[\text{L}]_0$ and $1/k_{2\text{z}}$ *vs.* $1/[\text{L}]_0$, the values of the constants of Eqs. 8 and 9 have been resolved (Table 4). The values of k_{calcd}, estimated using these resolved constants, match well the k_{obsd} values (Fig. 1).

The two-protonated oxidant species appears to react several orders of magnitude faster than the one-protonated one even though the abundance of the former species is very much lesser than the latter in the conditions employed. One probable reason for this reactivity order may be the structural difference in the protonated species. Whereas the one-protonated species continues to be almost pseudooctahedral, the two-protonated Ni(IV) complex is an unstable "kinetic intermediate" with a ring-opened structure.[10a,d] The latter species is, therefore, more prone to react either by a substitution-controlled mechanism or by an outer-sphere route, resulting in a higher reactivity. This is also borne out of the fact that the magnitudes of $k_{2\text{y}}$ and $k_{2\text{z}}$ almost

Table 4. Average values of the various constants (Aqueous medium, 35 °C, $\mu=0.25$ M)

10^3[Hydrazine]$_0$/M	$10^4 k_{2y}$/s^{-1}	$10^{-2} k_{2z}$/s^{-1}
1	1.0	6
4	2.8	9
10	7.5	10
20	8.1	10.5
40	10.1	10.7
K_{1H}/M^{-1}	7.08×10^{10}	
K_{2H}/M^{-1}	4.46	
K_a/M	$10^{-8.1}$	
k'_{2y}/s^{-1}	1.3×10^{-3}	
K_{2c}/M^{-1}	$77(\approx10^{1.9})$	
k'_{2z}/s^{-1}	1.1×10^{3}	
K_{2D}/M^{-1}	1.2×10^{3} $(\approx10^{3.1})$	

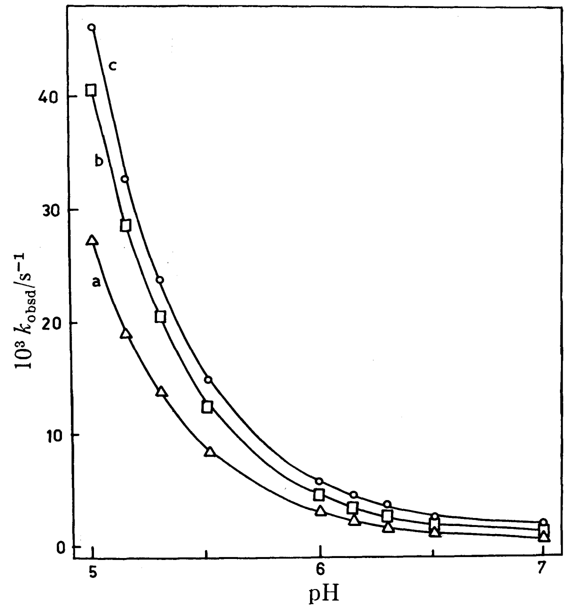


Fig. 1. The k_{obsd} *vs.* pH plots.
Aqueous medium, $\mu=0.25$ M, 35 °C, [Ni(IV)]$_0=(3-5)\times10^{-5}$ M, 10^3 [Hydrazine]$_0$/M : 1 (a), 4 (b), 10 (c) (representative). (The solid lines are drawn through the calculated values).

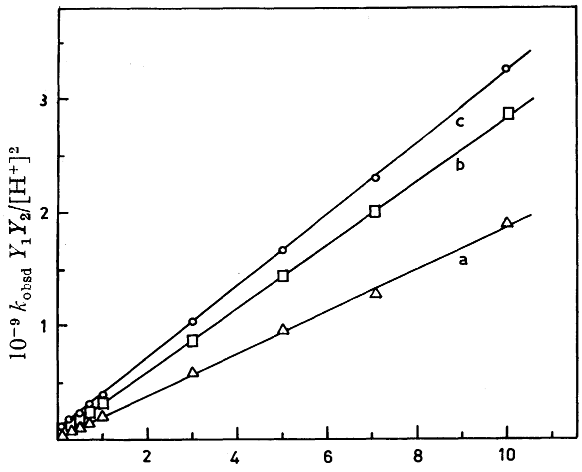


Fig. 2. The plots of k_{obsd} $Y_1Y_2/[H^+]^2$ *vs.* [H$^+$]. (*cf.*, text) Aqueous medium, $\mu=0.25$ M, 35 °C, [Ni(IV)]$_0=(3-5)\times10^{-5}$ M, 10^3 [Hydrazine]$_0$/M : 1 (a), 4 (b), 10 (c) (representative).

parallel (but are higher than) the k_{1d} and k_{2d} values pertaining to the one-protonated and two-protonated Ni(IV) complex respectively.

It is well established[15] that hydrazine transfers two electrons to an oxidant to form the diimide intermediate which on further very rapid two-electron loss gives nitrogen; the overall stoichiometry for this process would be e/[N$_2$H$_4$]=4. On the other hand, the loss of one electron (hydrogen atom) from hydrazine results in the incumbent hydrazyl radical,[8] two units of which give nitrogen and ammonia as products with a stoichiometric ratio of e/[N$_2$H$_4$]=1. The observed stoichiometry ratio

$$N_2H_4 - 2e \longrightarrow N_2H_2 + 2H^+ \tag{10}$$

$$N_2H_2 - 2e \longrightarrow N_2 + 2H^+ \tag{10a}$$

$$N_2H_4 - e \longrightarrow N_2H_4^{\cdot+} \longrightarrow N_2H_3 + H^+ \tag{11}$$

$$2N_2H_3 \longrightarrow 2NH_3 + N_2 \tag{11a}$$

(Δ[Ni(IV)]/Δ[hydrazine]) of $\approx$2 and nitrogen as the product of oxidation of hydrazine suggest that two-electron transfers might have taken place. If there would have been a discernible one-electron loss, two reactive species, Ni(III) and hydrazyl radical, would have been produced in the rate-limiting step for which the activation enthalpy would have been much too higher than what has been observed here.

Even though the kinetic observations have been most plausibly explained in terms of the rate equations (Eqs. 5—9), and the mechanism of an analogous redox reaction of Ni(IV) with phenylhydrazine was definitely established to be outer-sphere in nature,[10a] the actual mechanistic routes in the present redox system are complicated by several factors.

1. Whether C$_1$ and C$_2$ of Eqs. 6 and 7 represent (a) precursor complexes with inner-sphere substitution by the substrate unit at a ring-opened site of the Ni(IV) complex species (followed by rate-determining decomposition of the precursors with electron transfer), or (b) structures in which the Ni(IV) species and the substrate are held together (in an outer-sphere manner) by means of hydrogen bonding between a dioximate oxygen and a substrate unit, cannot be easily distinguished. Both routes (a) and (b) will exhibit almost negligible ionic strength effect and limiting kinetics at higher relative [L]$_0$, as have been observed.

2. Since the k_{obsd} values are tremendously retarded when the reactions are carried out in the presence of added EDTA (Table 1) and are enhanced in the presence of catalytic amounts of added aquacopper(II), an alternative to Scheme 1 can be written as in Scheme 2.

$$M^{n+} + LH^+ \overset{K_C}{\rightleftharpoons} [MLH]^{(n+1)+}$$

$$[MLH]^{(n+1)+} + [NiD_3(H)]^- \xrightarrow{k''_{2y}} \text{Intermediate products}$$

$$[MLH]^{(n+1)+} + [NiD_3(H)H] \xrightarrow{k''_{2z}} \text{Intermediate products}$$

$$\text{Intermediate products} + \text{Ni(IV)} \xrightarrow{\text{fast}} \text{products}$$

(M^{n+} represents the trace metal ion impurities present or Cu(II) added in catalytic concentrations).

Scheme 2.

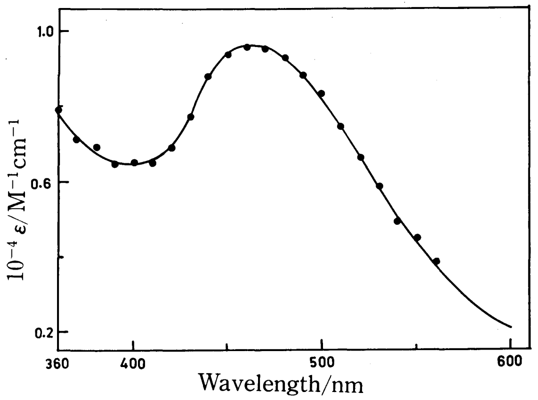


Fig. 3. Spectra of the nickel(IV) complex and reaction mixture.
Line: The Ni(IV) complex (1×10^{-4} M), points: the reaction mixture. ($[Ni(IV)]_0=1\times10^{-4}$ M, $[Hydrazine]_0 = 1\times10^{-3}$ M)
Aqueous medium, $\mu=0.25$ M, 35 °C, pH=7 (50 ms mode).

From the rate law of Scheme 2 it can be easily written that

$$k_{2y} = \frac{k''_{2y}K_C[L]_0}{1+K_C[L]_0} \tag{12}$$

and

$$k_{2z} = \frac{k''_{2z}K_C[L]_0}{1+K_C[L]_0}, \tag{13}$$

where k''_{2y} and k''_{2z} are the reaction constants of the metal ion-hydrazine complex with the one-protonated and two-protonated Ni(IV) complex under limiting (or trace impurity) concentrations of M^{n+}, and K_c is the formation constant of a 1 : 1 complex of metal ion and hydrazine. If the [L]-dependence of small quantities of k_{2y} (Eq. 12) is neglected, the K_c value from Eq. 3 is obtained as $\approx 10^{3.1}$ M^{-1} at 35 °C and $\mu=0.25$ M (K_c and K_{2D} being identical). The 1 : 1 complex of Cu(II)-N_2H_4 has a reported value[14] of $10^{3.18}$ at 30 °C and $\mu=1.0$ M of ClO_4^-. Since the presence of Cu(II) in the reaction at an impurity level of $10^{-8}-10^{-7}$ M cannot be ruled out, these two values appear to be in excellent agreement.

3. Point-by-point spectra of reaction mixtures on the stopped-flow apparatus (in the 380—550 nm range) at pH 5.2, 6.3 and 7.0 are not different from those of the original Ni(IV) under the same pH conditions. For example, Fig. 3 presents representative spectra of the original Ni(IV) complex and a reaction mixture containing the Ni(IV) complex and hydrazine at pH= 7, 35 °C and $\mu=0.25$ M in aqueous medium. The Aminco stopped-flow assembly used[10] has a nominal mixing time of 2 ms and the point-by-point absorbance values were recorded at 10 nm wavelength intervals using a time scale on 50 ms mode.

4. Many apparently "uncatalyzed" redox systems have actually been found to be metal ion-catalyzed.[16]

5. The reactivity of $[Ni(dmg)_3(H)H]$ being several order higher than that of $[Ni(dmg)_3(H)]^-$ is also compatible with Scheme 2.

The inherent complexities of the redox system studied and the kinetics observed make unambiguous assignment of the reaction scheme difficult. Schemes 1(a) or (b) and 2 appear equally probable. Since the formation of Cu(II)-hydrazine complexes are well established,[17] Scheme 2 appears more likely in the presence of catalytic concentrations of Cu(II). However, further probes are needed for a definite choice.

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