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Studies in Nickel(IV) Chemistry. V.[**] Kinetics of Electron Transfer in Redox Systems Containing Tris(dimethylglyoximato)-nickelate(IV), Hydroxylamine, and Catalytic Amounts of Copper(II) in Aqueous Alkaline Media

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Kinetics of electron transfer in the redox system containing hydroxylamine and tris(dimethylglyoximato)-nickelate(IV) ($[Ni(dmg)_3]^{2-}$), in the presence of catalytic amounts of added copper(II) ions, have been studied in aqueous medium in the pH range 8.04—11.81. The kinetics exhibit pseudo-zero-order disappearance of $[Ni(dmg)_3]^{2-}$ when excess $[NH_2OH]_0$ is present, in the presence and absence of added metal ions. While addition of Cu(II) results in significant catalysis, that of Co(II)/Co(III), Fe(II)/Fe(III), Ni(II) or Zn(II) does not. The pseudo-zero-order rate constants (k_0) are found to be linearly dependent on $[NH_2OH]_0$ and on added [Cu(II)]. The k_0 values register a decrease as $[OH^-]$ is increased in the pH range 8.04—*ca.*9.42, attaining a limiting value in the pH range *ca.* 9.8—*ca.*11.81. Results are interpreted in terms of a probable mechanism involving formation of precursor complexes from hydroxylamine and Cu(II) species, followed by rate-determining breakdown of the precursors with concomitant electron transfer. The Cu(II)·aq species reacts several orders of magnitude faster than the $Cu(OH)_2$·aq species. The Ni(IV) does not appear to have any kinetic role in the redox system and is involved only in rapid product formation steps. The stoichiometric ratios ($\Delta[Ni(IV)]/\Delta[NH_2OH]$) of *ca.* 1.0 in the lower pH region (7.8—8.6) and *ca.* 0.5 in the higher pH region (9.1—11.6) are explained in terms of differential product formation.

Hydroxylamine and its derivatives are versatile reducing agents and numerous reports are available on kinetics of their oxidation by various metal ions.[1–15] The electron transfer kinetics, as well as products of oxidation of hydroxylamine and their distribution and stoichiometry, are, among other factors, strongly pH-dependent, but most of these studies are restricted to reaction media of "acidic" pH conditions. A few studies[7,8,16] were, however, reported on metal ion-catalyzed reactions of hydroxylamine in aqueous alkaline media. Bridgart *et al.*[8] reported that the oxidation of hydroxylamine by alkaline hexacyanoferrate(III) exhibits first-order kinetics with respect to the initial stage of disappearance of hexacyanoferrate(III) and that the reaction is strongly catalyzed by copper(II). We have currently been interested[17–20] in the chemistry of tris(dimethylglyoximato)nickelate(IV), $[Ni(dmg)_3]^{2-}$ (dmg^{2-} =dimethylglyoximate dianion) and came across an early qualitative mention by Simek[21] that hydroxylamine and hydrazine effectively reduce Ni(IV)[22] by two-electron transfer. While studying the kinetics of oxidation of hydroxylamine by Ni(IV), we observed that the disappearance of Ni(IV) was always zero-order irrespective of the source of samples employed, and that the reactions were tremendously retarded in the presence of added edta.[23] To substantiate the suspected extensive metal ion-catalysis in the redox cycle, we have collected results of investigations on metal ion-catalyzed electron transfers involving hydroxylamine and Ni(IV) in aqueous media and are reporting them in this communication.

Experimental

Materials and Methods. Freshly prepared doubly distilled water, distilled from an all-glass apparatus containing a dilute solution (*ca.* 1×10^{-4} M) (1 M=1 mol dm^{-3}) of edta, was exclusively used for preparation of solutions and in kinetic runs. Characterization of $[Ni(dmg)_3]^{2-}$ and preparation of its aqueous solutions were performed as described earlier.[17,18] Hydroxylammonium chloride (Poole, England) was of guaranteed reagent grade, was recrystallized twice before use, and its solutions were freshly prepared; the solutions were standardized by the acid bromate method.[24] The substrate solutions were appropriately diluted and their pH adjusted, as required, when they were employed for kinetic runs. Fresh stock solutions of BDH AnalaR grade samples of MCl_2 (M= Cu, Fe, Ni, Co, or Zn) were prepared and standardized;[24] requisite amounts from the stock were taken to prepare M(II) solutions for kinetic runs. Other reagents were of analytical grade and were used as such. Standard buffer solutions were prepared in water using potassium salts (BO_3^{3-}—H^+/OH^-, acetate—OH^-, $H_2PO_4^-$—H^+/OH^-, and CO_3^{2-}—HCO_3^-).

The reactions were monitored for disappearance of Ni(IV) at 460 nm (ε_{460}=9,600 M^{-1} cm^{-1}), continuously as a function of time, in a VSU 2-P or Pye Unicam SP 1800 UV-VIS spectrophotometer or in an Aminco stopped-flow assembly as described previously.[17–19] In a typical run, an aqueous solution of Ni(IV) containing the metal ion at its requisite catalytic concentration was rapidly mixed[25] with the hydroxylamine solution at the appropriate temperature (±0.1 °C), ionic strength (μ, supporting electrolyte being KCl), and pH; the decrease in absorbance of Ni(IV) was monitored. The pH values of the reaction medium were maintained with standard buffers; they were determined by a Systronics 335 digital pH meter both before and after the reaction and the average (which did not differ by more than ±0.01 unit from the measured values) was taken into record. Correction for ionic strength contribution[26] was applied in calculating $[OH^-]$ from the average pH value. The pseudo-zero-order rate constants were calculated from least-squares fits of absorbance and time data in accordance with the following function which was found valid for the range over 90% of the disappearance of Ni(IV):

[**] Parts I—IV are Refs. 17—20.

$$(A_t - A_\infty) = (A_0 - A_\infty) - \varepsilon_{460}k_0t, \qquad (1)$$

where A_t, A_0, and A_∞, refer respectively to the absorbance at time t, the initial absorbance of Ni(IV) before commencement of reaction, and the absorbance at effective infinite time. $Ni(dmgH)_2$, a product from reduction of Ni(IV), was found to have a negligible absorbance at 460 nm. For the major part of Ni(IV) disappearance, the reaction medium was found to be homogeneous; slow precipitation of $Ni(dmgH)_2$ towards the later stage did not significantly influence the kinetics at least for three half-lives of reaction. The proton-assisted[17,19] and metal ion-mediated acid-decomposition[20] of Ni(IV) was negligible under the conditions of investigation. The k_0 values, calculated from data obtained through monitoring the disappearance of Ni(IV) at other wavelengths (440—480 nm), matched well those calculated similarly through monitoring the disappearance at 460 nm. Replicate runs (2 to 7) were reproducible to ±5%. Reproducibility (within ±10%) in zero-order rate constants in the uncatalyzed system was also observed when different freshly prepared stock solutions of the same samples were used and intercomparisons were made.

Computations were done using a DCM Data Products Minicomputer Microsystem 1121.

Results

Stoichiometry. The stoichiometric experiments were conducted in an inert atmosphere in the pH range 7.75—11.6. In experiments employing $[Ni(IV)]_0 \gtrsim [NH_2OH]_0$, the unreacted [Ni(IV)] was estimated spectrophotometrically (Table 1); 4×10^{-6} M of added Cu(II) was present in all the experiments. In experiments employing $[NH_2OH]_0 > [Ni(IV)]_0$, the reaction mixture was acidified with HCl after completion of reaction and the left-over $[NH_2OH]$ was estimated by rapid bromatometric titration.[24] (Under acidic conditions, the oxidation of $dmgH_2$ was found to be so slow as to be negligible.) The observed stoichiometric ratios, $\Delta[Ni(IV)]/\Delta[NH_2OH]$, of *ca.* 1.0 and *ca.* 0.5, would conform to the following equations:

$$2[Ni(dmg)_3]^{2-} + 2NH_2OH \xrightarrow{Cu(II)} 2[Ni(dmgH)_2] + 2\,dmg^{2-} + H_2O + N_2O, \qquad (2)$$

$$[Ni(dmg)_3]^{2-} + 2\,NH_2OH \xrightarrow{Cu(II)} [Ni(dmgH)_2] + dmg^{2-} + 2\,H_2O + N_2. \qquad (3)$$

In another set of experiments at pH 8.0, 8.6, 9.1, 10.4, and 11.5, a solution of Ni(IV) (0.2 M, 50 mL) was allowed to react with a solution of hydroxylamine (0.2 M, 50 mL) in the presence of 4×10^{-6} M of added Cu(II), and the produced gases were qualitatively identified by a gas chromatographic procedure[27] using a Packard 377 instrument. $Ni(dmgH)_2$ was identified by IR after being filtered from the reaction mixture, recrystallized, and dried.

Kinetics. Even though a pseudo-first-order excess of $[NH_2OH]_0$ over $[Ni(IV)]_0$ was maintained, the disappearance of Ni(IV) in the Ni(IV)–NH_2OH reaction never followed a first-order pattern as evidenced from nonlinearity of log $(A_t - A_\infty)$ *vs.* time plots. Instead, plots of A_t *vs.* time were perfectly linear for several half-lives of disappearance. The zero-order disappearance of Ni(IV) was observed irrespective of the source of the samples employed, and in the absence of any added

TABLE 1. STOICHIOMETRY DATA[a] FOR THE OXIDATION OF HYDROXYLAMINE
(Addded[Cu(Ni(II)]=(4—5)×10^{-6}, μ=0.25[b], and 35 °C)

pH	$10^5[Ni(IV)]_0$[c]	$10^5[NH_2OH]_0$[d]	$\frac{\Delta[Ni(IV)]}{\Delta[NH_2OH]}$[e]
7.75	2.6	2	1.04
7.8	14.1	4	1.02
7.85	3.8	2	1.01
8.0	10.0	50	0.9
8.24	14.1	4	0.85
8.3	2.6	2	0.88
8.6	5.3	4	1.04
8.6	10.0	50	0.8
9.1	14.1	4	0.53
9.5	10	50	0.55
10.43	2.6	2	0.65
10.5	10	50	0.55
11.4	3.8	4	0.50
11.4	14.1	4	0.52
11.5	2.6	2	0.51
11.61	5.3	6	0.50
11.6	14.1	4	0.51
11·6	10	50	0.51

a) Average of three determinations for each entry. b) All concentration units are expressed in M. c) Initial analytical concentration fixed by spectrophotometry. d) Initial analytical concentration fixed by the bromatometric titration. stoichiometric ratio of the [Ni(IV)] reacted to $[NH_2OH]$ reacted.

TABLE 2. AVERAGE[a] PSEUDO-ZERO-ORDER RATE CONSTANT FOR THE OXIDATION OF HYDOXYLAMINE

pH[c]	$10^2[NH_2OH]_0$	$\frac{10^8k'_0}{M\,s^{-1}}$	pH[c]	$10^2[NH_2OH]_0$	$\frac{10^8k'_0}{M\,s^{-1}}$
7.7	(1—1.2)	14.8	7.44	2	25.8
8.3		7.6	9.3	2	5.0
8.32		(7.3)[d]	9.3	2	4.5[e]
8.7		4.2	9.3	2	4.3[f]
8.75		3.6	9.3	2	2.5[g]
8.95		(3.5)	9.3	2	0.7[h]
9.05		3.3	9.35	0.4	1.1
9.1		(3.2)	9.35	1	2.6
9.2		3.1	9.35	1	(2.6)
9.25		(3.0)	9.35	2	(4.7)
10.6		2.4	9.35	3	6.8
11.3		2.3	9.35	10	24.9
11.7		2.3	9.83	2	4.6
11.7		(2.6)	12.25	3	5.8
11.9		2.3	12.6	3	4.1
11.9		(2.6)	12.77	3	4.6
12.0		2.4	12.78	3	(4.6)
13.0		2.0	12.85	3	5.0

a) Deviations from the average value of 2 to 4 replicates are within ±10%. b) All concentration units are expressed in M. c) Corrected pH. Buffers used (pH range): $H_2PO_4^-$—OH^- (7.4—7.7), BO_3^{3-}—H^+/OH^- (8.3—10.6), and HPO_4^{2-}—OH^- (11.3—13.0). d) Values in parentheses were obtained by employing different batches of solutions of the same samples. e—h) In the presence of 2×10^{-6}, 4×10^{-6}, 8×10^{-6}, and 20×10^{-6} M of added edta, respectively.

metal ion. There was progressive retardation of the pseudo-first-order rate constants (k_0', in the absence of any added metal ion) in the presence of added edta (Table 2) and this conformed to the empirical equation:

$$k_0' = p[\text{edta}]^{-1}/(1+q[\text{edta}]^{-1}), \tag{4}$$

where p and q are functions of NH_2OH, OH^-, and M^{n+} concentrations. (M^{n+} refers to metal ion impurities present in the reaction system). Thus there is significant metal ion-catalysis in the redox reaction.

Zero-order disappearance of Ni(IV) was also observed in the presence of a metal ion (M=Cu(II), Fe(II)/Fe(III), Ni(II), Co(II)/Co(III), or Zn(II)) added in small concentrations. Some representative plots are shown in Fig. 1. The pseudo-zero-order rate constants (k_0) were found to remain almost constant in the range $1\times10^{-5}\leq[\text{Ni(IV)}]_0\leq1.9\times10^{-4}$ M ($k_0 \gg k_0'$). The k_0 values were linearly dependent on $[NH_2OH]_0$ (Table 3) as well as on added [Cu(II)] (Table 4). The pH dependence of k_0 is presented in Table 5 and that of k_2 ($=k_0/([NH_2OH]_0\,[\text{Cu(II)}])$) in Fig. 2. In the range $11.81 \gtrsim \text{pH} \gtrsim 9.8$, k_0 registered a marginal increase by only *ca.* 7% for a hundred-fold decrease in $[OH^-]$, but the increase was more prominent below pH *ca.* 8.9.

The k_0 values were found to remain almost constant when different buffers were employed at the same pH (Table 5). The k_0 values were also insensitive to variation of ionic strength of the medium (Table 3), indicating that at least one of the reactants might be neutral in charge.

Table 3. AVERAGE[a] PSEUDO-ZERO-ORDER RATE CONSTANTS FOR THE OXIDATION OF HYDROXYLAMINE
($[\text{Ni(IV)}]_0=(4—6)\times10^{-5}$, added$[\text{Cu(II)}]=(5—6)\times10^{-7}$, $\mu=0.25$[b], and 35 °C)

pH[c]	$10^4[NH_2OH]_0$	10^8k_0[d]	pH[c]	$10^4[NH_2OH]_0$	10^8k_0[d]
8.5	5	21.7	9.0	5	5.2
	10	37.4		10	10.0
	10	90.8[e]		10	19.9[e]
	10	251[f]		10	40.2[f]
	10	33.8[g]		10	10.3[g]
	10	34.5[h]		10	10.1[h]
	10	35.1[i]		10	10.5[i]
	10	35.8[j]		10	9.8[j]
	15	50.3		20	19.5
	20	69.5		50	49.2
	30	106		100	95.4
	50	175		200	198
	100	350		400	400
	200	743		600	578
10.2[c]	1	0.5	10.2[c]	10	5.4[j]
	5	2.6		20	10.3
	7	3.6		50	25.6
	10	5.2		90	46.0
	10	10.0[e]		120	62.0
	10	18.7[f]		160	82.1
	10	5.5[g]		200	103
	10	5.1[h]		400	202
	10	5·2[i]		800	410

a) Deviations from the average value of 2 to 7 replicates are within ±5%. b) All concentration units are expressed in M. c) Corrected pH. Buffers used: BO_3^{3-}—H^+/OH^-. d) Units are $M\,s^{-1}$. e, f) At 40 and 45 °C, respectively. g) In the presence of 1×10^{-4} M of added acrylonitrile. h—j) At 0.1, 0.5, and 1.0 M of ionic strength, respectively.

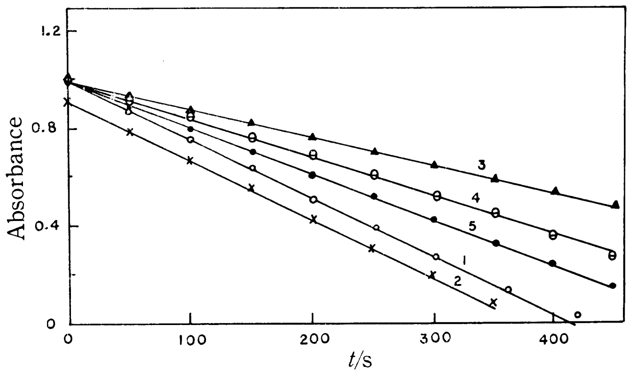

Fig. 1. Absorbance *vs.* time plots.
$[NH_2OH]_0=2\times10^{-3}$ M, $\mu=0.25$ M, 35 °C, Aqueous medium, $[M^{n+}]=2\times10^{-6}$ M.
1): Without added metal ion, pH=7.44; 2): Zn(II), pH=7.2; 3): Fe(II)/Fe(III), pH=7.6; 4): Co(II)/Co(III), pH=7.2; 5): Ni(II), pH=7.4.

Table 4. AVERAGF[a] PSEUDO-ZERO-ORDER RATE CONSTANTS FOR THE OXIDATION OF HYDROXYLAMINE
($[\text{Ni(IV)}]_0=(4—6)\times10^{-5}$, $[NH_2OH]_0=(1—1.1)\times10^{-3}$, $\mu=0.25$[b], 35 °C, and pH=10.2)

10^7[Cu(II)] (added)	$\frac{10^8k_0}{M\,s^{-1}}$
5	5.2
6	5.4
7	7.0
10	9.9
11	10.2
15	14.3
21	20.2
30	29.0
45	45.0
74	71.0

a) Deviations from the average value of 2 to 7 replicates are within ±5%. b) All concentration units are expressed in M.

The temperature dependence of k_0 was studied in the range 35—45 °C. The average values of the activation parameters $\Delta H^{\neq}$ (in kJ mol^{-1}) and $\Delta S^{\neq}$ (in J K^{-1} mol^{-1}) were calculated, respectively, to be 69 and −83 at pH=8.5, 47 and −165 at pH=9.0, and 43 and −184 at pH=10.2.

Table 6 compares the rate constants for the Ni(IV)–NH_2OH reaction in the presence of various added metal ions Ni(II), Fe(II)/Fe(III), Co(II)/Co(III), and Zn(II)). Cu(II) only appears to have a catalytic effect on the redox system.

Discussion

Mechanism and Rate Law. One scheme consistent with the observed kinetics can be given by Scheme 1. In the pH range of the study, hydroxylamine would

TABLE 5. AVERAGE RATE CONSTANTS FOR THE OXIDATION OF HYDROXYLAMINE
($[\mathrm{Ni(IV)}]_0=(4–6)\times10^{-5}$, $[\mathrm{NH_2OH}]_0=(1–1.1)\times10^{-3}$, added$[\mathrm{Cu(II)}]=(5–6)\times10^{-7}$, $\mu=0.25$[b], and 35 °C)

pH[c]	10^8k_0[d] / $\mathrm{M\,s^{-1}}$	$10^{-2}k_2$[e] / $\mathrm{M^{-1}\,s^{-1}}$	$10^{-2}k_2$ (calcd)[f] / $\mathrm{M^{-1}\,s^{-1}}$
8.04	103	20.6	22.1
8.15	83.3	16.7	15.6
8.23	69.4	13.9	12.2
8.31	59.5	10.9	9.8
8.32[g]	52.1	10.4	9.5
8.35	41.7	8.3	8.7
8.50	37.4	6.9	6.3
8.65	20.2	4.0	4.3
8.84	13.2	2.7	3.0
9.00	10.0	2.0	2.3
9.15	8.7	1.7	1.9
9.24	7.4	1.5	1.7
9.31	6.7	1.4	1.6
9.42	6.4	1.3	1.5
9.81	5.2	1.0	1.2
9.98[h]	5.2	1.0	1.1
10.06[i]	5.7	1.1	1.1
10.11	5.1	1.0	1.1
10.20	5.1	1.0	1.1
10.47[i]	5.4	1.1	1.1
11.04[j]	5.1	1.0	1.0
11.41[j]	5.1	1.0	1.0
11.81[j]	5.5	1.1	1.0

a) Deviations from the average value of 2 to 7 replicates are within ±5%. b) All concentration units are expressed in M. c) Corrected pH. Buffers used: $\mathrm{BO_3^{3-}}$-$\mathrm{H^+/OH^-}$ (unless otherwise mentioned). d) Observed pseudo-zero-order rate constants. e) $k_2=k_0/([\mathrm{NH_2OH}]_0[\mathrm{Cu(II)}])$. f) Calculated from a least-square fit of data to Eq. 10. g—j) Refer to buffers of acetate-$\mathrm{OH^-}$, $\mathrm{HCO_3^-}$-$\mathrm{CO_3^{2-}}$, $\mathrm{HCO_3^-}$-$\mathrm{OH^-}$, and $\mathrm{HPO_4^{2-}}$-$\mathrm{OH^-}$, respectively.

$$\begin{tikzcd}
\mathrm{Cu^{2+} + L} \arrow[r, rightleftharpoons, "K_{1c}"] \arrow[d, shift left, "\mathrm{OH^-}"] & \mathrm{[CuL]^{2+}} \arrow[r, "k_{1x}"] & \text{Intermediate products} \\
\mathrm{Cu(OH)^+ + L} \arrow[u, shift left, "K_1"] \arrow[r, rightleftharpoons, "K_{2c}"] \arrow[d, shift left, "\mathrm{OH^-}"] & \mathrm{[HOCuL]^+} \arrow[r, "k_{2x}"] & \text{Intermediate products} \\
\mathrm{Cu(OH)_2 + L} \arrow[u, shift left, "K_2"] \arrow[r, rightleftharpoons, "K_{3c}"] & \mathrm{[(HO)_2CuL]} \arrow[r, rightleftharpoons, "k_{3x}"] & \text{Intermediate products}
\end{tikzcd}$$

$$\text{Intermediate products} + \mathrm{Ni(IV)} \xrightarrow[\text{fast}]{k_p} \text{products}$$

($\mathrm{L = NH_2OH}$; aqua ligands are omitted for convenience.)

Scheme 1.

exist almost totally in the form of $\mathrm{NH_2OH}$ species since the proton-dissociation constant of $\mathrm{NH_3OH^+}$ is $10^{-5.8}$ M at 35 °C.[28] The values of K_1 and K_2 employed for the calculation in the present study are $1.6\times10^7\ \mathrm{M^{-1}}$ and $3.9\times10^{11}\ \mathrm{M^{-1}}$, respectively, assuming enthalpy changes with temperature for the steps of Eqs. 5 and 6 to be minimal. The K_1 value was calculated using the reported[29] constant K_5 for Eq. 5 and the ionic product of water K_w, and the K_2 value was calculated from Eq. 6 and the value of K_1:

$$\mathrm{Cu^{2+} + H_2O \rightleftharpoons [CuOH]^+ + H^+},\ K_5 = 10^{-6.8}\ \mathrm{M}, \tag{5}$$

$$\mathrm{Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-},\ K_6 = (K_1K_2)^{-1} = 1.6\times10^{-10}\ \mathrm{M^2}. \tag{6}$$

The operation of other equilibria,[29] Eqs. 7 and 8, related to this system was considered negligible in the experimental concentration ranges of Cu(II) and $\mathrm{OH^-}$ employed in the present investigation:

$$\mathrm{Cu(OH)_2 + 2OH^- \rightleftharpoons CuO_2^{2-} + 2OH_2},\ K_7 = 1.2\times10^{-3}\ \mathrm{M^{-2}}, \tag{7}$$

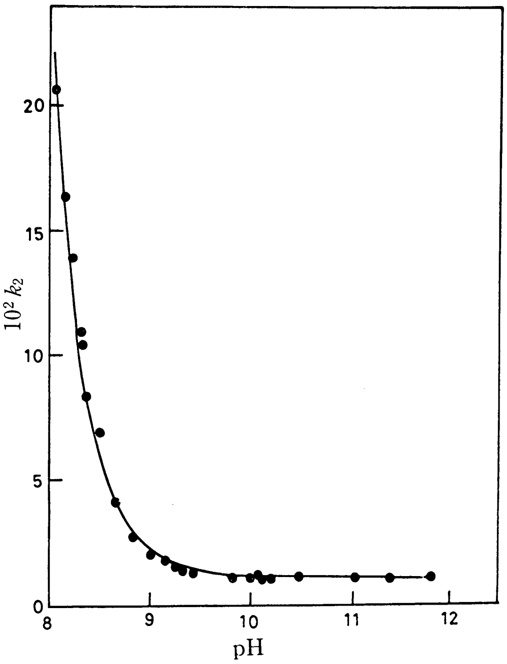

Fig. 2. The k_2 *vs.* pH Plot.
$k_2=k_0/([\mathrm{Cu(II)}][\mathrm{NH_2OH}]_0)$.
Point and line respectively refer to experimental and calculated k_2.

TABLE 6. AVERAGE PSEUDO-ZERO-ORDER RATE CONSTANTS FOR THE OXIDATION OF HYDROXYLAMINE
($[\mathrm{Ni(IV)}]_0=(4–6)\times10^{-5}$, $[\mathrm{NH_2OH}]_0=2\times10^{-2}$, $\mu=0.25$, and 35 °C)

Added metal Ion (M^{n+})	$10^6[\mathrm{M}^{n+}]$	pH	$10^8k_0/\mathrm{M\,s^{-1}}$
Co(II)/Co(III)	2	7.2	17.0
Fe(II)/Fe(III)	2	7.6	12.1
	2	8.6	7.0
	10	8.7	8.0
Ni(II)	2	6.6	40.0
	2	7.4	20.0
	2	9.7	4.1
	10	9.7	3.6
Zn(II)	2	7.2	25.0
	10	7.2	24.0

a) Deviations from the average value of 2 to 4 replicates are within ±5%. b) All concentration units are expressed in M.

$$2\,\mathrm{Cu^{2+}} + 2\,\mathrm{H_2O} \rightleftharpoons [\mathrm{Cu_2(OH)_2}]^{2+} + 2\mathrm{H^+},$$
$$K_8 = 1.38 \times 10^{-11}\,\mathrm{M}. \qquad (8)$$

If it is assumed that $k_{nx} \gg k_{-nc}$ (where k_{-nc} is defined by $K_{nc}=k_{nc}/k_{-nc}$), a rate law can be derived from Scheme 1 as follows:

$$\frac{k_0}{[\mathrm{Cu(II)}]_T[\mathrm{NH_2OH}} = \frac{k_{1x}K_{1c}+k_{2x}K_{2c}K_1[\mathrm{OH^-}]+k_{3x}K_{3c}K_1K_2[\mathrm{OH^-}]^2}{1+K_1[\mathrm{OH^-}]+K_1K_2[\mathrm{OH^-}]^2}, \qquad (9)$$

which on rearrangement becomes

$$\frac{k_0(1+K_1[\mathrm{OH^-}]+K_1K_2[\mathrm{OH^-}]^2)}{[\mathrm{Cu(II)}]_T[\mathrm{NH_2OH}]} = k_{1x}K_{1c} + k_{2x}K_{2c}K_1[\mathrm{OH^-}] + k_{3x}K_{3c}K_1K_2[\mathrm{OH^-}]^2. \qquad (10)$$

A least-squares fit of the data of Table 5 results in the values of $k_{1x}K_{1c}$, $k_{2x}K_{2c}$, and $k_{3x}K_{3c}$ as $(7.8\pm0.4)\times10^9$ $\mathrm{M^{-1}\,s^{-1}}$, $(4.6\pm0.2)\times10^8$ $\mathrm{M^{-1}\,s^{-1}}$, and $(1.0\pm0.4)\times10^2$ $\mathrm{M^{-1}\,s^{-1}}$, respectively. The calculated values of rate constants are found to match well those obtained experimentally, lending credence to the proposed rate law.

The envisaged mechanism in Scheme 1 depicts the reaction to proceed through equilibrium precursor complex formation involving the various species of Cu(II) and $\mathrm{NH_2OH}$ prior to rate-determining breakdown of the precursor complex(es) with concomitant electron transfer. The intermediate products containing Cu(I) species and $\mathrm{NH_2O\cdot}$ radical[15] are rapidly oxidized by Ni(IV) in subsequent kinetically insignificant step(s) (*i.e.*, the composite reaction constant $k_p \gg k_{nx}$), thus resulting in zero-order disappearance kinetics of Ni(IV).

The overall picture of product formation can be formulated as

$$2\mathrm{Cu(I)} + [\mathrm{Ni(dmg)_3}]^{2-} + 2\mathrm{H_2O} \longrightarrow$$
$$2\mathrm{Cu(II)} + [\mathrm{Ni(dmgH)_2}] + \mathrm{dmg^{2-}} + 2\mathrm{OH^-}, \qquad (11)$$
$$\mathrm{NH_2O\cdot} - \mathrm{e} \longrightarrow \mathrm{HNO} + \mathrm{H^+}, \qquad (12)$$
$$2\mathrm{HNO} \longrightarrow \mathrm{N_2O} + \mathrm{H_2O}, \qquad (13)$$
$$\mathrm{HNO} + \mathrm{NH_2OH} \longrightarrow \mathrm{N_2} + 2\mathrm{H_2O}, \qquad (14)$$
$$2\mathrm{NH_2O\cdot} \longrightarrow \mathrm{N_2} + 2\mathrm{H_2O}. \qquad (15)$$

The Cu(I) in Eq. 11 may either be a Cu(I) hydroxo species or a Cu(I)–$\mathrm{NH_2OH}$ complex. Equations 11—15 will be very rapid and the magnitudes of their rates relative to the rates of the reaction are such that the present redox system in a nitrogen atmosphere does not initiate polymerization of a radical-trapping agent, *viz.*, acrylonitrile, nor was there any significant influence of added acrylonitrile on rates of the reaction (Table 3). Nevertheless, the formation of radicals is not precluded on the basis of this negative finding, because if k_{12}, k_{13}, k_{14}, or $k_{15} \gg k_{\text{(induced polymerization)}}$, which is quite probable, the extent of the induced change may lie well below the limit of detectability, even under conditions favorable for this induced reaction, and also because that the absence of polymerization is not connected with a lack of radicals since measurements[30] show that in an acidic medium in the presence of dissolved oxygen, acrylonitrile does not polymerize even if the process is initiated by gamma-radiolysis or by thermal decomposition of peroxodisulfate.

It can be inferred from the stoichiometric experiments of Table 1 that the molar ratios of the reactants (and the product distribution) depend to a great extent on the ratio of the initial concentration of Ni(IV) to $\mathrm{NH_2OH}$ (at constant [Cu(II)]) and the pH of the reaction medium. The stoichiometric ratio of *ca.* 1.0 in the lower pH range (*ca.* 7.8—8.6) decreases to *ca.* 0.5 in the higher pH range (*ca.* 9.1—11.6) of the study. While $\mathrm{N_2O}$ appears to be the predominant product in the lower pH region, $\mathrm{N_2}$ is predominantly formed in the higher pH region. When $[\mathrm{NH_2OH}]_0$ is in excess over $[\mathrm{Ni(IV)}]_0$, there is a tendency to form more $\mathrm{N_2}$ in the lower pH region than is observed when $[\mathrm{Ni(IV)}]_0 \geq [\mathrm{NH_2OH}]_0$. The stoichiometric observations of the present study are in line with those predicted in several earlier reports.[15,16]

The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ at different pH values give some indication to the nature of the transition states formed in the reaction; the larger negative $\Delta S^{\neq}$ values at pH 9.0 and 10.2 are presumed to reflect an increased restriction in the transition state imposed by the formation of the (unstable) intermediate complex.

In deriving the rate law (Eq. 9), it was assumed that $k_{nc} \gg k_{-nc}$, *i.e.*, the precursor complex(es) would have only a limited stability under the conditions employed. In that event, the product of the equilibrium formation constant and the decomposition rate constant of the precursor complex, $K_{nc}k_{nx}$, is identifiable as a bimolecular second-order rate constant k'_{nx}. This assumption finds support from the observed kinetics which demonstrate that even over a wide range of $[\mathrm{NH_2OH}]_0$ (*viz.*, 800-fold at pH 10.2), the k_0 values do not show any tendency to saturate at high relative $[\mathrm{NH_2OH}]_0$.

The ligating properties of hydroxylamine have been shown earlier[31] and the formation of $[\mathrm{Cu(NH_2OH)}_n]^{2+}$ ($n=1$, 2, or 4) complexes is firmly established in many reaction systems such as the Cu(II)-catalyzed $[\mathrm{Fe(CN)_6}]^{3-}$–$\mathrm{NH_2OH}$ reaction,[8] the metal ion-catalyzed decomposition of hydroxylamine in strongly alkaline aqueous media,[16] and in oxidation reactions[9,10] of $\mathrm{NH_2OH}$ by Cu(II). However, the reported equilibrium constants[32] for the complexes of $[\mathrm{Cu(NH_2OH)}_n]^{2+}$ ($n=1$ or 2) should be strongly pH-dependent. In a recent report, the state of Cu(II) in solutions containing hydroxylamine has been well documented;[10] while in ethanolic solution the $[\mathrm{Cu(NH_2OH)}_n]^{2+}$ complexes appear to be stable, in aqueous solutions they decompose instantaneously with a tendency towards stabilization of Cu(I)–$\mathrm{NH_2OH}$ complexes.

Unfortunately, the Cu(II)–$\mathrm{NH_2OH}$ redox system could not independently be studied (to compare the results with those observed in the present study) due to the low molar absorptivity of Cu(II) and the precipitation of $\mathrm{Cu_2O}$ if high concentration of Cu(II) was employed. However, if the values of the (intercept)/(slope) of the plots of $[\mathrm{Cu(II)}]/k_0$ *vs.* $1/[\mathrm{NH_2OH}]_0$ are thought as representing the formation constants of the precursor in the medium, then the approximate values are ≤2, 40, and 220 (all expressed in $\mathrm{M^{-1}}$) at pH 10.2, 9.05, and 8.35, respectively. Even though much importance cannot be attached to these values (which have been obtained from small values of intercepts of the plots), their magnitudes show the relative order of stability of the precursors with respect to the pH of the medium. Incidentally, the formation constant of $[Cu(NH_2OH)]^{2+}$ has been reported as $10^{2.4}$ at 20 °C and $\mu=0.5$ M ($NaNO_3$) in aqueous medium.[32)]

The reaction rate remains almost constant when different buffers are employed at the same pH and hence the reaction is subject to general acid catalysis. General acid catalysis should be observed when $k_{17} \gg k_{-16}$ $[A^-]$ with respect to

$$[CuLOH]^{(n-1)+} + HA \underset{k_{-16}}{\overset{k_{16}}{\rightleftarrows}} [CuLOH_2]^{n+} + A^-, \qquad (16)$$

$$[CuLOH_2]^{n+} \xrightarrow{k_{17}} \text{products}. \qquad (17)$$

This inference also draws its testimony from the fact that in the present reaction system, the rate is accompanied by an increase when the pH is lowered. The magnitudes of the resolved rate constants ($k_{1x}K_{1c} > k_{2x}K_{2c} \gg k_{3x}K_{3c}$) do follow the trend predicted by the electrostatic theory and are much below the rate constant for the exchange of water from the first coordination sphere of $Cu^{2+}\cdot aq$ ion (*ca.* 8×10^9 s^{-1} at 25 °C),[33)] showing that the $Cu(II)$–NH_2OH precursors are indeed formed in the redox system.

In the reaction scheme presented, the Cu(II) species represent the aqua species. The dimethylglyoxime complexes of Cu(II) might be thought as being produced from a trace dimethylglyoxime impurity (which might have been produced due to proton-assisted decomposition[17,19)] or Cu(II)-mediated acid-decomposition[20)] of $[Ni(dmg)_3]^{2-}$). However, since the rates of the latter two reactions are insignificant in comparison with those of the present redox system, such a possibility, if at all exists, does not alter the discussion presented here. (The rate constants for proton-assisted decomposition of the $[Ni(dmg)_3]^{2-}$ range from 1.3×10^{-5} s^{-1} to 2.6×10^{-7} s^{-1} in the pH range 8.3—12.3 at 35 °C and $\mu=0.25$ M;[17,19)] the rate constant for Cu(II)-mediated acid-decomposition[20)] of Ni(IV) is 2.2×10^{-3} s^{-1} at 35 °C, $\mu=0.57$ M, pH=6.15, and $[Cu(II)]=4\times10^{-5}$ M).

The possibility of involvement of Cu(III) as an intermediate in the present system is also ruled out since strict zero-order kinetics in Ni(IV) have been observed. Moreover, the redox potential of Ni(IV)/Ni(III) (*ca.* 0.4 V)[34)] is not sufficient to oxidize $Cu(II)\cdot aq$ to $Cu(III)\cdot aq$.

It may be pertinent to remark here that in previous studies involving Cu(II)-catalyzed oxidation of hydroxylamine, the authors[6,8)] were either not interested in considering the pH dependence of rate or were silent on this aspect. Another aspect which needs mention is that, while the Cu(II)-catalyzed oxidation of hydroxylamine by hexacyanoferrate(III) in aqueous alkaline media[8)] exhibited first-order kinetics on $[Fe(CN)_6]^{3-}$ (with respect to the initial stage of disappearance of $[Fe(CN)_6]^{3-}$), the present system shows perfect zero-order kinetics with respect to several half-lives of disappearance of Ni(IV). Inasmuch as the oxidation potentials for the couples ($[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}=$ 0.36 V[29)] and $[Ni(dmg)_3]^{2-}/[Ni(dmgH)_2]=0.7$ V[35,36)] in aqueous alkaline solutions are comparable, the reason for the above behavior is not clear. Some probable explanation may lie in the different methods of analysis of the experimental rate data and/or in the fact that, whereas in the former system $[Fe(CN)_6]^{3-}$ (d^5 low-spin O_h) is capable of forming with Cu(II) (a d^9 system) a heteronuclear intermediate[37)] before the electron transfer process occurs, the $[Ni(dmg)_3]^{2-}$ (d^6 low-spin D_3) will participate only in rapid outer sphere oxidation of Cu(I) species and $NH_2O\cdot$ radicals formed. However, further probe appears necessary to authenticate the argument.

In sum, (1) the main course of the redox reaction involving $[Ni(dmg)_3]^{2-}$ and hydroxylamine is mediated by trace metal ion impurities present in solution and is strongly catalyzed by Cu(II); (2) the mechanism of the Cu(II)-catalyzed reaction proceeds through equilibrium formation of precursor complex and its rate-determining decomposition with concomitant electron transfer; (3) Ni(IV) does not have any kinetic role in the mechanism and is involved only in rapid product formation steps; (4) the hydroxo species of Cu(II) are less effective in catalysis of the redox system than the aqua species of Cu(II).

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