Kinetics of Oxidation of Hydrazine and of t-Butylhydrazine using Tris(dimethylglyoximato)nickelate(IV) in the Presence of Added Cu^{2+}(aq)

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The kinetics of the oxidation of hydrazine and t-butylhydrazine using tris(dimethylglyoximato)-nickelate(IV), $[Ni(dmg)_3]^{2-}$, in the presence of added Cu^{2+}(aq), and in the pH range 5.0—7.0 at 35 °C and I = 0.25 mol dm^{-3} in aqueous medium, follow pseudo-first-order and pseudo-zero-order disappearance of the Ni^{IV} complex, respectively. Results of the Cu^{2+}(aq)-promoted oxidation of hydrazine by $[Ni(dmg)_3]^{2-}$ are consistent with a probable scheme involving pH-dependent equilibrium formation of intermediate adducts between the Ni^{IV} and Cu^{II}–hydrazine complex species present in the solution and subsequent rate-determining electron transfer(s) to the adduct(s) from the hydrazine species in the presence of H^+. Results of the Cu^{2+}(aq)-catalyzed oxidation of t-butylhydrazine are interpreted in terms of a probable mechanism involving a rate-determining decomposition of the 1 : 1 intermediate complex between the Cu^{II} and t-butylhydrazine species in the solution, with a concomitant electron transfer. While the oxidation of hydrazine leads to nitrogen, the main products of the t-butylhydrazine oxidation are nitrogen and t-butyl alcohol.

Recently we have been interested [1–4] in the chemistry of tris(dimethylglyoximato)nickelate(IV), $[Ni(dmg)_3]^{2-}$. An early qualitative report [5] states that hydroxylamine and hydrazine effectively reduce a 'nickel(IV)' complex by two-electron transfer. However, it was recently observed that the kinetics of the oxidation of hydroxylamine [6] using $[Ni(dmg)_3]^{2-}$ in aqueous medium followed a pseudo-zero-order disappearance of Ni^{IV} both in the absence and presence of added Cu^{2+}(aq) and that the reactions were subject to extensive Cu^{2+}(aq) catalysis. While the kinetics of the oxidation of phenylhydrazine by $[Ni(dmg)_3]^{2-}$ in the absence of added metal ions exhibited a unit-order dependence [7] on the disappearing Ni^{IV} (the pseudo-first-order rate constants being only marginally influenced in the presence of ethylenediaminetetra-acetate), the same for the phenylhydrazine oxidation were seen to become pseudo-zero-order [8] in Ni^{IV} in the presence of added Cu^{II}. A preliminary study of the $[Ni(dmg)_3]^{2-}$–hydrazine reaction [9] showed that the disappearance kinetics of the Ni^{IV} complex were pseudo-first-order and the rates were accelerated in the presence of added Cu^{2+}(aq). We present in this paper the results of the oxidation of hydrazine (L^1) and of t-butylhydrazine (L^2) using $[Ni(dmg)_3]^{2-}$ in the presence of added Cu^{2+}(aq), in aqueous medium at 35 °C and an ionic strength of 0.25 mol dm^{-3}.

Experimental

Materials.—Freshly prepared doubly-distilled water, distilled from an all-glass apparatus containing a dilute solution of ethylenediaminetetra-acetate, $Na_2(H_2edta)$ (*ca.* 1×10^{-4} mol dm^{-3}), was used exclusively for the preparation of solutions and in kinetic runs. Preparation and characterization of $K_2[Ni(dmg)_3]$ and its aqueous solutions were as reported earlier; [1,2] freshly prepared aqueous solutions of the complex were employed. Hydrazinium chloride (B.D.H., AnalaR) and t-butylhydrazine (E. Merck) were recrystallized twice before use, their solutions were freshly prepared, and standardized by the acid bromate method.[10] The substrate solutions were appropriately diluted and their pH adjusted, as required, when employed for kinetic runs. Fresh stock solutions of a B.D.H. (AnalaR) grade sample of $CuCl_2$ were prepared and standardized; [11] requisite amounts from the stock were taken to prepare Cu^{2+}(aq) solutions for kinetic runs. In experiments conducted in the presence of Cu^{II}, the following procedures were adopted. Small concentrations of Cu^{II} were taken, immediately before use, either (*a*) along with the solution containing the substrate or (*b*) along with the aqueous solution of $[Ni(dmg)_3]^{2-}$; a known aliquot of one reactant solution was mixed with an equal volume of the other at the desired temperature (±0.1 °C), pH, and ionic strength (I, the supporting electrolyte being KCl), and the progress of the reaction monitored. (*c*) In a set of representative runs, Cu^{II}, substrate, and Ni^{IV} solutions were taken in separate precalibrated syringes and allowed rapidly to mix at the same time in the cell (so as to obtain a constant volume) by a fast motor-driven device, and the disappearance of the Ni^{IV} complex was followed. The kinetic results in all the three cases remained almost the same and were also independent of the order of mixing of the solutions. Other reagents used were of reagent grade. Standard buffer solutions were prepared in water. The pH values were recorded before and after the reactions, and found to be reproducible; a correction due to ionic strength effect [12a] was applied in calculating $[H^+]$ from the mean pH. Throughout the work, the pH refers to the corrected mean value (±0.01 unit). Buffers used (pH range) were potassium hydrogen phthalate–KOH (5.0—6.0) and $K[H_2PO_4]$–KOH (6.0—7.0).

Kinetics.—Reactions were monitored for the disappearance of the Ni^{IV} complex at 460 nm (ε_{460} = 9 600 dm^3 mol^{-1} cm^{-1}), as described earlier.[2–4] Pseudo-first-order [2–4] and pseudo-zero-order [6] rate constants were calculated using the usual expressions and were found to remain almost constant for more than three half-lives of Ni^{IV} disappearance in the ranges: 1×10^{-5}—1.4×10^{-4} mol dm^{-3} of initial concentration of $[Ni(dmg)_3]^{2-}$ ($[Ni^{IV}]_0$), 440—480 nm, I = 0.25—1.0 mol dm^{-3}, or when the reactions (in representative runs) were conducted in a nitrogen atmosphere. The rate constants were significantly retarded in the presence of $Na_2(H_2edta)$, but they remained practically unaltered in the presence of acrylonitrile (in a nitrogen atmosphere). Rate constants in replicate runs (two to seven) were reproducible to ±5%. Reproducibility in rate constants was also observed when different batches of the freshly prepared stock solutions of the same samples were used and intercomparison was possible. The rates for the proton-assisted [2] and those for the Cu^{II}-mediated acid-decomposition [3] reactions were negligible, compared to the

Table 1. Pseudo-first-order rate constants for the oxidation of hydrazine (L^1) by $[Ni(dmg)_3]^{2-}$ in the absence of added metal ion; $[Ni^{IV}]_0 = (3—5) \times 10^{-5}$ mol dm^{-3}

		$10^3k_{uo}/s^{-1}$				
pH	$10^3[L^1]_0$/mol dm^{-3} =	1	4	10	20	40
5.0		27 ± 1	40 ± 2	46 ± 2	47 ± 2	49 ± 2
5.15		19 ± 1	28 ± 1	32 ± 1	34 ± 1	35 ± 1
5.15 [a]		0.8 ± 0.03	—	1.3 ± 0.05	—	—
5.3		14 ± 0.6	20 ± 1	23 ± 1	24 ± 1	25 ± 1
5.52		8 ± 0.4	12 ± 0.4	14 ± 0.7	15 ± 0.7	15 ± 0.6
			(12 ± 0.4) [b]			
6.0		2.8 ± 0.1	4.2 ± 0.1	5.5 ± 0.2	5.5 ± 0.2	5.7 ± 0.3
6.15		2.0 ± 0.1	3.0 ± 0.1	4.5 ± 0.2	4.5 ± 0.1	4.5 ± 0.2
6.15 [a]		0.1 ± 0.004	—	0.2 ± 0.009	—	—
6.3		1.3 ± 0.06	2.2 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	3.2 ± 0.2
			(2.1 ± 0.1) [b]			
6.52		0.9 ± 0.04	1.4 ± 0.07	2.3 ± 0.1	2.3 ± 0.1	2.4 ± 0.1
6.52 [a]		—	0.06 ± 0.003	0.09 ± 0.004	—	—
7.0		0.4 ± 0.01	0.6 ± 0.02	1.4 ± 0.06	1.4 ± 0.06	1.4 ± 0.07
			(0.6 ± 0.03) [b]			

[a] In the presence of 6×10^{-5} mol dm^{-3} added $Na_2(H_2edta)$. [b] In the presence of 1×10^{-4} mol dm^{-3} acrylonitrile (N_2 atmosphere).

rates of the present investigation, under the conditions employed. {For example, the pseudo-first-order rate constants for the proton-assisted decomposition (k_{ad}) and those for the Cu^{II}-mediated acid decomposition [k_{dec}(Cu)] of the Ni^{IV} complex in the absence of the substrates had the following average values in aqueous medium at 35 °C and $I = 0.25$ mol dm^{-3}: $k_{ad} = 1.6 \times 10^{-3}—2.3 \times 10^{-5}$ s^{-1} (pH 5.1—7.1); k_{dec}(Cu) (with added $[Cu^{II}] = 6 \times 10^{-6}$ mol dm^{-3}) = 1.9×10^{-4} s^{-1} (pH 5.0), 4.8×10^{-4} s^{-1} (pH 5.6), and 3.8×10^{-5} s^{-1} (pH 7.0).} All kinetic data reported are at 35 °C and $I = 0.25$ mol dm^{-3} in aqueous medium.

Stoicheiometry and Products.—Stoicheiometric runs were conducted using solutions previously flushed with nitrogen gas. In a set of experiments at each of the pH values of 5.3, 6.2, and 7.0 and with $[Ni^{IV}]_0 > [L^1]_0$ ($[Ni^{IV}]_0 = 0.8 \times 10^{-4}—1.6 \times 10^{-4}$ mol dm^{-3}, $[L^1]_0 = 0.1 \times 10^{-4}—0.6 \times 10^{-4}$ mol dm^{-3}), the unreacted Ni^{IV} was spectrophotometrically estimated at the end of the reactions. Keeping $[L^1]_0 > [Ni^{IV}]_0$ ($[L^1]_0 = 1 \times 10^{-3}—4 \times 10^{-3}$ mol dm^{-3}, $[Ni^{IV}]_0 = 0.4 \times 10^{-3}—1 \times 10^{-3}$ mol dm^{-3}), the remaining L^1 was estimated by the acid bromate method. One mol of hydrazinium(1+) was found to have reacted with 2.0 ± 0.1 mol of the Ni^{IV} complex [equation (i)].

$$N_2H_5^+ + 2\,[Ni(dmg)_3]^{2-} + 3H^+ \longrightarrow N_2 + 2\,[Ni(Hdmg)_2] + 2\,H_2dmg \quad \text{(i)}$$

Nitrogen was qualitatively identified by a gas-chromatographic procedure. The other products were identified by a procedure similar to that described previously.[2] Tests for ammonia by Nessler's reagent method[12b] gave negative results. The stoicheiometric and product results were almost the same when the runs were conducted in the presence of small concentrations of Cu^{2+}(aq) ($[Cu^{II}] = 2 \times 10^{-6}—6 \times 10^{-6}$ mol dm^{-3}).

One moi of t-butylhydrazinium(1+) was found to have reacted with 2.0 ± 0.2 mol of the Ni^{IV} complex [equation (ii)] under the conditions: $[Ni^{IV}]_0 > [L^2]_0$ ($[Ni^{IV}]_0 = 0.8 \times 10^{-4}—1.6 \times 10^{-4}$ mol dm^{-3}, $[L^2]_0 = 1 \times 10^{-5}—6 \times 10^{-5}$ mol dm^{-3}) at pH 5.1, 6.0, or 7.0.

$$Bu^tNHNH_3^+ + 2\,[Ni(dmg)_3]^{2-} + 3\,H^+ + H_2O \longrightarrow Bu^tOH + N_2 + 2\,[Ni(Hdmg)_2] + 2\,H_2dmg \quad \text{(ii)}$$

In another set of experiments at pH 6 or 7, a solution of the Ni^{IV} complex (0.04 mol, 50 cm^3) was allowed to react with a solution of L^2 (0.02 mol, 50 cm^3) in the presence of added Cu^{II} (5×10^{-6} mol dm^{-3}). Evolution of nitrogen gas and the formation of $[Ni(Hdmg)_2]$, which slowly precipitates from the solution towards the end of the reaction, were observed. After the reaction was complete, a dilute solution of nickel(II) chloride was added and the precipitate of $[Ni(Hdmg)_2]$ was filtered off, washed, dried, and identified by i.r. spectroscopy.[2] The filtrate was brought to pH *ca.* 7, repeatedly extracted with small portions of light petroleum (b.p. 40—60 °C), and the extract was subjected to gas-chromatographic analysis. The major product obtained was t-butyl alcohol.

Stoicheiometric experiments were also conducted, in representative runs in the absence of Ni^{IV}, employing $[Cu^{II}]_0 > [L^2]_0$ (*e.g.*, $[Cu^{II}]_0 = 5 \times 10^{-2}—0.1$ mol dm^{-3}, $[L^2]_0 = 5 \times 10^{-3}—1 \times 10^{-2}$ mol dm^{-3}, pH 5). At the end of the reaction, the unreacted Cu^{II} was determined iodometrically after appropriate adjustments of the reaction solutions. One mol of $(HL^2)^+$ was found to have reacted with 4.0 ± 0.4 mol of Cu^{II}. Nitrogen and t-butyl alcohol were also qualitatively identified as the products of the oxidation of $(HL^2)^+$.

Proton-dissociation Constants.—The first proton-dissociation constants (K_a) of the substrates were determined potentiometrically in an atmosphere of nitrogen gas with a Systronics 335 digital pH meter. The values of pK_a were found to be 8.0 ± 0.2 for $N_2H_5^+$ and 8.1 ± 0.2 for $Bu^tNHNH_3^+$, respectively, at 35 °C and $I = 0.25$ mol dm^{-3} (KCl) in aqueous medium, in agreement with earlier reported values for $N_2H_5^+$ [13,14] and $MeNHNH_3^+$.[15]

Results

The Cu^{2+}*(aq)-promoted* $[Ni(dmg)_3]^{2-}$*-Hydrazine Reaction.*—The kinetics of the oxidation of hydrazine (L^1) by $[Ni(dmg)_3]^{2-}$, both in the absence and presence of added Cu^{2+}(aq), exhibited a perfect pseudo-first-order disappearance of Ni^{IV}. The values of the pseudo-first-order rate constant ($k_{obs.}$) for the oxidation of hydrazine in the *presence* of added Cu^{II} were higher than the values of k_{uo} (the pseudo-first-order rate constants in the *absence* of added metal ions, presented in Table 1) under similar conditions of $[L^1]_0$, pH, temperature, and I. The pseudo-first-order rate constants corresponding to

Table 2. Pseudo-first-order rate constants for the Cu^{II}-promoted oxidation of hydrazine by $[Ni(dmg)_3]^{2-}$; $[Ni^{IV}]_0 = (3—5) \times 10^{-5}$ mol dm^{-3}, added $[Cu^{II}] = 2 \times 10^{-6}$ mol dm^{-3}

pH	$10^3[L^1]_0$/ mol dm^{-3}	$10^3k_{obs.}$/s^{-1}	10^3k_{pr}/s^{-1} [a]	$k_{pr}/[L^1]_0$ (dm^3 mol^{-1} s^{-1})
5.0	4	129 ± 4	89	21.5 ± 0.2
	10	257 ± 7	211	
	20	470 ± 20	423	
	40	900 ± 40	851	
5.15	4	91 ± 3	63	15.2 ± 0.3
	10	180 ± 5	148	
		(52 ± 2) [b]	(51) [b]	
	20	337 ± 8	303	
	40	640 ± 20	606	
5.3	4	65 ± 2	45	10.9 ± 0.2
	10	130 ± 4	107	
	20	240 ± 10	216	
	40	460 ± 10	435	
5.52	4	39 ± 1	27	6.6 ± 0.1
	10	79 ± 2	65	
	20	147 ± 4	132	
	40	280 ± 7	265	
6.0	4	14 ± 0.4	9.8	2.34 ± 0.02
	10	29 ± 0.7	23.5	
	20	52 ± 2	46.6	
	40	99 ± 3	93	
6.15	4	10 ± 0.3	7.0	1.70 ± 0.02
	10	21 ± 0.5	16.5	
		(5 ± 0.2) [b]	(4.8) [b]	
	20	38 ± 1	33.2	
	40	73 ± 3	69	
6.3	4	7 ± 0.2	4.8	1.34 ± 0.03
	10	16 ± 0.5	13.2	
	20	30 ± 1	26.8	
	40	57 ± 3	53.8	
6.52	4	4.7 ± 0.1	3.3	0.81 ± 0.01
		(0.8 ± 0.04) [b]	(0.74) [b]	
	10	11 ± 0.3	8.7	
		(3 ± 0.1) [b]	(2.9) [b]	
	20	18 ± 0.5	15.7	
	40	35 ± 1	32.6	
7.0	4	2 ± 0.1	1.4	0.39 ± 0.01
	10	6 ± 0.2	4.4	
	20	9 ± 0.2	7.6	
	40	17 ± 0.4	15.6	

[a] $k_{pr} = k_{obs.} - k_{uo}$. The k_{uo} values are listed in Table 1. [b] In the presence of 6×10^{-5} mol dm^{-3} $Na_2(H_2edta)$.

the Cu^{II}-promoted oxidation of hydrazine by $[Ni(dmg)_3]^{2-}$, k_{pr}, were obtained using equation (iii).

$$k_{pr} = k_{obs.} - k_{uo} \qquad \text{(iii)}$$

Table 2 lists $k_{obs.}$ and k_{pr} at different $[L^1]_0$ and pH. The k_{pr} values were almost linearly dependent on $[L^1]_0$ in the range employed. [Since the concentrations of hydrazine taken were much higher than those of Cu^{II}, the concentrations of Cu^{II}–L^1 complexes (see later) in aqueous medium were assumed to be negligible compared to those of hydrazine.] A plot of $k_{pr}/[L^1]_0$ *vs.* pH registered a steep decrease with increasing pH, but the decrease tended to become almost minimal with increasing pH at higher relative pH values (Figure 1).

The dependence of k_{pr} on added $[Cu^{II}]$ with variable pH is presented in Table 3 and Figure 2. k_{pr} increased with increasing amounts of added $[Cu^{II}]$, but showed a tendency towards saturation at higher relative $[Cu^{II}]$ in the range employed. The saturation effect was dependent on pH as seen from the values of intercept/slope, (intercept/*m*), from the plots of $1/k_{pr}$ *vs.* $1/[Cu^{II}]$, which are listed in Table 3.

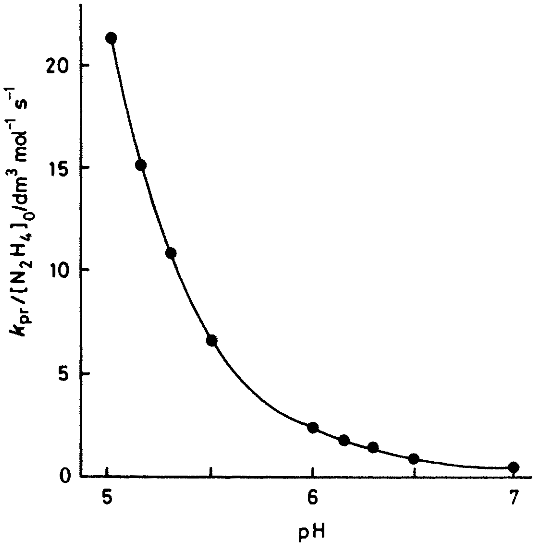

Figure 1. Plot of $k_{pr}/[N_2H_4]$ *vs.* pH. Added $[Cu^{II}] = 2 \times 10^{-6}$ mol dm^{-3}. The solid line is drawn through the calculated values

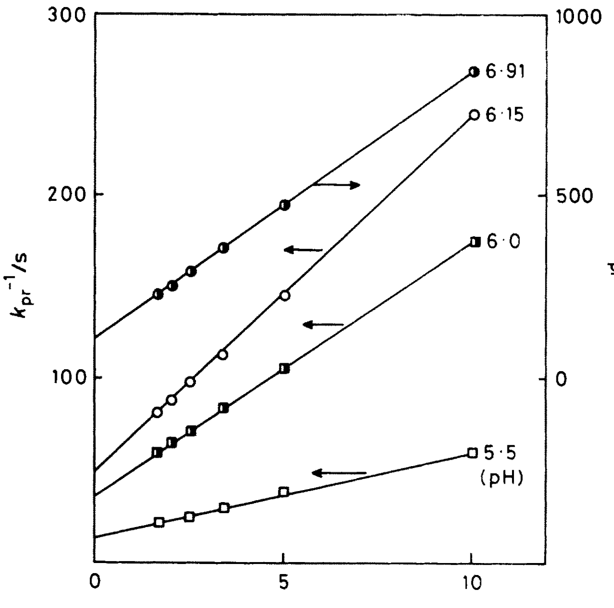

Figure 2. Plots of k_{pr}^{-1} *vs.* $[Cu^{II}]^{-1}$ at various pH; $[N_2H_4]_0 = 4 \times 10^{-3}$ mol dm^{-3}

The observed kinetic data of the Cu^{II}-promoted oxidation of hydrazine by $[Ni(dmg)_3]^{2-}$ can be rationalized in terms of Scheme 1. The Scheme envisages pH dependent equilibrium interactions of various species of Ni^{IV} with the (1 : 1) intermediate complex of Cu^{II} and hydrazine, existing in the solution under the employed conditions, to form adducts; the electron transfer from the reductant species to the latter, in the presence of H^+, may constitute the rate-controlling step(s). If it can be assumed that the reactions involving the $[Ni(dmg)_3]^{2-}$, $Cu(OH)^+(aq)$ and L^1 species have negligible contribution to the overall reaction in the pH range employed, a rate law [equation (iv)] can be derived from Scheme 1 which reduces to equation (v) (where k_{nx} and K_{An} are pH-dependent quantities) as $(1 + K_{2H}[H^+]) \approx 1$, $([H^+] + K_a) \approx [H^+]$,

Table 3. Pseudo-first-order rate constants for the Cu^{II}-promoted oxidation of hydrazine by $[Ni(dmg)_3]^{2-}$; $[Ni^{IV}]_0 = (3—5) \times 10^{-5}$ mol dm^{-3}, $[L^1]_0 = 4 \times 10^{-3}$ mol dm^{-3}

pH	10^6 [Cu^{II}]/ mol dm^{-3} (added)	10^3 $k_{obs.}$/s^{-1}	10^3 k_{pr}/s^{-1} [a]	10^{-5} (intercept/m)/ dm^3 mol^{-1} [b]
5.5	0	(12 ± 0.4) [c]		
	1	29 ± 1	17	
	2	39 ± 1	27	
	3	47 ± 1	35	
	4	52 ± 1	40	
	5	56 ± 2	44	
	6	59 ± 2	47	2.88
6.0	0	(4.2 ± 0.1) [c]		
	1	10 ± 0.2	5.8	
	2	14 ± 0.4	9.8	
	3	16 ± 0.5	11.8	
	4	18 ± 0.7	13.8	
	5	20 ± 0.6	15.8	
	6	21 ± 0.7	16.8	2.68
6.15	0	(3.0 ± 0.1) [c]		
	1	7 ± 0.3	4	
	2	10 ± 0.3	7	
	3	12 ± 0.4	9	
	4	13 ± 0.4	10	
	5	14 ± 0.3	11	
	6	15 ± 0.6	12	2.50
6.91	0	(0.8 ± 0.02) [c]		
	1	2.0 ± 0.06	1.2	
	2	2.9 ± 0.1	2.1	
	3	3.6 ± 0.1	2.8	
	4	4.2 ± 0.1	3.4	
	5	4.6 ± 0.1	3.8	
	6	5.0 ± 0.2	4.2	1.55

[a] $k_{pr} = k_{obs.} - k_{uo}$. [b] The average values of intercept/slope of the plots of $1/k_{pr}$ *vs.* 1/[Cu^{II}]. [c] Value of k_{uo}.

$$(HL^1)^+ \overset{K_a}{\rightleftharpoons} L^1 + H^+$$

$$Cu^{2+}(aq) \overset{K_{Cu}}{\rightleftharpoons} Cu(OH)^+(aq) + H^+$$

$$Cu^{2+} + (HL^1)^+ \overset{K_C}{\rightleftharpoons} [Cu(HL^1)]^{3+}$$

$$[Ni(dmg)_3]^{2-} \xrightleftharpoons{H^+,\ K_{1H}} [Ni(dmg)_3(H)]^- \xrightleftharpoons{H^+,\ K_{2H}} [Ni(dmg)_3(H)H]$$

$$[Ni(dmg)_3(H)]^- + [Cu(HL^1)]^{3+} \xrightleftharpoons[H^+]{K_{A1}} \text{adduct} \xrightarrow[k_{1x}]{(HL^1)^+,\ H^+} \text{intermediate products}$$

$$[Ni(dmg)_3(H)H] + [Cu(HL^1)]^{3+} \xrightleftharpoons[H^+]{K_{A2}} \text{adduct} \xrightarrow[k_{2x}]{(HL^1)^+,\ H^+} \text{intermediate products}$$

Scheme 1. Aqua ligands have been omitted for convenience; $K_{1H} = 7.08 \times 10^{10}$ dm^3 mol^{-1} and $K_{2H} = 4.46$ dm^3 mol^{-1} (ref. 2)

Table 4. Average values of the resolved constants for the Cu^{II}-promoted oxidation of hydrazine by $[Ni(dmg)_3]^{2-}$

Constant	Value
K_{A1}	7×10^{-3}
k_{1x}/dm^6 mol^{-2} s^{-1}	5.7×10^7
$k_{1x}K_{A1}$/dm^6 mol^{-2} s^{-1}	4×10^5
K_{A2}	6.7×10^4
k_{2x}/dm^6 mol^{-2} s^{-1}	5.7×10^6
$k_{2x}K_{A2}$/dm^6 mol^{-2} s^{-1}	3.8×10^{11}
K_{Cu}/mol dm^{-3}	$10^{-6.85}$

$$k_{pr} = \left[\frac{[L^1]_0^2[H^+]^2}{(K_a + [H^+])^2}\right] \cdot \left[\frac{(k_{1x}K_{A1}K_C[H^+] + k_{2x}K_{A2}K_{2H}K_C[H^+]^2)(K_a + [H^+])[Cu^{II}][H^+]}{[H^+](K_{Cu} + [H^+])(1 + K_C[L^1]_0)(1 + K_{2H}[H^+])(K_a + [H^+]) + \{(K_{A1}K_C[H^+] + K_{A2}K_{2H}K_C[H^+]^2)[Cu^{II}][L^1]_0[H^+]\}}\right] \quad \text{(iv)}$$

and $(1 + K_C[L^1]_0) \approx K_C[L^1]_0$ [*viz.*, $K_C = 10^{3.18}$ dm^3 mol^{-1} (ref. 13)—$10^{4.2}$ dm^3 mol^{-1} (ref. 14)], under the experimental conditions employed.

$$k_{pr} \approx \frac{(k_{1x}K_{A1} + k_{2x}K_{A2}K_{2H}[H^+])[Cu^{II}][L^1]_0[H^+]}{(K_{Cu} + [H^+]) + (K_{A1} + K_{A2}K_{2H}[H^+])[Cu^{II}]} \quad \text{(v)}$$

Treatment of the data furnished the various resolved constants, the average values of which are listed in Table 4. Calculated values of $k_{pr}/[L^1]_0$ thus obtained agreed well with the observed $k_{pr}/[L^1]_0$ values (Figure 1). The average value of K_{Cu}, calculated as *ca.* $10^{-6.85}$ mol dm^{-3} at 35 °C, is in good agreement with the reported value[16] of $10^{-6.8}$ mol dm^{-3} at 25 °C if it is assumed that the enthalpy variation of K_{Cu} is negligible in this small temperature range.

Even though much importance cannot be attached to the values of the statistically resolved constants for such a complicated reaction system, some qualitative comparison of the reactivity orders can be made. For example, it appears that the involvement of the diprotonated species, $[Ni(dmg)_3(H)H]$, is several orders of magnitude higher than the monoprotonated Ni^{IV} species, $[Ni(dmg)_3(H)]^-$, in the Cu^{II}-promoted oxidation of hydrazine (as $K_{A2} \gg K_{A1}$ and $k_{2x}K_{A2} \gg k_{1x}K_{A1}$). It has been shown earlier[2] that the first (outside) protonation of $[Ni(dmg)_3]^{2-}$ occurs (without much alteration of the pseudo-octahedral structure of the complex) at a dioximate oxygen forming an intramolecular hydrogen-bonding network, O–H ··· O, between dioximate oxygens of two ligands, and the second protonation most probably takes place *via* a direct proton addition to a ring-opened (ligand) nitrogen site. Since the diprotonated species derived from the Ni^{IV} complex is a 'kinetic intermediate', its higher reactivity is understandable. Moreover, the present Cu^{II}-promoted redox system can be regarded as being related to the Cu^{II}-mediated acid decomposition[3] of the Ni^{IV} complex, a representative sequence for the latter reaction being shown in equation (vi)

$$[Ni(dmg)_3(H)]^- + Cu^{2+}(aq) \xrightleftharpoons[H^+]{K_{3M}} [Ni(dmg)_3Cu] \xrightarrow[k_{3p}]{H^+} \text{products (decomposition)} \quad \text{(vi)}$$

($K_{3M} = 4.2 \times 10^{-3}$, $k_{3p} = 2.4 \times 10^3$ dm^3 mol^{-1} s^{-1}).[3] The apparent equilibrium constant, K_{A1}, for the formation of the 1 : 1 adduct involving the monoprotonated Ni^{IV} species and $[Cu(HL^1)]^{3+}$(aq) (Scheme 1) is of the same order of magnitude as K_{3M}. The third-order rate constant, k_{nx}, may either be due to a termolecular step or be a product of a small equilibrium constant and a large second-order rate constant. It is interesting to note that $k_{3p} \ll (k_{1x}[L^1]_0)$ even at the lowest $[L^1]_0$ employed in the reaction, implying that the Cu^{II}-mediated acid decomposition of the Ni^{IV} complex[3] is negligible compared to the Cu^{II}-promoted reduction of $[Ni(dmg)_3]^{2-}$ under the conditions studied.

The Cu^{2+}(aq)-*catalyzed Oxidation of t-Butylhydrazine using* $[Ni(dmg)_3]^{2-}$.—The disappearance of the Ni^{IV} complex

Table 5. Pseudo-zero-order rate constants for the oxidation of t-butylhydrazine (L^2) using $[Ni(dmg)_3]^{2-}$ in the absence of added metal ion; $[Ni^{IV}]_0$ = (4—5) × 10^{-5} mol dm^{-3}

		10^8k_0/mol dm^{-3} s^{-1}			
pH	$10^3[L^2]_0$/mol dm^{-3} =	0.5	1.0	5.0	10
5.0		3.0 ± 0.1	6.0 ± 0.3	17 ± 0.8	26 ± 1
		(3.0 ± 0.1) [a]			(25 ± 2) [a]
		(0.04 ± 0.002) [b]			(0.4 ± 0.03) [b]
5.3		1.7 ± 0.08	3.4 ± 0.2	10 ± 0.4	15 ± 0.8
5.5		1.2 ± 0.06	2.4 ± 0.1	7.9 ± 0.3	12 ± 0.6
6.0		0.64 ± 0.03	1.3 ± 0.06	6.5 ± 0.3	7.2 ± 0.4
		(0.6 ± 0.03) [a]			(7.1 ± 0.4) [a]
		(0.01 ± 0.0005) [b]			(0.1 ± 0.006) [b]
6.3		0.51 ± 0.02	1.0 ± 0.04	4.3 ± 0.2	6.2 ± 0.3
6.5		0.46 ± 0.02	0.9 ± 0.04	4.0 ± 0.2	5.8 ± 0.3
7.0		0.41 ± 0.02	0.8 ± 0.03	3.7 ± 0.2	5.4 ± 0.3
		(0.4 ± 0.02) [a]			(5.8 ± 0.3) [a]
		(0.007 ± 0.0004) [b]			(0.09 ± 0.005) [b]

[a] In the presence of 1 × 10^{-4} mol dm^{-3} acrylonitrile (N_2 atmosphere). [b] In the presence of 1 × 10^{-5} mol dm^{-3} $Na_2(H_2edta)$.

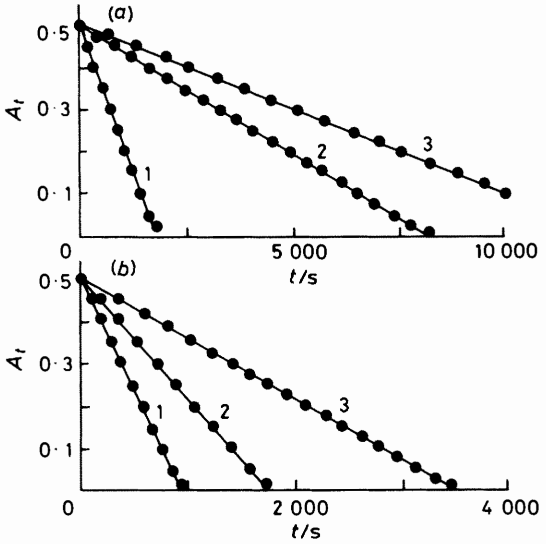

Figure 3. Representative pseudo-zero-order plots (*a*) in the absence of any added metal ion, and (*b*) in the presence of 2 × 10^{-6} mol dm^{-3} of added Cu^{II}. pH 5.0 (1), 6.0 (2), and 7.0 (3); $[Ni^{IV}]_0$ = 5.2 × 10^{-5} mol dm^{-3}, $[L^2]_0$ = 5 × 10^{-4} mol dm^{-3}, I = 0.25 mol dm^{-3}, at 35 °C

$$Cu^{2+} + (HL^2)^+ \underset{}{\overset{K_1}{\rightleftharpoons}} [Cu(HL^2)]^{3+} \xrightarrow{k_1} \text{intermediate products}$$

$$\text{intermediate products} + [Ni(dmg)_3]^{2-} \xrightarrow{\text{rapid}} \text{products}$$

Scheme 2. $(HL^2)^+ = Bu^tNHNH_3^+$; aqua ligands are omitted

in the oxidation of t-butylhydrazine (L^2) exhibited pseudo-zero-order kinetics. The zero-order disappearance of Ni^{IV} was observed irrespective of the sources of the samples employed, both in the absence and presence of added Cu^{2+}(aq). Figure 3 presents representative zero-order plots. It was observed that the zero-order rate constants in the absence of added metal ions were enhanced when small amounts of Cu^{II} were added. The observed pseudo-zero-order rate constants (k_z) were found to conform to equation (vii) where k_0 and k_{Cu} are the

$$k_z = k_0 + k_{Cu} = k_0 + k_{Cu}'[Cu^{II}] \qquad \text{(vii)}$$

pseudo-zero-order rate constants in the absence and presence of added Cu^{II}, respectively. Table 5 lists representative values of k_0. (Since the nature and extent of trace-metal ion impurities present in the solution are not known, the data collected in the absence of added metal ions are of little importance; they are only utilised to calculate the rates of the Cu^{II}-catalysed reaction.) Values of k_{Cu} were calculated from k_z using equation (vii) and are presented in Table 6. The k_{Cu} values exhibited linear kinetics on added [Cu^{II}], and a tendency to limiting kinetics on $[L^2]_0$ at high relative $[L^2]_0$. The decrease in k_{Cu} with increasing pH was less pronounced in the lower pH region, but became more prominent at higher relative pH, in the range employed.

The observed kinetic data of the oxidation of L^2 in the presence of added Cu^{2+}(aq) can be interpreted in terms of a probable mechanism, which envisages the equilibrium formation of 1 : 1 intermediate complex(es) involving Cu^{II} and the substrate species predominantly present in the solution, followed by a rate-determining decomposition of the intermediate complex(es) with a concomitant electron transfer to give intermediate products (including the reduced form of the metal ion species). The Ni^{IV} complex species is presumed to be involved in subsequent and rapid, and kinetically insignificant, steps of product formation. If it is assumed that the contributions of L^2 and $Cu(OH)^+$(aq) species to the reaction rate are negligible in comparison with those of $(HL^2)^+$ and Cu^{2+}(aq), respectively, then the rate law (viii) can be derived from Scheme 2. Equation (viii) fits the experimental data with the values of the resolved constants (Table 7).

$$\frac{k_{Cu}}{[Cu^{II}]} \approx \frac{k_1K_1[H^+][L^2]_0}{K_{Cu} + (1 + K_1[L^2]_0)[H^+]} \qquad \text{(viii)}$$

Although we could not study the kinetics of the Cu^{II}–L^2 redox system independently {in the absence of $[Ni(dmg)_3]^{2-}$} to compare the results with those observed in the present study (due to the non-homogeneous reaction medium), the magnitude of the resolved second-order rate constant (k_1K_1) in the case of the Cu^{II}-catalysed oxidation of L^2 is much smaller than the rate constant for the exchange of water from the first co-ordination sphere of Cu^{2+}(aq) (*ca.* 8 × 10^9 s^{-1} at 25 °C [17]) and suggests that the intermediate complex species involving Cu^{II} and L^2 might indeed be formed in the redox system. Information on the formation of 1 : 1 intermediate

Table 6. Pseudo-zero-order rate constants for the oxidation of t-butylhydrazine using $[Ni(dmg)_3]^{2-}$ in the presence of added Cu^{II}; $[Ni^{IV}]_0 = (3—4) \times 10^{-5}$ mol dm^{-3}

pH	$10^6[Cu^{II}]$/mol dm^{-3} (added)		10^8k_{Cu}/mol dm^{-3} s^{-1} *			
		$10^3[L^2]_0$/mol dm^{-3} =	0.5	1.0	5.0	10
5.0	1		1.3 ± 0.06	2.3 ± 0.1	6.0 ± 0.3	7.5 ± 0.4
	2		2.6 ± 0.1	7.4 ± 0.2	12 ± 0.5	15 ± 0.7
	5		6.6 ± 0.3	12 ± 0.5	29 ± 1	37 ± 2
5.15	1		1.3 ± 0.06	2.4 ± 0.1		
	2		2.6 ± 0.1	4.6 ± 0.2		
	5		6.5 ± 0.3	11 ± 0.6		
5.3	1		1.3 ± 0.06	2.3 ± 0.1	5.8 ± 0.2	7.6 ± 0.3
	2		2.6 ± 0.1	4.6 ± 0.2	12 ± 0.5	15 ± 0.7
	5		6.6 ± 0.3	11 ± 0.5	28 ± 1	38 ± 2
5.5	1		1.3 ± 0.06	2.3 ± 0.1	5.9 ± 0.3	7.5 ± 0.3
	2		2.6 ± 0.1	4.6 ± 0.2	12 ± 0.5	15 ± 0.6
	5		6.6 ± 0.3	11 ± 0.4	30 ± 1	37 ± 1
6.0	1		1.2 ± 0.05	2.2 ± 0.1	5.6 ± 0.2	7.4 ± 0.3
	2		2.4 ± 0.1	4.2 ± 0.2	11 ± 0.5	15 ± 0.7
	5		6.1 ± 0.3	10 ± 0.4	29 ± 1	36 ± 2
6.15	1		1.1 ± 0.05			
	2		2.2 ± 0.1			
	5		5.3 ± 0.2			
6.3	1		1.0 ± 0.04			
	2		2.1 ± 0.1	3.8 ± 0.2	11 ± 0.3	14 ± 0.6
	5		5.3 ± 0.2			
6.5	1		0.9 ± 0.04	1.7 ± 0.08	5.2 ± 0.2	6.8 ± 0.3
	2		1.9 ± 0.1	3.4 ± 0.1	10 ± 0.5	13 ± 0.6
	5		4.7 ± 0.2	8.5 ± 0.4	25 ± 1	34 ± 1
7.0	1		0.6 ± 0.03	1.1 ± 0.05	3.7 ± 0.1	5.5 ± 0.2
	2		1.1 ± 0.04	2.1 ± 0.1	7.5 ± 0.3	11 ± 0.4
	5		2.7 ± 0.1	5.2 ± 0.2	19 ± 1	27 ± 1

* $k_{Cu} = k_z - k_0$; k_z is the measured pseudo-zero-order rate constant, k_0 values are presented in Table 5.

Table 7. Average values of the resolved constants for the Cu^{II}-catalyzed oxidation of t-butylhydrazine using $[Ni(dmg)_3]^{2-}$

Constant	Value
k_1/s^{-1}	0.1
K_1/dm^3 mol^{-1}	3×10^2
k_1K_1/dm^3 mol^{-1} s^{-1}	30
K_{Cu}/mol dm^{-3}	$10^{-6.85}$

$$RNHNH_2 - e^- \longrightarrow RNHNH_2^{\cdot +} \longrightarrow RNHNH^{\cdot} + H^+$$

$$RNHNH^{\cdot} - e^- \longrightarrow RN{=}NH + H^+$$

$$RN{=}NH + H_2O - 2e^- \longrightarrow ROH + N_2 + 2H^+$$

Scheme 3. R = H or Bu^t; the reductant may represent either the free reductant or its metal-ion complexes

complexes involving Cu^{II} and the reducing substrate was also obtained from oxidation kinetics of analogous reductants, phenylhydrazine[8] and hydroxylamine,[6] in the presence of added Cu^{2+}(aq) and in numerous other studies. From the observed zero-order Ni^{IV} disappearance kinetics, it was also shown that the hydrolysed species $[Cu(OH)^+(aq)]$ reacted much slower than the unhydrolysed metal-ion species $[Cu^{2+}(aq)]$, suggesting that there might be a one-electron change in the rate-determining step [15,18] in each such case.

Discussion

The overall picture of formation of oxidation products of L^1 and L^2 can probably be formulated in terms of Scheme 3, which accounts for the observed stoicheiometric ratios of $\Delta[Ni^{IV}]/\Delta[L] \approx 2$ and $\Delta[Cu^{II}]/\Delta[L] \approx 4$. The product formation steps will presumably be very rapid and the magnitude of their rates relative to the rates of the reactions are such that the present redox systems do not initiate the polymerization of a radical-trapping agent (*viz.*, acrylonitrile) under a nitrogen atmosphere; nor was there any significant influence of added acrylonitrile on rates observed (both in the absence and the presence of added Cu^{II}).

Several important reports [14,15,18–21] are available on the kinetics of oxidation of hydrazines by various oxidants. It is generally established that hydrazine or a substituted hydrazine transfers two electrons to an oxidant, forming the diazene intermediate,[22,23] which on a further very rapid two-electron loss gives nitrogen (and water or ROH); the overall stoicheiometry for this process is $e^- : L = 4 : 1$. On the other hand, the loss of one electron (as a hydrogen atom) from hydrazine results in the hydrazyl radical,[15,24,25] two of which give nitrogen and ammonia (or RNH_2) as products, and a stoicheiometric ratio $e^- : L = 1 : 1$. Alternatively, the hydrazyl radical may suffer a rapid one-electron loss to produce the diazene which will lead to nitrogen (and water or ROH) as oxidation products, and a stoicheiometric ratio $e^- : L = 4 : 1$. Thus the stoicheiometry and products in the oxidation of hydrazines are not definitive and are merely indicative of the number of electrons transferred. These results in the present investigation, therefore, do not give any conclusive information regarding a simultaneous two-electron transfer or two one-electron transfers in the rate-determining step(s).

In spite of the apparent complexity of the reaction schemes, some reasonably simple mechanistic inferences (*a*)—(*d*) emerge from the study.

(*a*) That the reducing substrates do not enter the co-ordination sphere of the substitution-inert [26] Ni^{IV} complex species is confirmed by spectral data. Point-by-point spectra of reac-

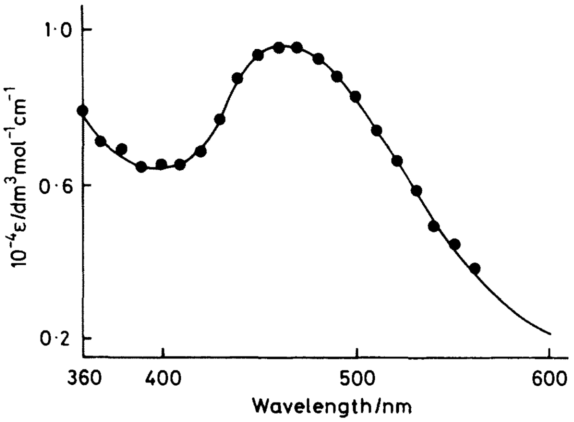

Figure 4. Visible spectra of $[Ni(dmg)_3]^{2-}$ (———) (1×10^{-4} mol dm^{-3}) and a reaction mixture (●) containing $[Ni^{IV}]_0 = 1 \times 10^{-4}$ mol dm^{-3} and $[L^1]_0 = 1 \times 10^{-3}$ mol dm^{-3} (aqueous medium, $I = 0.25$ mol dm^{-3}, 35 °C, pH 7, time-scale on 50-ms mode)

tion mixtures containing $[Ni(dmg)_3]^{2-}$ and hydrazine (in the absence of added Cu^{II}) on the stopped-flow apparatus (in the range 360—560 nm) at pH 5.2, 6.3, and 7.0 were almost the same as those of the original $[Ni(dmg)_3]^{2-}$ under identical conditions. For example, Figure 4 shows representative spectra of the original Ni^{IV} complex and a reaction mixture containing $[Ni(dmg)_3]^{2-}$ and hydrazine at pH 7, 35 °C, and $I = 0.25$ mol dm^{-3} in aqueous medium. (The Aminco stopped-flow assembly [1] used has a nominal mixing time of 2 ms and the point-by-point absorbance values were recorded at wavelength intervals of 10 nm using a time-scale on 50-ms mode. The original Ni^{IV} complex does not undergo any appreciable decomposition under these conditions.[2]) It can be seen that the ligand-to-metal charge-transfer band [1] at 460 nm of the original $[Ni(dmg)_3]^{2-}$ is not altered (λ or ε) in the presence of hydrazine.

(*b*) On the basis of spectral and kinetic data, it has been shown earlier [3] that Cu^{2+}(aq) and Ni^{IV} species in solution are involved in pH-dependent equilibrium interactions to form 1 : 1 adduct(s), in which the Cu^{II} is ligated to the dioximate oxygen or the ring-opened (ligand) nitrogen of the nickel complex species. There was an abrupt absorbance jump [3] at 460 nm when aqueous solutions of $[Ni(dmg)_3]^{2-}$, Cu^{II}, and hydrazine were mixed at pH 7, but the absorbance change could not be monitored due to the rapidity of the reactions. (The mixture of Cu^{II} and hydrazine was almost transparent at 460 nm under identical conditions.) Although spectral details for the adducts in the present system could not be independently obtained, it is very likely that such adducts (Scheme 1) are formed involving the Ni^{IV} and $[Cu(HL^1)]^{3+}$(aq) species, similar to the formation of adducts {*e.g.* $[Ni(dmg)_3Cu]$ from the $[Ni(dmg)_3(H)]^-$ and Cu^{2+}(aq) species: [3] equation (vi)}. Rate-determining electron transfer from the reductant species to the adduct(s) can take place in the presence of H$^+$. The apparent equilibrium constants (K_{A_n}) for the adducts are found to be much larger than the overall equilibrium constants (K_C) [13,14] for the formation of $[Cu(HL^1)]^{3+}$, *i.e.* $K_{A_n}/[H^+] \gg K_C$. The latter, therefore, will not have a significant effect (with respect to the concentrations of the various reactant species or to the contribution to the overall reactivity) in the Cu^{II}-promoted oxidation of hydrazine.

(*c*) In numerous studies, the oxidation of hydrazines has been shown to proceed through the formation of intermediate complexes with metal ions; *e.g.*, binary complexes [14,27] involving the metal ion and hydrazines, and ternary complexes [21] involving these with another oxidant. Various 1 : 1 and 1 : 2 metal-ion complexes of hydrazine [21,28] and its derivatives [28,29] have been prepared and characterized. Furthermore, protonated species of the hydrazines have been shown to be involved in ligation to metal ions at the nitrogen site away from that of protonation.[30] The formation constant of the 1 : 1 complex involving Cu^{II} and t-butylhydrazine obtained from the kinetics ($K_1 \approx 10^{2.5}$ dm^3 mol^{-1} at 35 °C) appears to be in order with such values reported earlier for similar reducing substrates such as hydrazine, $10^{3.1}$ at 35 °C,[9] $10^{3.18}$ at 30 °C,[13] $10^{4.2}$ at 25 °C; [14] phenylhydrazine, $10^{1.5}$—$10^{1.7}$ at 35 °C; [8] and hydroxylamine, $10^{2.3}$ at 35 °C,[6] $10^{2.4}$ dm^3 mol^{-1} at 20 °C.[13]

(*d*) The possibility of the kinetic involvement of other higher oxidation states of metal ions, as in the reaction $Cu^{II} + Ni^{IV} \rightleftharpoons Cu^{III} + Ni^{III}$, is ruled out since the redox potential of the Ni^{IV}–Ni^{III} couple (*ca.* 0.4 V [31]) is not sufficient to oxidise Cu^{2+}(aq) to Cu^{3+}(aq) [Cu^{2+}(aq)–Cu^{3+}(aq) $\gtrsim -1.8$ V [32]].

The exact reason for the differential behaviour of the observed kinetics and the envisaged mechanistic routes in the oxidation of hydrazine and other related reducing substrates, Y (where Y = hydroxylamine,[6] phenylhydrazine,[9] or t-butylhydrazine), using $[Ni(dmg)_3]^{2-}$ in the presence of added Cu^{2+}(aq) is not clear, but a qualitative explanation may be attempted. It is well established that complexes of Cu^{II}–Y have significant successor character. For example, complexes of Cu^{II}–Y$_n$ (Y = NH_2OH, n = 1, 2, or 4) have significant Cu^I character and decompose readily in aqueous solutions to Cu^I and oxidation products of hydroxylamine.[33] Similarly, in aqueous acid medium a mixture of Cu^{2+}(aq) and phenylhydrazine forms (1 : 1) complexes of Cu^I–phenyldiazene and Cu^{II}–phenyldiazene (with an excess of Cu^{2+}).[34] In the oxidation of substituted hydrazines, the formation of diazene derivatives,[35] and the metal–diazene complexes involving them, is favoured. The stability of metal-ion complexes of hydrazine derivatives decreases [35] in general with steric crowding (due to a decreased formation constant) and in the presence of electron-releasing groups in the hydrazine derivative (due to an increased decomposition). The oxidation of the reduced metal ion (Cu^I) species or the intermediate products of oxidation of Y by $[Ni(dmg)_3]^{2-}$ may be facile, and most probably very rapid under the conditions employed, leading to the zero-order disappearance of Ni^{IV} in the 'metal-ion-catalyzed' mechanistic route. On the other hand, it is known that the complexes of $[Cu^{II}(N_2H_4)_n]$ (n = 1 or 2) do not have significant successor character and are stable in aqueous medium with almost no change in the metal oxidation state.[21,28] Therefore, these complexes do not decompose with accompanying electron transfer so easily to the Cu^I species. In that event, the course of the formation of $[Cu^{II}(N_2H_4)]$–Ni^{IV} adducts and electron transfer to them from the reductant hydrazine species would predominate in aqueous acid medium, exhibiting the first-order Ni^{IV} disappearance as in the 'Cu^{2+}(aq)-promoted' oxidation of hydrazine. Corroboration of the arguments requires further investigation on the preparation of various metal-ion complexes of these substrates and establishing their metal oxidation states.

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