

One-Electron Reduction of Ni(III) by Hydroxylamine & Hydrazine via Addition/Elimination: An Example of an Inorganic Inner Sphere Electron Transfer Reaction

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The rates of oxidations in aqueous solution of hydroxylamine (HA) and hydrazine (HZ) by Ni(III) ion have been measured iodometrically in the presence and absence of 2,2'-bipyridine (BP). In the presence and absence of BP the order in [Ni(III)] is unity. In the absence of BP the order in [HA] and [HZ] is fractional which changes to unity in the presence of BP. The rates are acid-catalysed and marginally affected by added SO_4^{2-} ions. The rate of oxidation for HA is greater than that of HZ. Based on the results a suitable mechanism has been proposed for these oxidation reactions.

Several kinetic studies were reported on the oxidation of hydroxylamine and hydrazine by various one- and two-electron oxidising agents¹⁻⁸. Different mechanisms have been proposed in all these studies in tune with the observations made. But so far no kinetic studies have been reported on the oxidation of hydroxylamine (HA) and hydrazine (HZ) by Ni(III), except for a report⁹ on the oxidation of HN_3 by Ni^{3+} (bipy) complex. Hence, the title reactions were studied in detail to get an insight in to the mode of the redox process.

Materials and Methods

Nickel oxyhydroxide $[\text{NiO}(\text{OH})]$ was prepared according to literature procedure^{10,11}. It was dissolved in aqueous acid to give Ni(III) ions in solution. All other chemicals were of AR grade and used as such. All the solutions were prepared in doubly distilled water. The course of the reaction was followed by estimating the unreacted Ni(III) iodometrically. The presence of free radicals was confirmed by acrylamide polymerisation test. The activation parameters were evaluated from Arrhenius plots in the temperature range 303° K-323° K.

Results and Discussion

The kinetics of oxidation of HA by Ni(III) was studied in 0.5 mol dm^{-3} H_2SO_4 at 30°C. Under the conditions $[\text{Ni}(\text{III})] \ll [\text{HA}]$, the plot of $\log [\text{Ni}(\text{III})]$ versus time was linear ($r=0.998$) indicating the order in $[\text{Ni}(\text{III})]$ is one (Fig. 1A). From such plots the pseudo-first order rate constants (k_{obs}) were calculated. Also the plot of $\log k_{\text{obs}}$ versus $\log [\text{HA}]$ was linear ($r=0.989$) with a slope of 0.680 indicating the order in $[\text{HA}]$ to be fractional (Fig. 1B). The plot of $1/k_{\text{obs}}$

versus $1/[\text{HA}]$ was also linear ($r=0.985$) with a positive intercept on $1/k_{\text{obs}}$ axis (Fig. 1C). Therefore based on these observations an initial rapid formation of a complex between the substrate and the oxidant is proposed.

The nature of the reactive species of Ni(III) ion in aqueous acid solutions is now well established¹² as

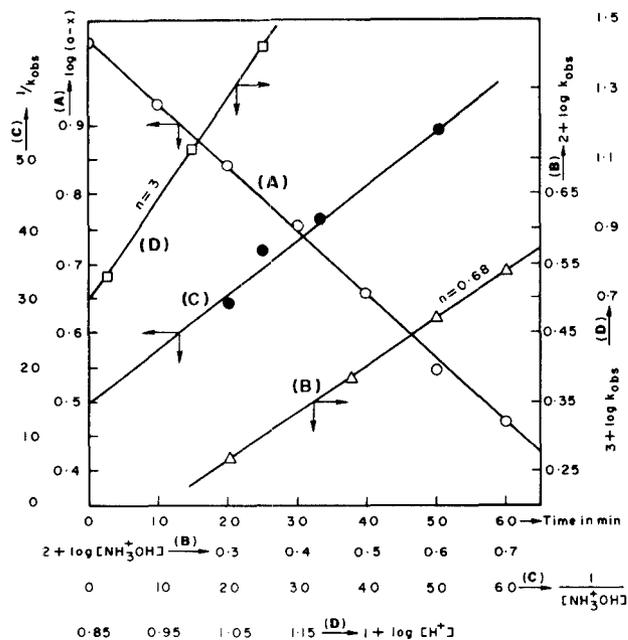
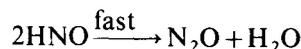
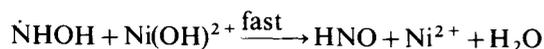
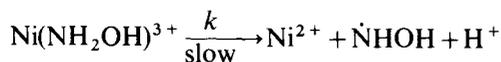
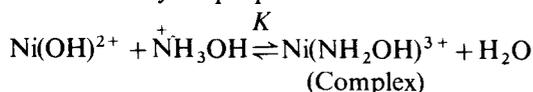


Fig. 1—(A) Plot of $\log(a-x)$ versus time ($[\text{Ni}(\text{III})]=3.00 \times 10^{-4}$ mol dm^{-3} ; $[\text{HA}]=0.020$ mol dm^{-3} ; $[\text{H}_2\text{SO}_4]=0.500$ mol dm^{-3} ; and temp. = 303° K)

(B) Plot of $\log k_{\text{obs}}$ versus $\log [\text{HA}]$ (Conditions as in A above)
(C) Plot of $1/k_{\text{obs}}$ versus $1/[\text{HA}]$ (Conditions same as in A above)
(D) Plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ ($[\text{Ni}(\text{III})]=3.00 \times 10^{-4}$ mol dm^{-3} ; $[\text{HA}]=0.010$ mol dm^{-3} ; and temp. = 303° K)

$\text{Ni}(\text{OH})^{2+}$, in accordance with the equilibrium $[\text{NiO}(\text{OH}) + 2\text{H}^+ \rightleftharpoons \text{Ni}(\text{OH})^{2+} + \text{H}_2\text{O}]$. Further NH_2OH is known to exist in acid solutions in equilibrium with its protonated species ($\text{NH}_2\text{OH} + \text{H}^+ \rightleftharpoons \text{NH}_3\text{OH}^+$).

In the present study we have observed a total third order in $[\text{H}^+]$ ($r=0.991$; Fig. 1D). This result based on $[\text{H}^+]$ effect studies led the authors to conclude that the complex formation occurred between $\text{Ni}(\text{OH})^{2+}$ and NH_3OH^+ by liberation of a water molecule. Under the experimental conditions no ammonia was found to be detectable as a product, hence it was concluded that the products of oxidation may be N_2O and H_2O . From the stoichiometry $[\text{Ni}(\text{III}) : \text{NH}_3\text{OH}^+] = 2:1$ and forgoing kinetic results a mechanism suggested in Scheme 1 may be proposed.



Scheme 1

Scheme 1 leads to the rate law (1)

$$\text{Rate} = \frac{kK[\text{Ni}(\text{OH})^{2+}][\overset{+}{\text{N}}\text{H}_3\text{OH}]}{1 + K[\overset{+}{\text{N}}\text{H}_3\text{OH}]} \quad \dots(1)$$

The rate law (1) explains the first order and fractional order dependences of rate on $[\text{Ni}(\text{OH})^{2+}]$ and $[\overset{+}{\text{N}}\text{H}_3\text{OH}]$ respectively. From Eq. (1) it follows that

$$\frac{-2.303 d \log [\text{Ni}(\text{OH})^{2+}]}{dt} = k_{\text{obs}} = \frac{kK[\overset{+}{\text{N}}\text{H}_3\text{OH}]}{1 + K[\overset{+}{\text{N}}\text{H}_3\text{OH}]} \quad \dots(2)$$

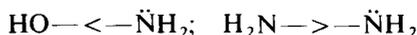
Therefore,

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK[\overset{+}{\text{N}}\text{H}_3\text{OH}]} + \frac{1}{k} \quad \dots(3)$$

Now Eq. (3) predicts a linear plot of $1/k_{\text{obs}}$ versus $1/[\overset{+}{\text{N}}\text{H}_3\text{OH}]$ with an intercept $(1/k)$. This is found to be true (see Fig. 1C).

The N-H bond breaking (H is removed as H^+) in the decomposition of the complex in a slow step gets further support from the following arguments.

There appears two other possible reaction paths in the decomposition of the complex: (i) the O-H bond breaking and (ii) an electron transfer from the lone pair of nitrogen to Ni(III). If O-H bond breaking occurs in the complex, no reaction is expected between Ni(III) and NH_2NH_2 since latter does not contain any O-H bond. Hence, O-H bond breaking is ruled out in Ni(III)- NH_2OH reaction. Now, if one of the electrons from the lone pair of nitrogen is knocked away by Ni(III), the rate of oxidation of NH_2NH_2 would be higher than that of NH_2OH . This will be because of the more +I effect of NH_2 compared to that of OH which will be clear as follows:



Hence the removal of an electron from the lone pair is also ruled out.

Therefore, the only pathway which the present redox process involves the removal of one of the hydrogens on nitrogen as H^+ . This gets further support from the low reactivity of N_2H_4 .

Effect of complexing agents

Addition of 2,2'-bipyridine to the reaction system changes the order in $[\overset{+}{\text{N}}\text{H}_3\text{OH}]$ from fractional to unity. This implies that the complexing capacity of hydroxylamine with Ni(III) is less than that of bipyridine. Therefore, what appears to be pure addition/elimination reaction can be made pure electron transfer process by simply changing the bare Ni(III) ion as its complex using a stronger ligand like bipyridine than hydroxylamine. Under similar conditions no reaction is observed between Ni(III) and bipyridine.

Effect of temperature

The formation constant (K) for the complex remained unaltered with temperature; however the decomposition rate constant (k) increased with

Table I—Rate Constants and Thermodynamic Parameters

$[\text{Ni}(\text{III})] = 3.00 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{HA}] = [\text{HZ}] = 0.020 \text{ to } 0.050 \text{ mol dm}^{-3}$ $[\text{H}_2\text{SO}_4] = 0.500 \text{ mol dm}^{-3}$

Substrate	Temp. (K)	$k \times 10^2$ min ⁻¹	K litre mol ⁻¹	E_a kJ mol ⁻¹	ΔS^\ddagger at 303 J mol ⁻¹ K ⁻¹
HA	303	6.55 ± 0.41	18.1 ± 1.1	40.6 ± 1.74	-136 ± 0.02
	308	8.47 ± 0.33	17.4 ± 1.7		
	313	10.9 ± 0.17	16.7 ± 2.1		
HZ	303	2.42 ± 0.28	39.3 ± 2.4	—	—

increase in temperature. The more negative ΔS^\ddagger value (Table 1) is in good agreement with the liberation of a proton in the rate-determining step.

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