Kinetics of Oxidation of Hydrogen Azide (Hydrazoic Acid) by Tris(2,2'-bipyridine)nickel(III) Ions in Aqueous Perchlorate Media: Comparison with Oxidation by Aqua-cations

By **John K. Brown, David Fox, Malcolm P. Heyward,** and **Cecil F. Wells,*** Department of Chemistry, University of Birmingham, Edgbaston, P.O. Box 363, Birmingham B15 2TT

E.s.r. measurements on solutions of Ni^{II} containing 2,2'-bipyridine (bipy) confirm that anodic oxidation produces Ni^{III}. The stoicheiometry and kinetics of oxidation of HN_3 by $[Ni(bipy)_3]^{3+}$ have been investigated. Unlike the oxidations of H_2O_2 and Br^- by this cation, with HN_3 the rate varies with the concentration of $HClO_4$ at constant ionic strength. Under conditions where specific cation effects are eliminated, the rate is directly proportional to $[H^+]^{-1}$, suggesting that the kinetically active entity of the hydrazoic acid is N_3^-. No removal of bipy from the Ni^{III} occurs before the slow oxidative step, even though an outer-sphere intermediate complex may be formed between $[Ni(bipy)_3]^{3+}$ and N_3^-. This system is compared with the oxidations of HN_3 by aqua-cations and with the oxidations of other ligands by $[Ni(bipy)_3]^{3+}$.

THE oxidation of hydrazoic acid (hydrogen azide, HN_3) by aqua-cations $M^{n+}(aq)$ has been investigated for $M^{n+} = Mn^{III}$,[1] Co^{III},[2,3] and Ce^{IV}.[4] For Mn^{III} the rate is first order in $[Mn^{III}]$ and second order in $[HN_3]$ and the rate increases with increasing $[H^+]$ at constant ionic strength.[1] This shows that the reaction proceeds through a complex formed between $Mn^{3+}(aq)$ and HN_3 and that $[Mn(OH)]^{2+}(aq)$ is unreactive in the oxidation.[1] At high initial $[HN_3]/[M^{n+}]$, the reaction with Co^{III} resembles that with Mn^{III} under similar conditions in being first order in $[Co^{III}]$ and second order in $[HN_3]$,[2] but it differs [2] from the reaction with Mn^{III} in being zero order in $[H^+]$. At lower initial $[HN_3]/[M^{n+}]$ for Co^{III}, the reaction is first order in $[HN_3]$ as well as in $[Co^{III}]$ and the rate is proportional to $a + b[H^+]^{-1}$, where a and b are constants at constant temperature.[3] The reaction with Mn^{III} is relatively slow and the rates are entirely accessible to conventional spectrophotometric techniques, but for the faster reaction with Co^{III} stopped-flow techniques have to be used except at low temperatures. However, for the much faster reaction with Ce^{IV}, only stopped-flow measurements are possible, and the reaction is first order in $[Ce^{IV}]$ and zero order in both $[HN_3]$ and $[H^+]$.[4] In all cases for $M^{n+}(aq)$,[1-4] the overall stoicheiometry is represented by (1).

$$2M^{n+}(aq) + 2HN_3 \longrightarrow 2M^{(n-1)+}(aq) + 3N_2 + 2H^+(aq) \quad (1)$$

By comparing the rates of oxidation of various ligands L by Co^{III} at one temperature it has been argued [5,6] that they are all controlled by the rate of substitution of L into the inner co-ordination sphere of Co^{III}, *i.e.* the rate represents the rate of removal of a water molecule from this inner aqua-sphere. That this is an oversimplification is shown by the very significant differences [7] in the enthalpies $\Delta H^{\ddagger}$ and entropies $\Delta S^{\ddagger}$ of activation with varying L and by the observation that intermediate (Co^{III} + L) complexes participate in the rate-determining redox steps for some of the L cited: such complexes have been detected spectrophotometrically and kinetically for L = H_2O_2 [8] and kinetically for L = HN_3 [2] and Br^-.[9] It has been pointed out [9-11] that, since both redox processes and substitution processes of cations involve considerable movement of water molecules to achieve their respective transition states, it is not surprising that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (and therefore sometimes the rates) for the two types of process are of similar magnitude even if the redox process is not controlled by the substitution process. To investigate in a more general way the extent to which the water molecules in the inner co-ordination spheres of cations are involved in cation + ligand redox processes, the kinetics of the oxidation of H_2O_2 [10] and Br^- ions [11] by the tris(2,2'-bipyridine)nickel(III) ion have been compared with the kinetics of the oxidation of these ligands by aqua-cations. The kinetics of the oxidation of hydrazoic acid by the $[Ni(bipy)_3]^{3+}$ are now described and compared with the kinetics of the oxidation of HN_3 by aqua-cations.

EXPERIMENTAL

Materials.—Tris(2,2'-bipyridine)nickel(III) perchlorate was prepared by anodic oxidation under nitrogen.[10] The anode compartment consisted of a glass tube (length, 10 cm; diameter, *ca.* 3 cm) separated at its base from the cathode compartment by a no. 4 glass sinter. The electrodes were platinum, the anode being of area *ca.* 3.2 cm², and the current was normally 50 mA at 36 V. Nickel(II) perchlorate was dissolved in 2 mol dm^{-3} $HClO_4$, and the whole electrolytic apparatus was maintained at *ca.* 5 °C. Such a solution soon achieved the maximum yield of Ni^{III} which was always low: 1.33 mol dm^{-3} Ni^{II} in 2 mol dm^{-3} $HClO_4$ gave 2.5×10^{-4} mol dm^{-3} Ni^{III} after the current had passed for 10 min and this did not change after passage of current for 50 min (some precipitation of the bipyridinenickel(II) salt occurred at this concentration); 3.2×10^{-4} mol dm^{-3} Ni^{II} in 2 mol dm^{-3} $HClO_4$ gave 1.2×10^{-4} mol dm^{-3} Ni^{III} after 10 min, and this did not change after passage of current for 40 min. The spectrum of lime-green $[Ni(bipy)_3]^{3+}$ is shown in Figure 1.

AnalaR perchloric acid was used in the reaction mixtures; solutions of sodium and lithium perchlorates were prepared by neutralization of $HClO_4$ with $Na_2[CO_3]$ and $Li_2[CO_3]$ (all AnalaR). G. F. Smith magnesium perchlorate was used. Solutions of sodium azide were made up by weight. Water was distilled once in an all-glass still.

Procedure.—Practically all the kinetic measurements were made using a Durrum–Gibson stopped-flow spectrophotometer; all those at $I = 2.00$ mol dm^{-3} using added Li[ClO$_4$] were done on this instrument. Some of the other rate measurements employed a Unicam SP 500 series 2 spectrophotometer. All the rate measurements were carried out at 350 nm: the product of the oxidation in the stopped-flow experiments is $[\mathrm{Ni(bipy)_3}]^{2+}$ and interference from its absorption at this wavelength is negligible.[10] Errors arising from the oxidation of water by $[\mathrm{Ni(bipy)_3}]^{3+}$ on these time scales can be neglected.[10] The concentrations of solutions of $[\mathrm{Ni(bipy)_3}]^{3+}$ were determined as described earlier.[10]

E.s.r. spectra were run on a Hilger and Watts Microspin ESR-3 spectrometer operated at *X*-band frequencies. Determinations of the *g* value, were made by superimposing the resonance from diphenylpicrylhydrazyl (dpph) on the traces from the complexes and from proton resonance meter magnetic field calibrations.

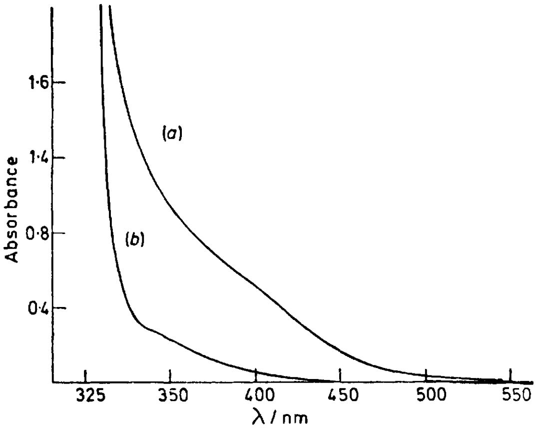

FIGURE 1 Spectra of Ni$^{\mathrm{II}}$ and Ni$^{\mathrm{III}}$ in 2 mol dm^{-3} HClO$_4$ for path length = 4 cm: (*a*) 3.0 × 10^{-5} mol dm^{-3} $[\mathrm{Ni(bipy)_3}]^{3+}$ containing *ca.* 1.3 × 10^{-3} mol dm^{-3} Ni$^{\mathrm{II}}$ as decomposed $[\mathrm{Ni^{II}(bipy)_3}]^{2+}$; (*b*) 1.33 × 10^{-3} mol dm^{-3} Ni$^{\mathrm{II}}$ as decomposed $[\mathrm{Ni(bipy)_3}]^{2+}$

RESULTS AND DISCUSSION

E.S.R. Measurements.—E.s.r. spectra were obtained from the bipyridinenickel complexes in frozen perchloric acid–water solution at 77 K. Comparison of the spectra recorded before and after electrochemical oxidation allowed an unambiguous identification of the most pronounced feature of the product of anodic oxidation. This resonance had a near symmetric lineshape of maximum slope width *ca.* 10mT and *g* 2.095 ± 0.002. Any other possible weak features at higher fields which would have indicated *g* anisotropy could not be discerned because of interference from the resonance from unoxidized Ni$^{\mathrm{II}}$ present in excess.

For a number of nickel complexes there has been discussion as to whether their e.s.r. spectra are to be understood as originating from low-spin d^7 Ni$^{\mathrm{III}}$ or as a nickel(II)-stabilized radical–ligand system.[12-19] There are a number of well authenticated examples where the stabilized radical–ligand structures are associated with highly isotropic *g* values close to that for the free-electron spin (2.002 3); in contrast, the low-spin d^7 complexes have anisotropic *g* tensors and significantly higher $\langle g \rangle$ values.[14,16-18] Although we have no definitive evidence of *g* anisotropy, on the grounds of the *g* value observed we propose that the oxidized bipyridine complexes should be formulated as being based on Ni$^{\mathrm{III}}$.

Stoicheiometry.—Working with an excess of [Ni$^{\mathrm{III}}$] (*ca.* 2.5 × 10^{-5} mol dm^{-3}) over hydrazoic acid (1.00 × 10^{-5} mol dm^{-3}), the consumption of Ni$^{\mathrm{III}}$ was measured for a range of acidities assuming that all the hydrazoic acid had disappeared. The observed consumption values $|\Delta[\mathrm{Ni^{III}}]|/|\Delta[\mathrm{HN_3}]|$ in Table 1 show that the stoicheiometry conforms to equation (1), analogous to the oxidations of hydrazoic acid by the aqua-cations.

TABLE 1

$[\mathrm{HClO_4}]$ / mol dm^{-3}	$\lvert\Delta[\mathrm{Ni^{III}}]\rvert/\lvert\Delta[\mathrm{HN_3}]\rvert$
	1.10, 0.90
1.00	1.10
2.00	0.94
3.00	

Mean = 1.01 ± 0.1

Rate Measurements.—The rate of reaction was first studied at $I = 5.00$ mol dm^{-3} with $[\mathrm{HN_3}] \gg$ initial [Ni$^{\mathrm{III}}$] over a range of temperature. Good linear plots of log(optical density) against time were obtained with initial [Ni$^{\mathrm{III}}$] ~ 1 × 10^{-4} mol dm^{-3}. At 25 °C a plot of the pseudo-first-order rate constant k_0 against [HN$_3$] over the range 0.05—0.25 mol dm^{-3} in 4.00 mol dm^{-3} HClO$_4$ was linear passing through the origin, showing that the reaction is first order in [HN$_3$]. However, in testing the dependence of rate on acidity, plots of the second-order rate constant k_2 against $[\mathrm{H^+}]^{-2}$ were linear and passed through the origin at 2.5, 13.0, 25.3, and 32.1 °C. Since the mechanistic interpretation of the latter variation is clearly difficult, a test for specific ion effects was carried out. The results for equivalent additions of Li[ClO$_4$] and Na[ClO$_4$] at constant [HClO$_4$] for $I = 5.00$ mol dm^{-3}, summarized in Table 2, show clearly that there is a specific cation effect. Due to the low solubility of Li[ClO$_4$], rates were then measured at $I = 2.00$ mol dm^{-3} at 29.7 °C when Mg[ClO$_4$]$_2$ was also used as the added salt. Table 2 shows that the accelerating effect of the cation is in the order $\mathrm{Mg^{2+}} > \mathrm{Na^+} >$

TABLE 2

Variation of rate with nature of added metal perchlorate at constant ionic strength; $[\mathrm{HN_3}] = 2.00 \times 10^{-3}$ mol dm^{-3}

$[\mathrm{HClO_4}]$ / mol dm^{-3}	I / mol dm^{-3}	θ_c / °C	Added salt (c/mol dm^{-3})	k_2 / dm^3 mol^{-1} s^{-1}	$k_2[\mathrm{H^+}]$ / s^{-1}
5.00	5.00	25.3		0.71	3.55
4.00	5.00	25.3	Li[ClO$_4$] (1.00)	0.78	3.12
			Na[ClO$_4$] (1.00)	1.18	4.72
3.00	5.00	25.3	Li[ClO$_4$] (2.00)	0.98	2.94
			Na[ClO$_4$] (2.00)	2.26	6.8
2.00	2.00	29.7		78	156
1.00	2.00	29.7	Li[ClO$_4$] (1.00)	153	153
			Na[ClO$_4$] (1.00)	203	203
			Mg[ClO$_4$]$_2$ (0.33)	322	322
1.00	1.00	29.7		78	78
0.50	1.00	29.7	Li[ClO$_4$] (0.05)	159	80
			Na[ClO$_4$] (0.05)	153	77

Li^+. However, it can also be seen that the rates at 29.7 °C with added $Na[ClO_4]$ or $Li[ClO_4]$ at $I = 1.00$ mol dm^{-3} are not dependent on the cation. Since Table 2 shows that $k_2[H^+]$ is constant, at $I = 1.00$ mol dm^{-3}, independent of the added cation H^+, Li^+, or Na^+, and that $k_2[H^+]$ is constant at $I = 2.00$ mol dm^{-3} for the cations Li^+ and H^+, a detailed kinetic investigation was carried out at 29.7 °C at $I = 2.00$ mol dm^{-3} maintained by the addition of $Li[ClO_4]$. In all these cases linear plots were obtained for log(optical density) against time.

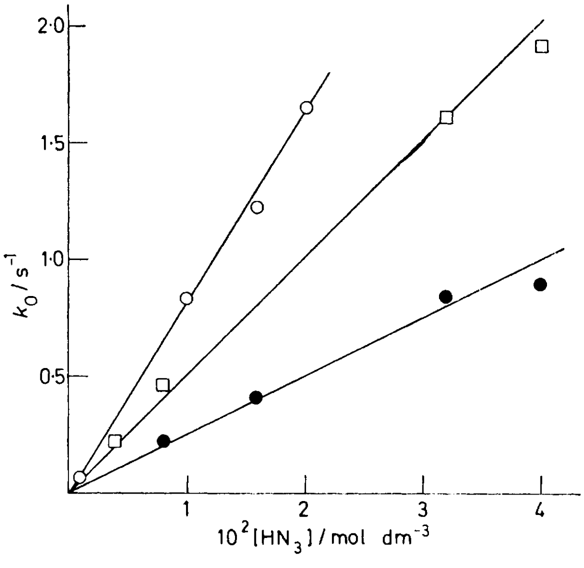

FIGURE 2 Variation of the pseudo-first-order rate constant k_0 with $[HN_3]$ at $I = 2.00$ mol dm^{-3} ($Li[ClO_4]$). $[HClO_4] = 2.00$ [(○) at 29.7, (●) at 17.0 °C] or 1.00 mol dm^{-3} (17.0 °C) (□)

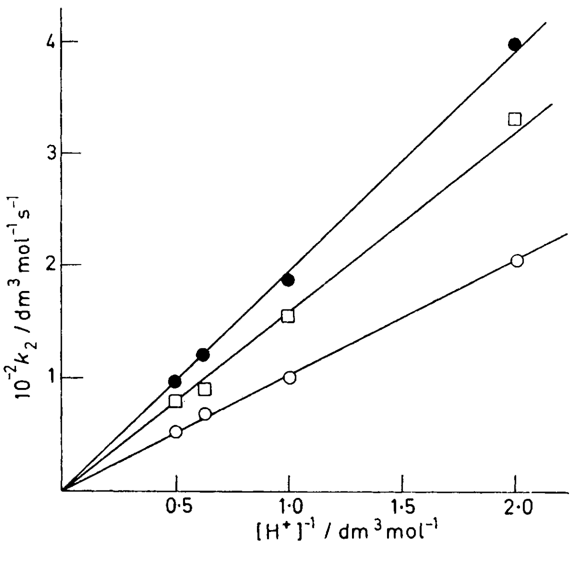

FIGURE 3 Variation of the second-order rate constant k_2 with $[H^+]^{-1}$ at $I = 2.00$ mol dm^{-3} ($Li[ClO_4]$) and 24.7 (○), 29.7 (□), or 35.5 °C (●)

Figure 2 shows that a plot of k_0 against $[HN_3]$ in 2.00 mol dm^{-3} $HClO_4$ at 29.7 °C is linear passing through the origin, and the values for k_2 over a range of acidity at $I = 2.00$ mol dm^{-3} ($Li[ClO_4]$) are collected in Table 3. Figure 3 shows that a plot of k_2 against $[H^+]^{-1}$ at $I = 2.00$ mol dm^{-3} ($Li[ClO_4]$) and 29.7 °C is linear. Linear plots for log (optical density) against time were obtained for $I = 2.00$ mol dm^{-3} with added $Li[ClO_4]$ over a range of temperature, and Figure 2 shows that plots for k_0 against $[HN_3]$ for 1.00 and 2.00 mol dm^{-3} $HClO_4$ at 17.0 °C are linear passing through the origin. From Table 3 it can be seen that values for k_2 are constant for varying $[HN_3]$ at constant acidity at both 24.7 and 35.5 °C, providing final confirmation that the reaction is first order in $[HN_3]$ as well as first order in $[Ni^{III}]$. Plots of k_2 against $[H^+]^{-1}$ at 24.7 and 35.5 °C (Figure 3) are also linear passing through the origin, and Table 3 confirms this inverse dependence of rate on acidity at $I = 2.00$ mol dm^{-3} with added $Li[ClO_4]$ for all the temperatures. Figure 4 shows that a plot of log k_3 against $1/T$ is linear (where $k_3 = k_2[H^+]$). From the gradient in Figure 4, determined using the least-squares procedure, the enthalpy of activation $\Delta H^\ddagger = 51 \pm 3$ kJ mol^{-1}; the entropy of activation $\Delta S^\ddagger = -36 \pm 10$ J K^{-1} mol^{-1}.

TABLE 3

Values of k_2 and k_3 at $I = 2.00$ mol dm^{-3} ($Li[ClO_4]$)

θ_c/°C	$[HClO_4]$/mol dm^{-3}	$10^3[HN_3]$/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}	k_3/s^{-1}
17.0	2.00	8.0	27.4	55
	2.00	16.0	25.5	51
	2.00	32.0	26.2	52
	2.00	40.0	22.4	44.8
	1.00	4.0	61	61
	1.00	8.0	59	59
	1.00	32.0	50	50
	1.00	40.0	47.8	47.8
			Mean =	53 ± 6
24.7	2.00	10.0	51	102
	2.00	5.00	54	108
	1.60	5.00	68	109
	1.60	2.50	68	109
	1.00	5.00	100	100
	1.00	2.50	100	100
	0.50	5.00	208	104
	0.50	2.50	200	100
			Mean =	104 ± 4
29.7	2.00	20.0	83	166
	2.00	16.0	76	152
	2.00	10.0	84	168
	2.00	1.00	68	136
	1.60	4.00	90	144
	1.00	8.00	146	146
	1.00	4.00	168	168
	1.00	1.00	152	152
	0.50	1.00	329	165
			Mean =	155 ± 12
35.5	2.00	5.00	101	202
	2.00	2.50	95	190
	1.60	5.00	124	198
	1.60	2.50	120	192
	1.00	2.50	196	196
	1.00	1.25	180	180
	0.50	2.50	396	198
			Mean =	194 ± 7

Mechanism of the Oxidation of HN_3 *by* $[Ni(bipy)_3]^{3+}$.—Although the oxidation of HN_3 by $[Ni(bipy)_3]^{3+}$ is sensitive to specific cation effects at high ionic strengths, unlike the oxidation by $Co^{III}(aq)$,[3] it seems clear that the rate is inversely dependent on $[H^+]$. For such a dependence in an oxidation by an aqua-cation there are a number of possibilities to account for the variation with $[H^+]$: acid dissociation of HN_3, hydrolysis of the aqua-cation, or dissociation of a proton from an intermediate complex. As in the oxidation of H_2O_2 [10] and Br^- [11] by $[Ni(bipy)_3]^{3+}$, intermediate complexes are not detected with HN_3: for H_2O_2 [10] and Br^-,[11] the oxidations by $[Ni(bipy)_3]^{3+}$ are independent of $[H^+]$, confirming that the acid dependence observed for the oxidations of these ligands by aqua-cations must arise from either of the last two possible causes given above. With HN_3 such a proton dependence operating on $[Ni(bipy)_3]^{3+}$ is not possible since there are no water molecules in the first co-ordination sphere and the rate of removal of bipy ligand is *directly* dependent on $[H^+]$.[20] However, the experimental inverse dependence shows that a proton is removed from the reactants in the transition state. Although the azide must be present as HN_3 in the bulk solution at these acidities, since the acid-dissociation constant of HN_3 at $I = 2.00$ mol dm^{-3} is *ca.* 1×10^{-4} mol dm^{-3} at 20 °C,[21] the form in the transition must be $[N_3]^-$ as in (2)—(4) with $k' \gg k$. The

$$HN_3 \overset{K}{\rightleftharpoons} H^+ + [N_3]^- \qquad (2)$$

$$[Ni(bipy)_3]^{3+} + [N_3]^- \xrightarrow{k} [Ni(bipy)_3]^{2+} + N_3\cdot \qquad (3)$$

$$2N_3\cdot \xrightarrow{k'} 3N_2 \qquad (4)$$

$$\text{Rate} = kK[Ni(bipy)_3{}^{3+}][HN_3][H^+]^{-1} \qquad (5)$$

rate is then given by (5), conforming to the observed kinetic orders, with $k_3 = kK$. Taking the experimental values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ above for k_3, and using $\Delta H^{\ominus} =$ 15.1 kJ mol^{-1} and $\Delta S^{\ominus} = -32.6$ J K^{-1} mol^{-1} found [22] for the acid dissociation (2), for the rate-determining step (3) we obtain $\Delta H^{\ddagger} = 36 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -3 \pm 10$ J K^{-1} mol^{-1}.

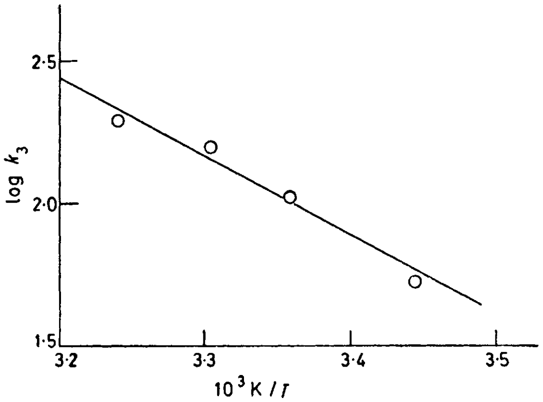

FIGURE 4 Plot of the logarithm of $k_3(= k_2[H^+])$ against $1/T$

Comparison with Oxidation of HN_3 *by Aqua-cations.*—For the oxidation of hydrazoic acid by $Co^{III}(aq)$ at high [2] $[HN_3]/[Co^{III}]$ and by $Mn^{III}(aq)$,[1] the rate-determining step is (6) followed by a rapid (7), and in the oxidation by

$$[M^{n+},HN_3] + HN_3 \longrightarrow M^{(n-1)+}(aq) + [H_2N_6]\cdot^+ \qquad (6)$$

$$M^n(aq) + [H_2N_6]^+ \longrightarrow M^{(n-1)+}(aq) + 3N_2 + 2H^+ \qquad (7)$$

$$M^{n+}(aq) + [N_3]^- \longrightarrow M^{(n-1)+}(aq) + N_3\cdot \qquad (8)$$

$Co^{III}(aq)$ at low $[HN_3]/[Co^{III}]$ the rate-determining step is (8),[3] which may or may not involve an intermediate complex and which is followed by rapid (4). The kinetics of the oxidation of hydrazoic acid by $Ce^{IV}(aq)$ do not tell us the form of the substrate ligand in the transition state, but they do require the reaction to go through an intermediate (cation + ligand) complex. The conclusion from the above, combined with the new information from the oxidation by $[Ni(bipy)_3]^{3+}$, appears to be that the oxidation of HN_3 requires two HN_3 molecules in the transition state, whereas oxidation of the azide ion requires only one. Since the kinetic requirements at high $[HN_3]/[M^{n+}]$ for $Mn^{III}(aq)$ and $Co^{III}(aq)$ is that, for

$$M^{n+}(aq) + HN_3 \overset{\beta}{\rightleftharpoons} [M^{n+},HN_3](aq) \qquad (9)$$

(9), $\beta[HN_3] \ll 1$, then at low $[HN_3]/[M^{n+}]$ for $Co^{III}(aq)$ any intermediate complex must have a very low concentration indeed, suggesting that, under the latter conditions, such an intermediate is not involved. However, the path involving the intermediate complex of HN_3 is energetically preferred with $Co^{III}(aq)$.[2] Since $[N_3]^-$ exists in such low concentrations in these strongly acidic solutions, the possibility of concerted electron and proton transfers taking place in a solvated outer-sphere $\{[Ni(bipy)_3]^{3+} + HN_3\}$ complex cannot be excluded.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are concerned with the rearrangement of the redox system and solvation in the transition state to allow electron tunnelling to occur between the ligand and the cation. The overall $\Delta H^{\ddagger}$ (kJ mol^{-1}) for HN_3 with aqua-cations, Ce^{IV} (zero) [4] < Co^{III} (53)[2] < Mn^{III} (80),[1] does not follow the reverse order of their redox potentials (V), Co^{III} (1.95) [23] > Ce^{IV} (1.76) [24] > Mn^{III} (1.56),[25] presumably because of the very high β for (9) with $M^{n+} = Ce^{IV}$. The overall $\Delta S^{\ddagger}$ reflects the balance between the lowering of restriction on the solvent in the transition state ($\Delta S^{\ddagger}_e$) to accommodate the lowering of charge on the cation and the increase in restriction imposed by any proton ejected ($\Delta S^{\ddagger}_p$).[10] Thus, although the overall $\Delta H^{\ddagger}$ for HN_3 with $Co^{III}(aq)$ and $[Ni(bipy)_3]^{3+}$ are very close (53 and 51 kJ mol^{-1}), the transfer of the proton to the solvent in the latter case produces greater restriction and a negative overall $\Delta S^{\ddagger}$ compared with an overall $\Delta S^{\ddagger} = 7$ J K^{-1} mol^{-1} for the protonic charge developing on $[H_2N_6]^+$ with $Co^{III}(aq)$.

Comparison with Oxidation of Other Ligands by $[Ni(bipy)_3]^{3+}$.—For oxidation by $[Ni(bipy)_3]^{3+}$, $\Delta S^{\ddagger} = -3$ J K^{-1} mol^{-1} for the rate-determining steps with both $[N_3]^-$ and Br^- without proton ejection being involved, but $\Delta S^{\ddagger} = -126$ J K^{-1} mol^{-1} for H_2O_2 with $|\Delta S^{\ddagger}_p| > |\Delta S^{\ddagger}_e|$ when a proton is transferred to solvent.

$\Delta H^{\ddagger}$ (kJ mol^{-1}) for these ligands with $[Ni(bipy)_3]^{3+}$, H_2O_2 (38) [10] $<$ HN_3 (51) $<$ Br^- (60),[11] does not follow the reverse order of their redox potentials (V),[26] Br^- (1.087) $>$ H_2O_2 (0.68) $>$ HN_3 (-3.1); presumably, the low $\Delta H^{\ddagger}$ for H_2O_2 arises from a large negative contribution from $\Delta H^{\ddagger}_{p}$.

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