Kinetics of the Oxidation of Hydrogen Azide (Hydrazoic Acid) by Bis(2,2′-bipyridine)manganese(III) Ions in Aqueous Perchlorate Media

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On mixing HN_3 with solutions containing $[Mn(bipy)_2]^{3+}$(aq) (bipy = 2,2′-bipyridine) the absorbance at 400 nm first increases before decreasing to zero. The analysis of the absorption coefficient extrapolated to zero time for the rise in absorbance shows that two 1 : 1 complexes are formed between N_3^- and $[Mn(bipy)_2]^{3+}$. The kinetics of the subsequent decay in absorbance show that both these complexes, $[Mn(bipy)_2(N_3)]^{2+}$ and $[Mn(bipy)_2(OH)(N_3)]^+$, are involved in the oxidation process producing free radicals $N_3^{\bullet}$. This oxidation is compared with the kinetics of the oxidation of HN_3 by aqua cations and by $[Ni(bipy)_3]^{3+}$.

Following the investigation of the kinetics of the oxidation of hydrazoic acid (hydrogen azide, HN_3) by tris(2,2′-bipyridine)nickel(III) ions[1] to compare with the kinetics of the oxidation of this substrate ligand by aqua cations, particularly by aquamanganese(III),[2] aquacerium(IV),[3] and aquacobalt(III),[4,5] we now report the results of our kinetic investigation of the oxidation of hydrazoic acid by a monomeric complex of manganese(III) complexed with 2,2′-bipyridine (bipy).[6] A spectrophotometric investigation has shown that this complex exists probably mainly as $[Mn(bipy)_2(H_2O)(OH)]^{2+}$ in solution.

Experimental

Materials.—Solutions of bis(2,2′-bipyridine)manganese(III) ions were prepared[6] by the anodic oxidation of tris(2,2′-bipyridine)manganese(II) ions under nitrogen at a Pt electrode using a current density of 0.022 A cm^{-2} at 36 V. Solutions of sodium and lithium perchlorates were prepared by neutralizing 12 mol dm^{-3} $HClO_4$ with the appropriate carbonate, boiling to dispel CO_2, followed by filtration to remove the precipitated trace impurities. AnalaR $HClO_4$ was used and water was distilled once in an all-glass still. Sodium azide was used. Acrylonitrile was purified by washing 100 cm^3 with three separate portions (25 cm^3) of 1.0 mol dm^{-3} NaOH followed by washing five times with distilled water (5 × 20 cm^3): after drying over AnalaR anhydrous sodium sulphate for 10 h, the sample was distilled under a reduced pressure of nitrogen and then stored in a dark bottle under nitrogen.

Procedure.—The decay of Mn^{III} was followed in the thermostatted cell housing of an SP800 or SP500 Series 2 spectrophotometer, the reaction trace being followed using pen recorders. Water was circulated from a thermostat for temperatures above room temperature and from a cryostat for temperatures below room temperature.

Results and Discussion

Stoicheiometry.—Excess of $[Mn(bipy)_2]^{3+}$(aq) was allowed to react with HN_3 in solutions containing various $[HClO_4]$ at 25 °C. The $[Mn^{III}]$ remaining after the reaction was estimated by sampling into a solution containing excess of Fe^{II} which was then back-titrated with a standard solution of Ce^{IV}; the initial $[Mn^{III}]$ was estimated by the same procedure using a mixture without HN_3 present. The values for the consumption ratio $|\Delta[Mn(bipy)_2{}^{3+}(aq)]|/|\Delta[HN_3]|$ obtained are given in Table 1. The mean value of the consumption ratio = 0.98 ± 0.07 confirms that the stoicheiometry conforms to that found for the oxidation of HN_3 by other transition-metal ions [equation (1)].[1-5]

$$2Mn^{III} + 2HN_3 \longrightarrow 2Mn^{II} + 3N_2 + 2H^+ \qquad (1)$$

Table 1. Consumption ratios for the $[Mn(bipy)_2]^{3+}$(aq) + HN_3 reaction at 25 °C with initial $[Mn^{III}] \approx (2.5—3.0) \times 10^{-4}$ mol dm^{-3} and ionic strength = $[H^+]$ at 25.0 °C

$[H^+]$/mol dm^{-3}	$10^4[HN_3]$/ mol dm^{-3}	$\frac{\lvert\Delta[Mn^{III}]\rvert}{\lvert\Delta[HN_3]\rvert}$
1.00	0.98	1.13
1.00	1.96	0.95
1.00	0.98	1.02
1.00	1.96	0.88
1.00	1.96	0.93
1.00	1.96	0.95
2.00	0.98	1.02
2.00	1.96	0.92

Preliminary Kinetic Observations.—Figure 1 shows two typical reaction traces at 400 nm for the reduction of $[Mn(bipy)_2]^{3+}$(aq) by hydrazoic acid. Two distinct regions are discernible: an initial rise in absorbance lasting no more than 2 min, followed by a slower decline in the absorbance. It is reasonable to suppose that the initial rise can be ascribed to complex formation between $[Mn(bipy)_2]^{3+}$(aq) and HN_3, whilst the slower decay is the decomposition of this complex, or of complexes arising from the oxidation of the ligand HN_3 (or N_3^-) and the conversion $Mn^{III} \longrightarrow Mn^{II}$.

It was found that such mixtures of $[Mn(bipy)_2]^{3+}$(aq) and HN_3 rapidly initiate the polymerization of acrylonitrile under anaerobic conditions. As neither of the reacting species will do this when added separately to an aqueous mixture of acrylonitrile, it can be assumed that the redox steps produce some free radicals which are capable of initiating the polymerization chain.

Rates of Decay of the Absorbance.—The decay of the absorbance with $[HN_3] \gg [Mn(bipy)_2{}^{3+}(aq)]$ was found to be first order at constant acidity, temperature, and ionic strength: the latter was maintained by the addition of $NaClO_4$. Values for the pseudo-first-order rate constant k_0 calculated from the slopes of these linear plots are collected in Table 2. This Table shows that there is no effect on the rate constant of changing sodium perchlorate for lithium perchlorate to maintain a constant ionic strength. Similar results were obtained at an ionic strength = 2.00 mol dm^3 at 25.0 °C. Plots of k_0^{-1} against

Table 2. Pseudo-first-order rate constants, $10^4k_0/s^{-1}$, for the oxidation of HN_3 (10^{-3} mol dm^{-3}) by $[Mn(bipy)_2]^{3+}$(aq) (initial concentration = *ca.* 2 × 10^{-4} mol dm^{-3}) for various $[H^+]$ (mol dm^{-3}) over a range of temperatures at an ionic strength = 1.00 mol dm^{-3}

	25.0 °C		17.7 °C		34.0 °C		43.5 °C	
$[H^+]$	$[HN_3]$	k_0	$[HN_3]$	k_0	$[HN_3]$	k_0	$[HN_3]$	k_0
0.100	2.00	7.2	20.0	7.4	2.00	14.1	1.00	23.5
0.100	2.00	7.0	30.0	8.2	4.00	23.5	2.00	41.0
0.100	3.90	11.1	40.0	8.7	8.00	34.5	4.00	60
0.100	3.90	11.2	80.0	10.3	20.0	48.0	8.00	92
0.100	7.80	14.9						
0.100	8.10	12.6						
0.100	12.2	14.5						
0.100	15.7	17.6						
0.100	19.6	18.1						
0.100	19.6	18.8						
0.200			20.0	7.1	2.00	9.4	1.00	17.2
0.200			30.0	8.9	4.00	16.7	2.00	30.0
0.200			40.0	10.3	8.00	32.5	4.00	45
0.200			80.0	11.5	20.0	49	8.00	68
0.300	2.00	4.30						
0.300	2.00	3.90						
0.300	3.90	7.4						
0.300	3.90	9.0						
0.300	3.90	7.8						
0.300	7.80	13.0						
0.300	7.80	14.4						
0.300	11.8	15.9						
0.300	15.7	20.3						
0.300	19.6	20.5						
0.500	2.00	3.20	20.0	7.4	2.00	7.3	1.00	9.2
0.500	2.00	3.00	30.0	9.0	4.00	11.6	2.00	17.0
0.500	2.00	3.30*	40.0	11.6	8.00	20.0	4.00	31.7
0.500	2.00	3.50*	80.0	13.7	20.0	41.0	8.00	58
0.500	3.90	5.8						
0.500	3.90	6.1						
0.500	3.90	6.0*						
0.500	3.90	6.2*						
0.500	7.80	10.0						
0.500	7.80	10.7*						
0.500	7.80	11.6*						
0.500	8.10	9.6						
0.500	11.8	12.7						
0.500	12.2	11.8						
0.500	15.7	17.2						
0.500	16.2	15.3						
0.500	19.6	19.4						
0.500	19.6	18.2						
0.500	19.6	17.2						
0.500	19.6	20.5*						
0.500	19.6	21.3*						
0.500	20.3	16.8						
0.700	2.00	2.90						
0.700	2.00	2.80						
0.700	3.90	6.2						
0.700	3.90	6.0						
0.700	3.90	5.6						
0.700	7.80	10.1						
0.700	7.80	10.0						
0.700	19.6	20.4						
0.700	19.6	18.5						
0.700	19.6	20.7						
1.00	2.00	2.40	7.80	3.60	2.00	6.5	1.00	7.3
1.00	2.00	2.70	7.80	3.80	2.00	6.3	1.00	7.8
1.00	2.00	2.60	19.6	7.3	2.00	6.0	1.00	7.8
1.00	3.90	4.60	19.6	6.9	3.90	11.1	2.00	17.2
1.00	3.90	5.3	39.2	11.4	3.90	11.7	2.00	14.5
1.00	3.90	4.40	39.2	12.4	7.80	22.8	2.00	13.9
1.00	7.80	8.5	78.3	16.3	7.80	22.5	3.90	26.2
1.00	8.10	8.7	78.3	18.2	19.6	45	3.90	27.2
1.00	8.10	9.3	156.6	24.2	19.6	45	7.8	52
1.00	11.8	12.3	156.6	19.7			7.8	45
1.00	12.2	12.3					7.8	56
1.00	12.2	12.9						
1.00	15.9	15.4						
1.00	16.2	19.7						
1.00	16.2	16.4						
1.00	19.6	19.1						
1.00	19.6	21.1						
1.00	20.3	18.7						
1.00	20.3	18.4						
1.00	39.2	30.6						
1.00	39.2	28.8						
1.00	78.3	64						
1.00	78.3	46						
1.00	117.5	57						
1.00	156.6	61						
1.00	195.8	330						

* With added $LiClO_4$.

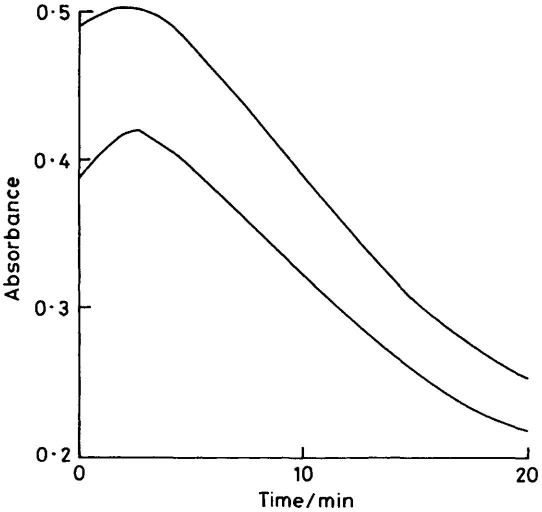

Figure 1. Change in absorbance with time for the reaction $[Mn(bipy)_2]^{3+}$ + HN_3 at 21.5 °C with $[H^+]$ = 0.100 mol dm^{-3} and $[NH_3]$ = 4.0 × 10^{-3} mol dm^{-3}

Table 3. Slopes and intercepts of plots of k_0^{-1} *vs.* $[HN_3]^{-1}$ for the oxidation of HN_3 by $[Mn(bipy)_2]^{3+}$(aq) ions at varying $[H^+]$ and temperature with ionic strength = 1.00 mol dm^{-3}

T/°C	$[H^+]$/ mol dm^{-3}	Slope/mol s dm^{-3}	Intercept/s
17.7	0.100	9.9 ± 1.2	800 ± 40
17.7	0.200	14.9 ± 1.9	640 ± 60
17.7	0.500	17.2 ± 2.0	500 ± 70
17.7	1.00	18.5 ± 0.5	374 ± 92
25.0	0.100	1.80 ± 1.94	480 ± 303
25.0	0.300	4.25 ± 0.16	228 ± 26
25.0	0.500	5.61 ± 0.15	292 ± 39
25.0	0.700	6.48 ± 0.17	139 ± 47
25.0	1.00	7.62 ± 0.01	141 ± 23
34.0	0.100	1.11 ± 0.02	152 ± 7
34.0	0.200	1.96 ± 0.08	93 ± 23
34.0	0.500	2.45 ± 0.21	176 ± 60
34.0	1.00	3.01 ± 0.08	73 ± 25
43.5	0.100	0.36 ± 0.01	70 ± 6
43.5	0.200	0.49 ± 0.01	91 ± 6
43.5	0.500	1.04 ± 0.03	52 ± 17
43.5	1.00	1.25 ± 0.04	30 ± 27

Table 4. Variation of the absorption coefficient, ε_0/dm^3 mol^{-1} cm^{-1}, at 400 nm with [HN$_3$] (10^{-3} mol dm^{-3}), [H$^+$] (mol dm^{-3}), and temperature (°C) for mixtures of [Mn(bipy)$_2{}^{3+}$(aq)] $\approx 2 \times 10^{-4}$ mol dm^{-3} and HN$_3$ at an ionic strength = 1.00 mol dm^{-3}

[H$^+$]	[HN$_3$]	21.5 °C	30.5 °C	39.3 °C
0.100	4.00	1 060	1 085	1 155
0.100	5.00		1 115	1 245
0.100	6.00	1 100	1 145	1 255
0.100	8.00		1 160	1 350
0.100	10.0	1 170	1 175	1 375
0.100	15.0		1 205	1 525
0.100	16.0	1 290		
0.100	20.0	1 235	1 245	1 560
0.100	40.0	1 345		
0.400	4.00	970	980	1 065
0.400	5.00	1 000	1 005	1 045
0.400	6.00	1 005	1 020	1 095
0.400	8.00	1 035	1 060	1 115
0.400	10.0	1 045	1 085	1 115
0.400	15.0	1 105	1 125	1 260
0.400	20.0	1 150	1 190	1 345
0.700	4.00	930	930	990
0.700	5.00	940	945	1 020
0.700	6.00	960	945	1 030
0.700	8.00	985	980	1 085
0.700	10.0	1 020	1 005	1 105
0.700	15.0	1 050	1 045	1 175
0.700	20.0	1 105	1 050	1 010
1.00	4.00	910	915	995
1.00	5.00	930	925	1 005
1.00	6.00	940	925	1 055
1.00	8.00	965	945	1 085
1.00	10.0		955	1 080
1.00	12.0	990		
1.00	15.0		970	1 160
1.00	20.0	1 045	1 010	1 270

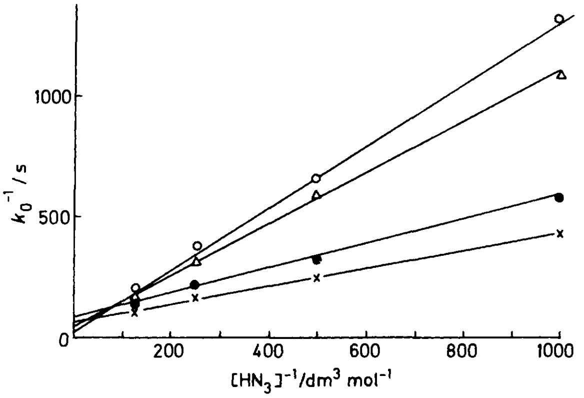

Figure 2. Variation of k_0^{-1} with [HN$_3$]$^{-1}$ for the reaction [Mn(bipy)$_2$]$^{3+}$ + HN$_3$ at 43.5 °C and I = 1.00 mol dm^{-3} with [H$^+$] (mol dm^{-3}) as follows: ×, 0.100; ●, 0.200; △, 0.500; ○, 1.00

[HN$_3$]$^{-1}$ for constant acidity and temperature are straight lines with intercepts on the k_0^{-1} axis: these are illustrated in Figure 2 at 43.5 °C.

The values of the slopes and intercepts of these plots for all the temperatures, calculated by applying the least-squares procedure are given in Table 3 together with their standard errors. At all temperatures, both the slopes and intercepts vary with acidity.

Initial Increase in the Absorbance.—This was investigated at 21.5, 30.5, and 39.3 °C by extrapolating log(absorbance) *vs.* time plots back to zero time and then calculating the value of the absorption coefficient, ε_0. These values for ε_0 are recorded in Table 4.

Possible pre-equilibria which may participate in this initial period are given by equations (2)—(6). Process (2) followed by

$$[\mathrm{Mn(bipy)_2}]^{3+}(\mathrm{aq}) \xrightleftharpoons{K_h} [\mathrm{Mn(bipy)_2(OH)}]^{2+}(\mathrm{aq}) + \mathrm{H^+(aq)} \quad (2)$$

$$[\mathrm{Mn(bipy)_2}]^{3+}(\mathrm{aq}) + \mathrm{HN_3} \xrightleftharpoons{\beta} [\mathrm{Mn(bipy)_2(HN_3)}]^{3+}(\mathrm{aq}) \quad (3)$$

$$[\mathrm{Mn(bipy)_2(HN_3)}]^{3+}(\mathrm{aq}) \xrightleftharpoons{K} [\mathrm{Mn(bipy)_2(N_3)}]^{2+}(\mathrm{aq}) + \mathrm{H^+(aq)} \quad (4)$$

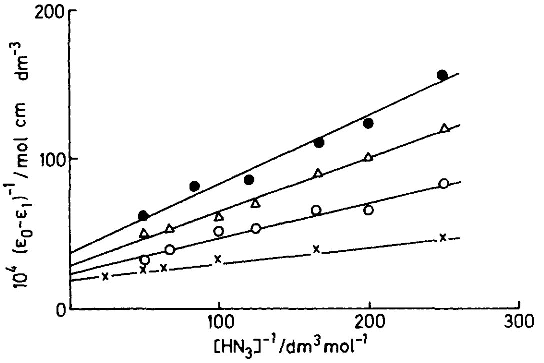

Figure 3. Variation of $(\varepsilon_0 - \varepsilon_1)^{-1}$ with [HN$_3$]$^{-1}$ for the rise in absorbance at zero time in [Mn(bipy)$_2$]$^{3+}$ + HN$_3$ mixtures at 21.5 °C and I = 1.00 mol dm^{-3} with [H$^+$] (mol dm^{-3}) as follows: ×, 0.100; ○, 0.400; △, 0.700; ●, 1.00

$$[\mathrm{Mn(bipy)_2(N_3)}]^{2+}(\mathrm{aq}) \xrightleftharpoons{K'} [\mathrm{Mn(bipy)_2(N_3)(OH)}]^{+}(\mathrm{aq}) + \mathrm{H^+(aq)} \quad (5)$$

$$[\mathrm{Mn(bipy)_2(OH)}]^{2+}(\mathrm{aq}) + \mathrm{HN_3} \xrightleftharpoons{\beta'} [\mathrm{Mn(bipy)_2(N_3)}]^{2+}(\mathrm{aq}) \quad (6)$$

(6) is indistinguishable from process (3) followed by (4). If it is assumed that $K_h h^{-1} \gg 1$, where h = [H$^+$], and that the concentration of [Mn(bipy)$_2$]$^{3+}$(aq) can be neglected relative to that of all other species of Mn$^{\mathrm{III}}$, and if absorption coefficients are assigned as follows, [Mn(bipy)$_2$(OH)]$^{2+}$(aq) ε_1, [Mn(bipy)$_2$(HN$_3$)]$^{3+}$(aq) ε_2, [Mn(bipy)$_2$(N$_3$)]$^{2+}$(aq) ε_3, and [Mn(bipy)$_2$(N$_3$)(OH)]$^+$ ε_4, then equation (7) can be deduced.

$$\frac{1}{\varepsilon_0 - \varepsilon_1} = \frac{K_h h}{\beta\{(\varepsilon_2 - \varepsilon_1)h^2 + (\varepsilon_3 - \varepsilon_1)Kh + (\varepsilon_4 - \varepsilon_1)KK'\}[\mathrm{HN_3}]} + \frac{h^2 + Kh + KK'}{(\varepsilon_2 - \varepsilon_1)h^2 + (\varepsilon_3 - \varepsilon_1)Kh + (\varepsilon_4 - \varepsilon_1)KK'} \quad (7)$$

It is assumed that all uncomplexed azide exists as HN$_3$ in these high acid concentrations. From equation (7), plots of $(\varepsilon_0 - \varepsilon_1)^{-1}$ *vs.* [HN$_3$]$^{-1}$ should be straight lines for constant acidity and constant temperature. Using ε_1 = 850 dm^3 mol^{-1}

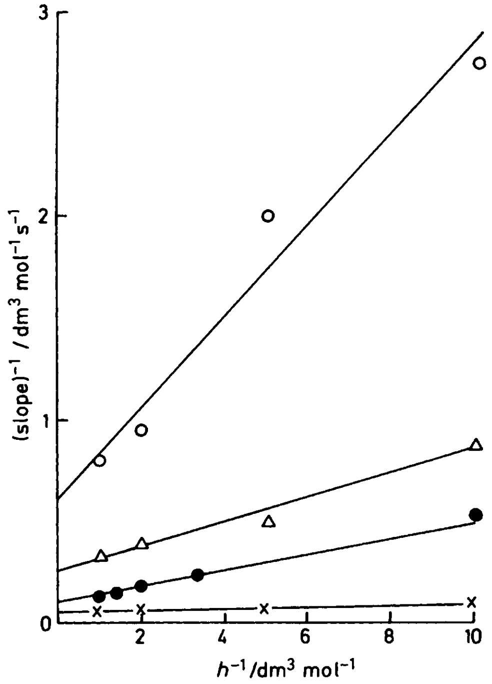

Figure 4. Variation in (slope)$^{-1}$, from Table 3, with $[H^+]^{-1}$ for the $[\mathrm{Mn(bipy)_2}]^{3+}$ + HN_3 oxidation at I = 1.00 mol dm^{-3} and the following temperatures: ×, 17.7; ●, 25.0; △, 34.0; ○, 43.5 °C

cm^{-1},[6] this is indeed found to be the case and the plots at 21.5 °C are shown in Figure 3.

From equation (7), the slopes and intercepts of these plots should be related *via* equation (8). Values for the slopes and

$$\frac{(\text{intercept})h}{\text{slope}} = \frac{\beta(h^2 + Kh + KK')}{K_h} \tag{8}$$

intercepts for varying acidity at each of the temperatures, calculated using the least-squares method, are collected in Table 5. Although the errors are large, the approximately linear plots of $\{(\text{intercept})h/(\text{slope})\}$ *vs.* h suggest that $h^2 \ll Kh + KK'$ in equation (8): in this case, the value for $\beta K/K_h$ ranges from 70 to 85 dm^3 mol^{-1} and that for $\beta KK'/K_h$ ranges from 6 to 8.5 in the temperature range 21.5—39.3 °C.

Mechanism of the Oxidation.—Bearing in mind the result of the analysis of the variation of ε_0 with h above, reactions (9) and (10) are suggested as rate-determining steps in the oxidation

$$[\mathrm{Mn(bipy)_2(N_3)}]^{2+}(\mathrm{aq}) \xrightarrow{k} \mathrm{Mn^{II}} + \mathrm{N_3^{\bullet}} \tag{9}$$

$$[\mathrm{Mn(bipy)_2(OH)(N_3)}]^{+}(\mathrm{aq}) \xrightarrow{k'} \mathrm{Mn^{II}} + \mathrm{N_3^{\bullet}} \tag{10}$$

leading to the decay of Mn^{III}. The free radicals, $N_3^{\bullet}$, will initiate the polymerization observed, and in the absence of monomer, and to account for the observed stoicheiometry, are probably removed by the rapid reaction (11), as found previously.[1-5]

$$\mathrm{N_3^{\bullet}} + \mathrm{N_3^{\bullet}} \xrightarrow{\text{fast}} 3\mathrm{N_2} \tag{11}$$

Assuming that the complex formation and the oxidative decay are adequately resolved, the rate of decay of the total concentration of all species of Mn^{III}, $[\mathrm{Mn^{III}}]_{\mathrm{total}}$, is given by equation (12),

Table 5. Values of the intercepts and the reciprocal of the slopes for plots of $(\varepsilon_0 - \varepsilon_1)^{-1}$ *vs.* $[HN_3]^{-1}$ for the initial change in absorbance for the reaction $[\mathrm{Mn(bipy)_2}]^{3+}$ + HN_3 with varying $[H^+]$ (mol dm^{-3}) and temperature (°C), with ionic strength = 1.00 mol dm^{-3}

Temperature/ °C	$[H^+]$	10^4(slope)$^{-1}$/dm^6 mol^{-2} cm^{-1}	10^4(intercept)/mol dm^{-3} cm
21.5	0.100	8.35 ± 0.64	17.9 ± 1.4
21.5	0.400	4.20 ± 0.26	23.6 ± 2.5
21.5	0.700	2.80 ± 0.24	28.9 ± 5.2
21.5	1.00	2.20 ± 0.17	37.2 ± 6.0
30.5	0.100	12.9 ± 1.0	22.3 ± 0.9
30.5	0.400	4.38 ± 0.05	19.5 ± 1.3
30.5	0.700	2.50 ± 0.17	27.9 ± 4.5
30.5	1.00	2.25 ± 0.17	48.5 ± 5.3
39.3	0.100	11.1 ± 0.8	9.3 ± 1.1
39.3	0.400	6.72 ± 0.95	15.5 ± 3.8
39.3	0.700	4.45 ± 0.21	15.1 ± 1.7
39.3	1.00	4.59 ± 0.45	16.7 ± 3.6

Table 6. Values for $k\beta KK_h^{-1}$ (dm^3 mol^{-1} s^{-1}) and for $k'\beta KK'K_h^{-1}$ (s^{-1}) with varying temperature (°C) for the reaction $[\mathrm{Mn(bipy)_2}]^{3+}$ + HN_3 at ionic strength = 1.00 mol dm^{-3}

Temperature/ °C	$k\beta KK_h^{-1}$	$k'\beta KK'K_h^{-1}$
17.7	0.047 ± 0.004	0.052 ± 0.001
25.0	0.106 ± 0.067	0.041 ± 0.014
34.0	0.259 ± 0.039	0.062 ± 0.007
43.5	0.612 ± 0.182	0.231 ± 0.032

$$-\frac{d[\mathrm{Mn^{III}}]_{\mathrm{total}}}{dt} = k_0[\mathrm{Mn^{III}}]_{\mathrm{total}} = \frac{(kh^{-1} + k'K'h^{-2})\beta K[\mathrm{Mn^{III}}]_{\mathrm{total}}[\mathrm{HN_3}]}{K_h h^{-1} + \beta K(h^{-1} + K'h^{-2})[\mathrm{HN_3}]} \tag{12}$$

assuming that $K_h h^{-1} \gg 1$ and $Kh^{-1} + KK'h^{-2} \gg 1$ from the variation of ε_0 with h. Equation (12) can be rearranged to give equation (13), which accounts for the linear plots of k_0^{-1} against $[HN_3]^{-1}$ at constant acidity and temperature.

$$\frac{1}{k_0} = \frac{K_h}{(k + k'K'h^{-1})\beta K[\mathrm{HN_3}]} + \frac{1 + K'h^{-1}}{k + k'K'h^{-1}} \tag{13}$$

The slopes of these plots should vary with h as given by equation (14). Figure 4 shows that plots of (slope)$^{-1}$ against h^{-1}

$$(\text{slope})^{-1} = \frac{(k + k'K'h^{-1})\beta K}{K_h} \tag{14}$$

are linear for varying h at each temperature using the data in Table 3. The values for $k\beta KK_h^{-1}$ and $k'\beta KK'K_h^{-1}$ obtained from the application of the least-squares method to these plots are given in Table 6. Applying the least-squares procedure to the linear variation of the plots of the logarithm of these composite functions against the reciprocal of the absolute temperature produces $\Delta H^{\ddagger}$ = 35.6 ± 0.4 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 16.4 ± 2.6 J K^{-1} mol^{-1} for $k\beta KK_h^{-1}$ and $\Delta H^{\ddagger}$ = 50 ± 10 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 63 ± 68 J K^{-1} mol^{-1} for $k'\beta KK'K_h^{-1}$.

From equation (13) the ratio intercept:slope of the linear plots of k_0^{-1} against $[HN_3]^{-1}$ should be given by equation (15).

$$\frac{\text{intercept}}{\text{slope}} = \frac{\beta K(1 + K'h^{-1})}{K_h} \tag{15}$$

Using the data in Table 3, there is considerable scatter on the points for a plot of intercept:slope against h^{-1} and only rough limits can be set for βKK_h^{-1} and $\beta KK'K_h^{-1}$ from the slopes and intercepts: these give 20—30 dm^3 mol^{-1} for βKK_h^{-1} and 4—10 for $\beta KK'K_h^{-1}$, which are in the same order as found above from the analysis of the variation of ε_0 with h.

Conclusions

The conclusions drawn from the kinetic and equilibrium studies here contrast with those for the oxidation of HN_3 by some aqua cations, $Mn^{III}(aq)$[2] and $Co^{III}(aq)$,[5] where, at high initial ratios of $[HN_3]/[\text{cation}]$, two HN_3 molecules are present in the transition state for each oxidizing cation. A reasonable explanation for this latter observation is that a 1:1 complex between the cation and HN_3 interacts oxidatively with another HN_3 molecule. The kinetics of the oxidation of HN_3 by $Ce^{IV}(aq)$ also suggest that intermediate complexes are involved.[3] To account for the variation of the rate constant with acidity in the oxidation of HN_3 by $[Ni(bipy)_3]^{3+}$ ions, it was suggested that an outer sphere 1:1 complex between the cation and N_3^- is involved in the rate-determining oxidative step. In the oxidation of HN_3 by $[Mn(bipy)_2]^{3+}(aq)$ investigated here, both approaches, that of the interpretation of the initial rise in the absorbance and that of the subsequent oxidation resulting in the decay of Mn^{III} to Mn^{II}, show that 1:1 complexes between $[Mn(bipy)_2]^{3+}$ and N_3^- ions are involved, with only one N_3^- in the transition state for the oxidation. In this repect, this oxidation resembles that by $[Ni(bipy)_3]^{3+}$: however, in that involving $[Mn(bipy)_2]^{3+}$, the initial change in the spectrum, resulting in a rise in the absorbance at 400 nm when the complex is formed, suggests that the N_3^- ion is in the first co-ordination sphere of the Mn^{III}, formed by the replacement of either an OH^- or an H_2O.

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