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Kinetics and Mechanism of Tris(pyridine-2-carboxylato)manganese(III) Reduction by Azide Ion in Sodium Pyridine-2-carboxylate–Pyridine-2-carboxylic Acid Buffer Media

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The kinetics and mechanism of the reduction of tris(pyridine-2-carboxylato)manganese(III) by azide ion in Na(pic)–picH [where Na(pic) = sodium salt of pyridine-2-carboxylic acid and picH = pyridine-2-carboxylic acid] have been studied. The reaction appears to proceed through the intermediate formation of a hepta-coordinated 1 : 1 complex between $[Mn^{III}(pic)_3]$ and N_3^- ion, which then decomposes to give the free radical ($\dot{N}_3$) and diaquabis(pyridine-2-carboxylato)manganese(II). The free radical $\dot{N}_3$ further reacts with $[Mn^{III}(pic)_3]$ to give nitrogen as the product of oxidation. During the reduction, pyridine-2-carboxylate ion is generated and the coordination sphere of the parent complex is altered, thereby indicating that the reaction takes place by an inner-sphere mechanism. The enthalpy change (ΔH°) and change in entropy (ΔS°) associated with the equilibrium step are -61 ± 4 kJ mol^{-1} and -169 ± 14 J K^{-1} mol^{-1}, whereas the enthalpy of activation ($\Delta H^{\neq}$) and the entropy of activation ($\Delta S^{\neq}$) associated with the slowest step are found to be 91 ± 4 kJ mol^{-1} and 11 ± 14 J K^{-1} mol^{-1}, respectively.

Kinetic studies of the reaction of HN_3 with Cr(II) and HNO_2 have been reported,[1—3] and in both reactions N_2 was formed. The oxidations of HN_3 by aqua ions of Mn(III),[4,5] Co(III)[6—8] and Ce(IV)[9] in acidic media have also been studied. The reaction between the tetrahydroxoargentate(III)[10] and azide ion proceeds via the formation of a monoazidosilver(III) complex, which undergoes an internal two-electron redox only after a reaction with an additional N_3^-. There have been some reports on the kinetics of aqueous electron-transfer reactions between substitution inert metal complexes and N_3^-.[11—13] In addition to this, the reaction of ClO_2 and excess N_3^- in aqueous media has been studied,[14] which proceeds with a complex kinetics, whereas in the presence of spin trap PBN (*N*-*t*-butyl-α-phenylnitrone) the reaction is much simpler. However, there is no literature data to date concerning the oxidation of N_3^- by tris(pyridine-2-carboxylato)manganese(III).[15] An attempt has therefore been made to study the kinetics and mechanism of the oxidation of azide ion by this oxidant. It will be interesting to see whether the oxidant is a substitution inert or labile complex. The complex is unstable in an acid or alkaline medium, but stable in a Na(pic)–picH buffer medium over the pH range of (4.22—6.45), which minimizes the possibility of a ligand-substitution reaction.

Experimental

Materials. A sodium azide (Loba) stock solution was prepared from solid NaN_3, which had been recrystallized twice from water. The azide concentration was determined by the addition of an excess standard cerium(IV) sulfate solution followed by back titration with standard iron(II) to a ferroin end point.[16] Pyridine-2-carboxylic acid (Lancaster) was used without purification and its sodium salt was prepared by the addition of the requisite amount of NaOH. All solutions were made in doubly distilled H_2O. The oxidation studies were carried out in Na(pic)–picH buffer, which was prepared by mixing pyridine-2-carboxylic acid ($pK_a = 5.52$)[17] with its sodium salt in calculated amounts. The pH of each buffer solution remained unaltered for a considerable period of time, indicating that the buffer solutions are stable in the pH range studied.

The complex, tris(pyridine-2-carboxylato)manganese(III) was prepared by a modified procedure, as mentioned in the literature.[18] 2.5 g $MnCl_2\cdot6H_2O$ was dissolved in 25 cm^3 of water. The solution was warmed, and 25 cm^3 of H_2O_2 was added to it. This was followed by the addition of 1 g NaOH dissolved in 25 cm^3 of water. The mixture was stirred vigorously for at least 30 min, and the precipitated MnO_2 was filtered through a sintered-glass crucible. The precipitate was washed thoroughly with water and then warmed with an aqueous solution of excess pyridine-2-carboxylic acid with vigorous stirring. It was then filtered through a sintered-glass crucible. The scarlet red filtrate deposited red crystals of tris(pyridine-2-carboxylato)manganese(III) on cooling.

C, H, N analysis of the complex yielded the results: Found: C, 49.95; H, 3.3; N, 9.4%. Calcd for $[Mn^{III}(C_5H_4NCO_2)_3]\cdot H_2O$: C, 49.2; H, 3.2; N, 9.6%. A thermogravimetric analysis of the solid product was carried out by heating a sample (10 mg) at a rate of 10 °C per min. The result indicates that a loss of the water of crystallisation takes place in one step; from a weight-loss calculation based on $[Mn^{III}(C_6H_4NO_2)_3(H_2O)]$ we confirm that one water molecule is lost in one step. The structure of the manganese(III) complex has been reported[15] to be a tetragonally distorted octahedron with the axial positions occupied by N-atoms and with the axial bonds elongated. The room-temperature magnetic moment (ca. 25 °C) of the solid compounds has been found to be 4.92 B.M.

This value is not different from those mentioned for octahedral Mn$^{\mathrm{III}}$ complexes (4.90 B.M.).[19] The existence of Mn(III) in the complex has thus been confirmed by the electronic spectra and the magnetic moment measurement.

The Mn(III) solution was estimated[20a,20b] as follows. To 25 ml of a solution containing [Mn$^{\mathrm{III}}$(pic)$_3$] was added a known excess of a standard ferrous ammonium sulfate solution. The excess of ferrous ammonium sulfate was determined by titration with a standard $K_2Cr_2O_7$ solution using phosphoric acid and a barium diphenylamine-4-sulfonate indicator.

All other inorganic materials were of the highest purities available. The solutions were made from doubly distilled water.

Instrumentation. The absorbances were measured on a Systronics (India) and Shimadzu UV-160 spectrophotometer. Analyses of C, H, and N were performed by the micro analytical laboratory using a Perkin–Elmer 240 C, H, N Analyser. T.g.a studies were performed in a Shimadzu Corporation (Japan) TG 50 in a normal atmospheric environment. A Cyclic voltammetric experiment was performed under dry nitrogen using a Bioanalytical system (BAS) CV-2 electrochemical analyser and a BAS Model X–Y recorder at 298 K. A standard three-electrode electrochemical cell consisting of a platinum disc working electrode (BAS), a platinum wire auxilliary electrodes and a Ag/AgCl reference electrode separated from the test solution by a salt-bridge containing the solvent and the supporting electrolyte. Ferrocence was used as an internal standard for a measurement of the ΔE_{p} value using the above setup. The cyclic voltammogram of [Mn$^{\mathrm{III}}$(pic)$_3$] in water in the presence of KCl as the supporting electrolyte exhibited an irreversible reductive response at -0.80 V; the corresponding oxidative response was observed at -0.47 V ($\Delta E_{\mathrm{p}} = 330$ mV; $E_{1/2} = -0.63$ V).

The oxidative potential[21] of $N_3^- = \frac{3}{2}N_2 + e^-$ is 3.4 volt, which clearly indicates that a reaction between Mn(III) and N_3^- is thermodynamically feasible. Raman spectra were recorded in a Ramalog double-grating monochromator fitted with an argon ion laser and a cooled photomultiplier detector. The excitation wavelength was 488 nm. EPR spectra were recorded with a Varian EPR spectrometer. The pH of the solution was measured at room temperature (ca. 25 °C) using an Elico, India (LI 120) pH meter calibrated with standard pH solutions.

Kinetic Measurements. The electronic absorption spectrum[19] of the Mn(III) complex exhibits two weak shoulders at approximately 21900 and 24800 cm^{-1} (ε = 257 and 407 cm^{-1} mol^{-1} dm^3). Since the extinction coefficients are small in this region, the progress of the reaction was followed spectrophotometrically at 350 nm (ε = 2710 cm^{-1} mol^{-1} dm^3), where the complex absorbs appreciably at the low concentration range of $(0.5\text{—}5.0)\times 10^{-4}$ mol dm^{-3}. Moreover Beer's law is obeyed in this concentration range. Kinetic studies were carried out under a pseudo-first-order condition with the concentration of azide in large excess compared to that of Mn(III). After the requisite volumes of the reactants at the appropriate temperature were mixed, the mixture was immediately transferred to a cell having a path length of 1 cm. The cell compartment of the spectrophotometer was kept at constant temperature. Other reactants and products were nearly transparent at this wavelength. The rate of decrease of Mn(III) was followed for at least two half lives. Pseudo-first-order rate constants were calculated from $\log A$ (A = absorbance) against time plots. The maximum error in the measurement of the rate constant was ±5%, depending upon the experimental conditions. However, for most experiments, duplicate measurements were reproducible to within ±3%.

Stoichiometry and Product Analysis. The stoichiometry of the reactions was studied both in excess of N_3^- and excess of the oxidant. The reaction mixture containing an excess of N_3^- was allowed to stand for 1 h. Blank experiments using the oxidant when kept for 1 h indicated that the compounds are stable towards reduction. A known excess of cerium(IV) solution was added to the mixture. The excess of Ce(IV) solution was then titrated as mentioned earlier. The average ratio from the different experiment are 1. Again, when the reaction was studied in an excess of oxidant and the mixture was allowed to stand for 1 h, the excess Mn(III) solution was then estimated titrimetrically, and the average ratios from three different experiments were $[N_3^-]:[\mathrm{Mn^{III}}] = 1:1$ (Table 1). The reaction may be expressed stoichiometrically by the following equation:

$$2\mathrm{Mn^{III}} + 2N_3^- \rightarrow 2\mathrm{Mn^{II}} + 3N_2. \tag{1}$$

The existence of Mn(II) in the reaction mixture was confirmed (Fig. 1) by the appearance of six typical lines in the EPR spectrum, and indicate Mn(II) as being the final product. The spectral pattern is in conformity with that reported earlier.[22] The fact that azide is oxidized to nitrogen gas was confirmed by the following experiment. A closed reaction cell containing the reactants and kept at constant temperature (298 K) was continuously purged with pure, dry argon and the outgoing gas passed for 1 h through a solution of $[\mathrm{Ru(NH_3)_5(H_20)}]^{2+}$ prepared by a standard procedure.[23a] A red complex $[\mathrm{(NH_3)_5Ru(N_2)Ru(NH_3)_5}]^{4+}$ was isolated from the solution.[23b] The Raman spectrum of this complex exhibited a strong band at around 3100 cm^{-1}, which is known to originate from the $\nu(\mathrm{N{\equiv}N})$[24] of the coordinated N_2, which must have been generated by oxidation of the azide ion by Mn$^{\mathrm{III}}$.

Test for Free Radicals. Acrylonitrile [50% (v/v)] was added during the course of the reactions. An immediate haziness appeared during the oxidation of N_3^- ion by Mn(III). When an excess of methanol was added to the reaction mixture, a thick precipitate of polyacrylonitrile was formed, demonstrating that free-radicals

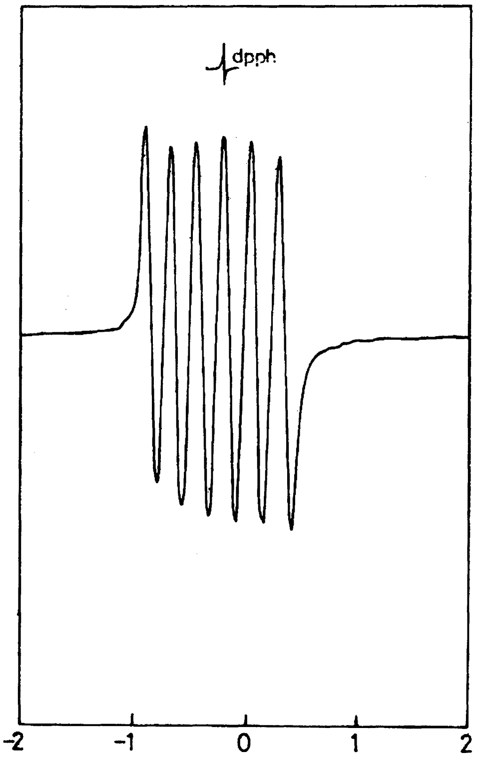


Fig. 1. EPR spectrum of the product Mn$^{\mathrm{II}}$ complex at 9.45 GHz.

Table 1. Stoichiometric Results for the Oxidation of N_3^- by Manganese(III) Complex

$\frac{[\mathrm{Mn^{III}}]}{10^{-3}\ \mathrm{mol\,dm^{-3}}}$	$\frac{[\mathrm{N_3^-}]}{10^{-2}\ \mathrm{mol\,dm^{-3}}}$	$\frac{[\mathrm{H^+}]}{\mathrm{mol\,dm^{-3}}}$	$\frac{[\mathrm{Mn^{III}}]_{\mathrm{left}}}{10^{-3}\ \mathrm{mol\,dm^{-3}}}$	$\frac{[\mathrm{N_3^-}]_{\mathrm{left}}}{10^{-2}\ \mathrm{mol\,dm^{-3}}}$	$\frac{\Delta[\mathrm{N_3^-}]}{\Delta[\mathrm{Mn^{III}}]}$
2.0	1.5		0.00	1.31	0.95
2.0	3.0		0.00	2.79	1.05
2.0	4.5	pH = 5.86	0.00	4.29	1.05
4.0	0.2		2.06	0.00	1.03
8.0	0.2		6.06	0.00	1.03

intervene in the oxidation process. Blank experiments from which either Mn(III) or azide were excluded gave no detectable polymers.

Results and Discussion

The pseudo-first-order rate constants were determined at different concentrations of $[\mathrm{Mn^{III}(C_6H_4NO_2)_3(H_2O)}]$ in the range $(0.5—5.0)\times10^{-4}$ mol dm^{-3}, but at constant $[\mathrm{N_3^-}]$, pH and temperature of 1.0×10^{-2} mol dm^{-3}, 5.86 and 308 K respectively. The values are $(1.95\pm0.06)\times10^{-3}$ s^{-1}, indicating that the rate is independent of the initial concentration of $[\mathrm{Mn^{III}(C_6H_4NO_2)_3(H_20)}]$. The reaction was also studied at different $[\mathrm{N_3^-}]$ and constant $[\mathrm{Mn^{III}(C_6H_4NO_2)_3(H_2O)}]$, pH and temperature. The results indicating that the rate increases with increasing $[\mathrm{N_3^-}]$. Plots of k_{obsd}^{-1} versus $[\mathrm{N_3^-}]^{-1}$ gave straight lines with positive intercepts on the y-axis at four different temperatures (Fig. 2) according to

$$-\frac{\mathrm{d}[\mathrm{Mn^{III}}]}{\mathrm{d}t}=\frac{k_{\mathrm{d}}K_{\mathrm{e}}[\mathrm{Mn^{III}}][\mathrm{N_3^-}]}{1+K_{\mathrm{e}}[\mathrm{N_3^-}]} \qquad (2)$$

The values of K_e and k_d, which denote the equilibrium constant for the formation of 1 : 1 complex between the reactants and the disproportionation constant of the complex, were then calculated. The reaction was also studied at different hydrogen-ion concentrations within the pH range (5.22—6.45), but at constant $[\mathrm{N_3^-}]$, $[\mathrm{Mn^{III}(C_6H_4NO_2)_3(H_2O)}]$ and temperature of 1.0×10^{-2} mol dm^{-3}, 2×10^{-4} mol dm^{-3} and 308 K respectively. The rate of the reaction remained unaffected at different hydrogen-ion concentrations.

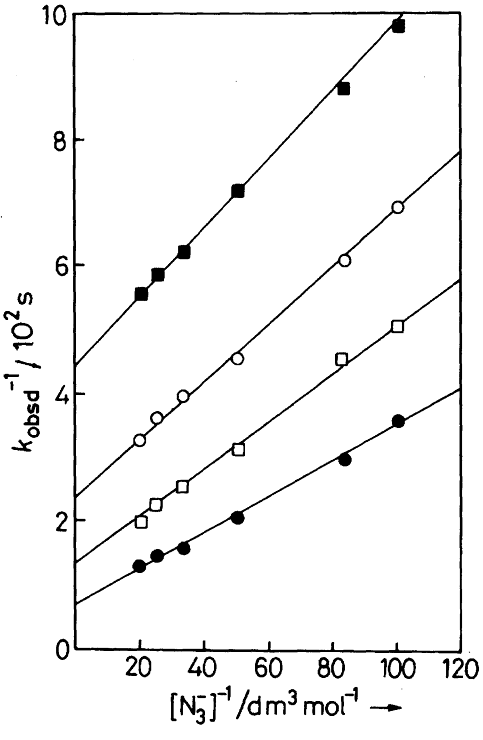


Fig. 2. Variation of pseudo-first-order rate constant with $[\mathrm{N_3^-}]$. Plots of k_{obsd}^{-1} vs. $[\mathrm{N_3^-}]^{-1}$ at 298 (■), 303 (○), 308 (□) and 313 K (●). $[\mathrm{Mn^{III}}]=2\times10^{-4}$ mol dm^{-3}, pH = 5.86.

The effect of the addition of 1,4-dioxane on the pseudo-first-order rate constant was studied for the oxidation of N_3^- by Mn(III). The rate increased about with an increase in the solvent composition (% v/v). The increase in the pseudo-first-order rate constant is small (Table 2). This result is to be expected, because the reaction takes place between an ion and a neutral molecule. No attempt was made to keep the ionic strength fixed, since the pseudo-first-order rate constant remains unaltered in the presence of different $\mathrm{NaClO_4}$ concentrations in the region (0.5 to 5)$\times10^{-1}$ mol dm^{-3}. The value of the pseudo-first-order rate constants, which are $(1.91\pm0.05)\times10^{-3}$ s^{-1}, indicates that the rate constant remains unchanged with increasing [H$^+$]. The values of K_e associated with step (5) and k_d associated with step (6) were then calculated from Fig. 2. The values of K_e are 79.2, 52.8, 35.4, and 23.4 (dm^3 mol^{-1}) at 298, 303, 308, and 313 K, respectively, whereas the values of k_d are 2.27×10^{-3}, 4.23×10^{-3}, 7.78×10^{-3}, and 14.6×10^{-3} (dm^3 mol^{-1} s^{-1}) at the respective temperatures. The values of ΔH° were calculated from a plot of log K_e against T^{-1} (Fig. 3), and then ΔS° from the relation

$$\log K_{\mathrm{e}}=1/2.303R[\Delta S^\circ-\Delta H^\circ/T]. \qquad (3)$$

The enthalpy change (ΔH°) and change in entropy (ΔS°) associated with the equilibrium step are -61 ± 4 kJ mol^{-1} and -169 ± 14 J K^{-1} mol^{-1}, respectively. The value of $\Delta H^{\neq}$ is calculated from the plot of log (k_d/T) against T^{-1} (Fig. 3)

Table 2. Effect of Solvent on the Rate of Reaction $[\mathrm{N_3^-}]=1.2\times10^{-2}$ mol dm^{-3}, $[\mathrm{Mn^{III}}]=2\times10^{-4}$ mol dm^{-3}, pH = 5.86, and Temp = 308 K.

% of 1,4-dioxane (v/v)	$k_{\mathrm{obsd}}/10^{-3}$ s^{-1}
10	2.15
20	2.3
30	2.55
40	2.7
50	2.9
60	3.0

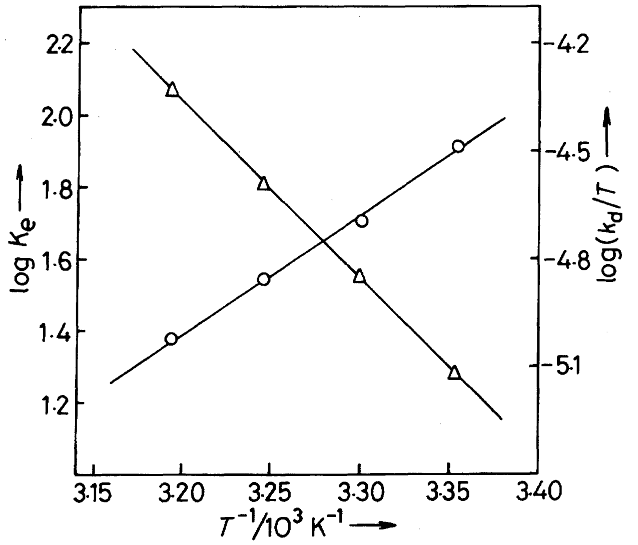
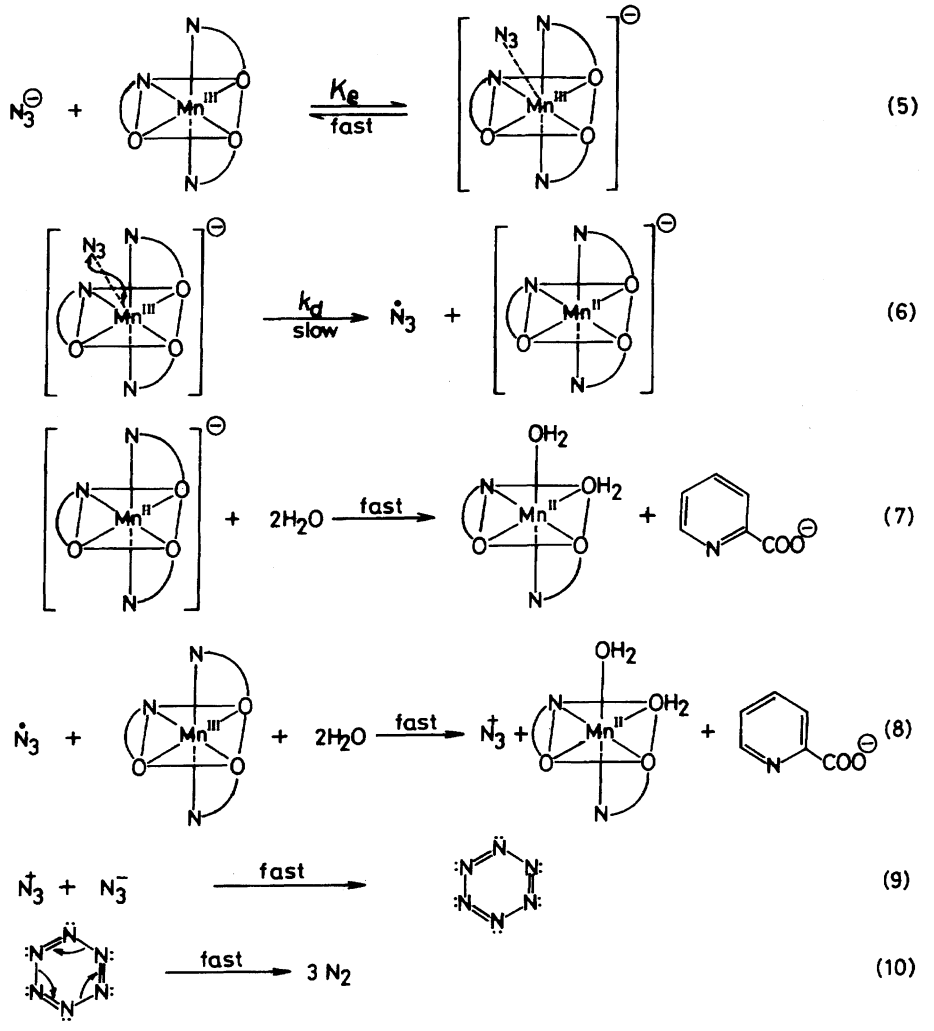


Fig. 3. Variation of equilibrium constant (K_e) and disproportionation constant (k_d) with temperature. (○) Plots of log K_e vs. T^{-1}, (△) Plots of log (k_d/T) vs. T^{-1}.

followed by a calculation of $\Delta S^{\neq}$ using the relation

$$k_d = \frac{RT}{Nh} e^{-\Delta H^{\neq}/RT} e^{\Delta S^{\neq}/R}, \tag{4}$$

where R, N, and h have their usual significance. The enthalpy of activation ($\Delta H^{\neq}$) and the entropy of activation ($\Delta S^{\neq}$) associated with the slowest step are found to be 91±4 kJ mol^{-1} and 11±14 J K^{-1} mol^{-1}, respectively. The dissociation constant[25] of hydrazoic acid to give H^+ and N_3^- is 1.8×10^{-5} mol dm^{-3}. The reaction involving the substrate and manganese(III) complex has been avoided at lower pH values, where both the HN_3 and N_3^- species may exist. It may be mentioned that hydrazoic acid is a colorless liquid (bp 37 °C) and dangerously explosive.[25] Since HN_3 is more reactive than N_3^-, the former may lead to an abrupt decomposition to nitrogen at higher temperatures. Consequently, most of the experiments were carried out at pH = 5.86 ($[N_3^-]:[HN_3] = 13:1$) where the predominating species is N_3^-. The reaction has thus been shown to occur involving N_3^- and the manganese(III) complex. The azide ion is a symmetrical linear molecule containing sixteen electrons.[26] The reaction takes place through the initial formation of an unstable hepta-coordinated complex[27,28] between the reactants.



Scheme 1.

Table 3. Effect of Acrylamide Concentrations on the Observed Pseudo-First-Order Rate Constant
$[\mathrm{N}_3^-] = 1\times10^{-2}$ mol dm^{-3}, $[\mathrm{Mn^{III}}] = 2\times10^{-4}$ mol dm^{-3}, pH = 5.86, and Temp = 308 K.

[Acrylamide]/mol dm^{-3}	$k_{\mathrm{obsd}}/10^{-3}$ s^{-1}
0.0	1.87
0.1	1.46
0.2	1.1
0.3	0.86
0.4	0.5
0.5	0.1

It is reasonable to propose the hepta-coordinated Mn(III) intermediate, because the $\mathrm{Mn^{III}}$ complex is formally a 16-electron species, and it produces an 18-electron species when N_3^- binds to it. The complex in step (5) then decomposes to give $\dot{\mathrm{N}}_3$, Mn(II) and salt of pyridine-2-carboxylic acid ($\mathrm{C_6H_4NO_2^-}$) in steps (6,7). The immediate formation of a polymeric suspension of acrylonitrile during the oxidation by manganese(III) suggests that the reaction proceeds via an intermediate formation of a free radical, $\dot{\mathrm{N}}_3$. The one-electron reduction of manganese(III) had been reported earlier.[4,5] The azide radical, $\dot{\mathrm{N}}_3$, is known to be involved in flash photolysis and molecular-beam studies.[29] This is further supported by the fact that the rate of the reaction was retarded by the addition of acrylamide (Table 3). This is possible because the polymer, when formed, may preferentially adsorb one of the reactants and abnormally reduce its bulk concentration in the aqueous phase. It may be mentioned that the addition of acrylamide to the reaction mixture gave a cloudy suspension only upon standing for nearly 1 h.

The fact that pyridine-2-carboxylic acid is generated during the reaction was confirmed by the following test.[30] One drop of the test solution containing the substrate and oxidant was mixed in a micro test tube with a drop of a solution of 1 g of $\mathrm{FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O}$ and 0.5 g of KF in 100 ml of 0.1 mol dm^{-3} acetic acid, to give a light yellow color, which was stable in acetic acid or dilute mineral acids. The color is believed to be due to the production of the inner complex cation between $\mathrm{Fe^{2+}}$ and the pyridine-2-carboxylate anion. Appropriate blank tests were also carried out to confirm that the pyridine-2-carboxylic acid was generated only as the result of the reaction (7,8), as shown in the Scheme 1. The $\dot{\mathrm{N}}_3$ radical which is formed reacts rapidly with another $\mathrm{Mn^{III}}$ complex to give N_3^+ and the diaquabis(pyridine-2-carboxylato)manganese(II) complex.[31] There is also literature evidence[4] to indicate that N_3^+ is then converted to hexazene ($\mathrm{N_6}$) by rapidly reacting with N_3^- in solution followed by the decomposition of $\mathrm{N_6}$. However, during the photoinduced reductive elimination of *cis*$[\mathrm{Pt(N_3)_2(PPh_3)_2}]$, transient formation of hexazene ($\mathrm{N_6}$) was suggested.[32] Although the formation of nitrogen has been shown to occur through the formation of a cyclic intermediate, the involvement of an open chain structure to give an oxidation product cannot be totally ruled out. The steps of the reaction are shown in the Scheme 1 Eqs. 5—10.

Upon standing the reaction mixture for several hours in excess N_3^-, the two coordinated aqua molecules were displaced by N_3^- ions. It is likely that the following reaction occurs:

$$[\mathrm{Mn^{II}(C_6H_4NO_2)_2(H_2O)_2}] + 2\mathrm{N}_3^- \rightarrow [\mathrm{Mn^{II}(C_6H_4NO_2)_2(N_3)_2}]^{2-} + 2\mathrm{H_2O} \qquad (11)$$

There is literature[33] evidence to indicate that manganese(II) reacts with azide to give anionic azide complex. All of the above-mentioned evidence corroborates the suggested mechanism.

Conclusion

The redox reaction involving tris(pyridine-2-carboxylato)manganese(III) and azide ion proceeds through the intermediate formation of a 1 : 1 complex followed by a one electron reduction to $[\mathrm{Mn^{II}(C_6H_4NO_2)_2(H_2O)_2}]$ and $\dot{\mathrm{N}}_3$. During the reaction pyridine-2-carboxylate ion is generated and the coordination sphere of the parent complex is altered, thereby indicating that the reaction takes place by an inner-sphere mechanism. It is likely that the Mn(II) complex, which is formed in the rate determining step, further reacts with excess N_3^- to form the anionic complex, $[\mathrm{Mn^{II}(C_6H_4NO_2)_2(N_3)_2}]^{2-}$.

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