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A study of the stability of Mn(III) and its redox reaction with Co(II) in aqueous azide medium

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Abstract

Mn(III) was generated in a coulometric cell by the oxidation of Mn(II) in azide medium at 2 M ionic strength and 22 °C. The system exhibited an excellent Nernst behaviour. The interaction of Mn(II/III) with Co(II/III) according to the overall reaction $Co(III)+Mn(II) \rightleftharpoons Co(II)+Mn(III)$ was studied as a function of azide concentration. The equilibrium constant for this reaction increases from 0.0239 at 2 M azide to 0.0289 at 0.1 M azide. Kinetic measurements were also performed to measure the forward and reverse rate constants for the equilibrium which resulted in an equilibrium constant of 0.0175 at 1 M azide. The results are discussed in reference to the catalytic role of Mn(II/III) in the sulfite catalyzed autoxidation of Co(II).

Introduction

It was reported in the literature [1–3] that Co(II)–azide complexes are slowly oxidized by dissolved oxygen to the corresponding Co(III)–azide complexes. It was shown that this process is markedly accelerated by sulfur(IV) oxides (SO_2, HSO_3^- and SO_3^{2-}), and can be used as a spot test for sulfite [1, 2]. In later work this reaction was used to develop a quantitative spectrophotometric method for the determination of S(IV) oxides in rain water [3]. The high molar absorptivity [4] of the produced Co(III)–azide complex (up to 2.2×10^4 M^{-1} cm^{-1} at 365 nm) formed the basis for an accurate analytical technique. Sulfite is oxidized to sulfate during the reaction to produce at least 1.3 mol of Co(III) per mole of S(IV).

Various investigations were undertaken to resolve the mechanism of the S(IV) catalyzed autoxidation of Co(II)–azide complexes. Formation constants for the various Co(II)–azide and Co(III)–azide complexes were determined potentiometrically [5, 6]. It was shown [3, 7] that the autoxidation process exhibits typical autocatalytic behaviour and that the process is further accelerated by the presence of Co(III) and Mn(II). A detailed understanding of these catalytic effects is still lacking [7]. We therefore undertook a systematic kinetic investigation of the observed effects [8]. In the present paper we studied the stability of Mn(II/III) in azide medium and its reactions with Co(II/III).

Reports on the formation of MnN_3^{2+} and its reaction with HN_3 in strongly acidic medium have appeared in the literature [9–12]. Since complex formation is very slow and unfavourable in such strong acidic medium, the present study was performed under conditions of high N_3^- concentrations, i.e. typically 0.5–2.0 M at pH 6.5 in the presence of 0.05 M Mn(II) and 1.0 mM Co(II).

Experimental

All chemicals used in this study were of analytical reagent or chemical pure grade (Merck). Sodium azide, manganese salts (hydrated chloride or sulfate) and sodium perchlorate (monohydrate) were weighed directly to prepare stock and test solutions. Standard $HClO_4$ was used to produce HN_3 in the test solutions and the ionic strength was adjusted to 2.0 M with the aid of $NaClO_4$. Solutions of Co(III) in N_3^-/HN_3 medium were prepared by acidification of solid $Na_3[Co(CO_3)_3]\cdot3H_2O$ which was synthesized according to standard literature methods [13].

A constant current source, adjustable at the mA level, was used in the coulometric cell to generate Mn(III). In the coulometric H shaped cell the compartments each have a volume of 150 ml and are

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separated by a fritted glass plate with a 2 M NaCl agar-agar plug. The cathodic compartment was filled with 2 M NaCl solution, and contained a 1 cm^2 platinum electrode. The anodic compartment was filled with 90 ml of the working solution containing Mn(II), and contained a closely-fitting 94 cm^2 platinum gauze electrode. This compartment also contained a Ag/AgCl reference electrode filled with 1 M KCl and a 2 M NaCl internal electrolyte bridge, and was operated under constant stirring. The working solution for the preparation of Mn(III) consisted of 0.01 M HN_3, 0.05 M Mn(II) and NaN_3 ranging from 0.5 to 2.0 M. The ionic strength was adjusted by the addition of 3.0 M $NaClO_4$. The constant current was adjusted to 14.3 mA for 0.5 M NaN_3 and to 28.1 mA for all other concentrations of NaN_3. Electrolysis was performed as a function of time at approximately constant logarithmic increments (usually from 5 until 300 s). After each period of applied current the potential of the platinum indicator electrode versus the reference electrode was measured. After completion of the electrolysis a small volume (0.09 ml) of a Co(II) solution was added to make it 1 mM and the new potential was measured after equilibrium was reached.

pH measurements were performed in order to estimate the free azide concentration present in solution. The glass electrode was calibrated with 0.010 M $HClO_4$ and 1.99 M $NaClO_4$ at pH = 2.00, thus reading $[H^+]$ instead of hydrogen activity. The pH of a solution containing the HN_3/N_3^- buffer was measured before and after addition of solid $MnCl_2$ to make it 0.05 M. This data was used to estimate the average number of azide ligands attached to the Mn(II) [5, 14]. All measurements were performed at 22 °C.

Kinetic measurements involving the reaction of Mn(II/III) with Co(II/III) in azide medium, were performed on a Durrum D 110 stopped-flow instrument equipped with an online data acquisition system [15]. All reactions were performed under pseudo-first-order conditions and the corresponding plots of $\ln(\Delta A)$ versus time were linear for at least two to three half-lives of the reaction. UV–Vis absorption spectra were recorded on a Shimadzu UV 250 spectrophotometer equipped with a thermostatted (±0.1 °C) cell holder.

Results and discussion

In order to prepare Mn(III) from Mn(II) in azide medium, anodic oxidation at controlled current can provide a known concentration of this species when the efficiency of the electrode reaction is close to 100%. According to the second Faraday law [16], the concentration of generated Mn(III) is given by ti/FV, where t is time in seconds, i is current in amp, F is the Faraday constant and V the volume of solution in litre. The Nernst equation for the potential of the cell outlined in (1) is given in eqn. (2) for measurements at 22 °C. $E^{\circ\prime}(Mn^{III}/Mn^{II})$ is the conditional standard potential of the Mn(III)/Mn(II) system in azide medium and will change with the free azide concentration due to the formation of different complexes in the two oxidation states similar to that found for the Co(III)/Co(II) system [6].

$$\begin{array}{l|l|l|l|l} \mathrm{Ag} & \mathrm{AgCl} & \mathrm{NaCl} & \mathrm{NaN_3+NaClO_4=2\ M} & \mathrm{Pt} \\ & \mathrm{1.0\ M\ KCl} & \mathrm{2.0\ M} & \mathrm{HN_3=0.01\ M} & \\ & & & \mathrm{Mn^{II}/Mn^{III}} & \end{array} \qquad (1)$$

$$E=E^{\circ\prime}(Mn^{III}/Mn^{II})+0.05857\log\{[Mn^{III}]/([Mn^{II}]_0-[Mn^{III}])\} \qquad (2)$$

Addition of Mn(II) (0.05 M) to solutions with higher azide concentrations leads to the spontaneous appearance of a red–brown colour which is characteristic for the formation of Mn(III) in azide medium presumably due to the oxidation by dissolved oxygen. The high Mn(II) and N_3^- concentrations suppress the formation of Mn(IV). Plots of E versus log t, where t is the time of the applied current and proportional to the Mn(III) concentration, were found to be linear with slopes very close to the theoretical value of 0.05857 V at 22 °C (see eqn. (2)). The first few experimental points usually deviated from this linear fit due to the spontaneous (non-electrochemical) formation of Mn(III) by dissolved oxygen. A correction procedure was developed to correct the Mn(III) concentration for this additional contribution and resolved the apparent deviations. In general these plots confirm that we are dealing with an efficient one-electron oxidation reaction as given in (3).

$$Mn(II) \longrightarrow Mn(III)+e^- \qquad (3)$$

At lower azide concentrations (<0.5 M) some deviations were observed due to the oxidation of HN_3 to N_2, but a decrease in the applied current from 28.1 to 14.3 mA resolved this problem. Figure 1 demonstrates the linearity of plots of E versus log $\{[Mn(III)]/([Mn(II)]_0-[Mn(III)])\}$ as a function of azide concentration at 0.05 M Mn(II).

Complex formation of Mn(II) with azide was calculated from pH measurements before and after the addition of Mn(II) and the obtained formation curve [5, 14] is presented in Fig. 2. This curve can be used to estimate the free azide concentration at a given total azide concentration. Although this experiment is not adequate for reliable equilibrium constant calculations it does demonstrate the formation of

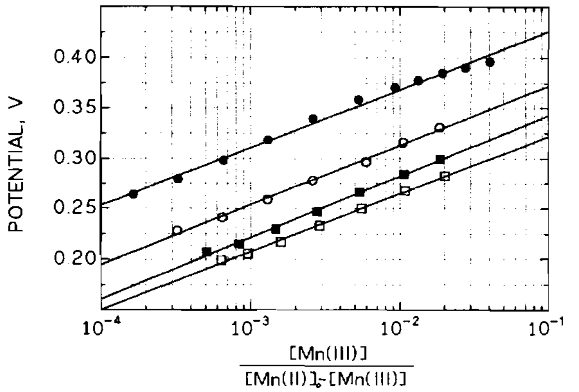

Fig. 1. Potential of the Pt vs. reference electrode as Mn(III) is generated coulometrically in the working solution containing 0.050 M Mn(II), 0.10 M HN_3 and 1.99 (□), 1.49 (■), 0.99 (○), 0.49 (●) M NaN_3. Temperature = 22 °C, ionic strength = 2.0 M ($NaClO_4$).

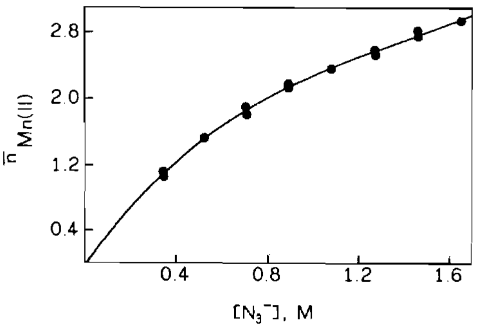

Fig. 2. Average number of azide ligands for the Mn(II) complexes as a function of azide concentration. Temperature = 22 °C, ionic strength = 2.0 M ($NaClO_4$).

1:1, 1:2 and 1:3 Mn(II):N_3^- complexes on increasing the azide concentration. Significantly more stable Mn(III) complexes are expected to be produced under such conditions, similar to that formed for Co(III) as compared to Co(II) [6].

Evidence for the interaction between Mn(III/II) and Co(III/II) in azide medium according to the reversible reaction (4) came from spectrophotometric observations (see Fig. 3) during the addition of Mn(II) to Co(III).

$$\text{Co(III)} + \text{Mn(II)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{Co(II)} + \text{Mn(III)} \qquad (4)$$

An excess of Mn(II) was required to reduce 4×10^{-5} M Co(III), which is accompanied by a decrease in the Co(III) peak at 365 nm and the formation of a new band at *c.* 420 nm characteristic for Mn(III) in azide medium. When Co(II) at a 1 mM level is added to the final electrochemically oxidized Mn(II) solution it consumes Mn(III) and causes a change in potential according to eqn. (2), from which the equilibrium concentration of Mn(III) can be determined. The consumed Mn(III) is equivalent to the produced Co(III), such that the equilibrium constant for (4) given in (5) can be determined. Such experiments resulted in values of approximately 0.025.

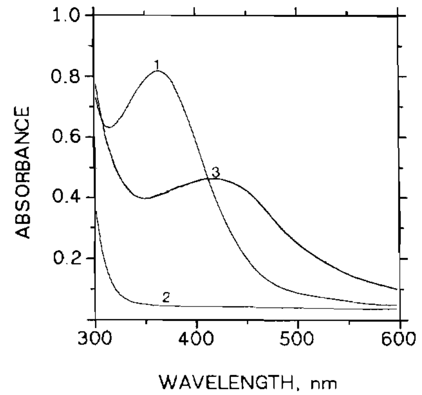

Fig. 3. Spectral changes observed during the reaction of Co(III) with Mn(II) in azide medium. 1: 4.6×10^{-5} M Co(III), 0.1 M N_3^- and 0.1 M HN_3; 2: 5×10^{-4} M Mn(II), 0.1 M N_3^- and 0.1 M HN_3; 3: 4.6×10^{-5} M Co(III), 5×10^{-4} M Mn(II), 0.1 M N_3^- and 0.1 M HN_3. Optical pathlength = 0.88 cm.

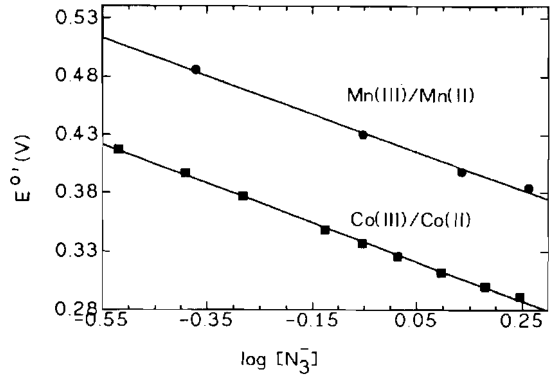

Fig. 4. Conditional standard potential of Mn(III)/Mn(II) and Co(III)/Co(II) vs. Ag/AgCl as a function of azide concentration (see eqn. (1) and ref. 6).

$$K = [\text{Co(II)}] \times [\text{Mn(III)}]/[\text{Co(III)}] \times [\text{Mn(II)}] \qquad (5)$$

More reliable values for K can be obtained from the expression given in (6).

$$E^{\circ\prime}(\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}) - E^{\circ\prime}(\text{Co}^{\text{III}}/\text{Co}^{\text{II}}) = -\frac{RT}{nF}\log K \qquad (6)$$

A measurement of the conditional potential of the Co(III)/Co(II) system in 1.5 M azide medium in the same cell used before, resulted in a difference of 38 mV compared to data obtained experimentally with another reference electrode [6]. Figure 4 reports the conditional potential of both systems as a function of azide concentration, and indicates a fairly constant potential difference that increases slightly at lower azide concentration. The equilibrium constant K was calculated from eqn. (6) and the results are summarized in Table 1. It follows that K increases from 0.0238 at 2 M azide to 0.0294 at 0.1 M azide.

The electrochemically generated Mn(III) enabled us to obtain spectral data on the Mn(III)–azide complexes. For instance an absorption maximum is reached at 427 nm ($\epsilon = 6 \times 10^3$ M^{-1} cm^{-1}) in 0.5–2.0 M azide and pH = 6.3. If the final solution is stored in the dark at 5 °C there is no significant spectral change over a period of 24 h. However, at room temperature and in the presence of light a black precipitate is formed which is probably MnO_2. Fresh solutions of Mn(III) could be used in kinetic experiments in order to measure the forward (k_f) and reverse (k_r) rate constants of reaction (4). The forward reaction could be followed at 365 nm by addition of an excess Mn(II) to Co(III) (see Fig. 3), whereas the reverse reaction was studied by addition of an excess Co(II) to Mn(III), prepared electrochemically. All reactions were followed using a stopped-flow instrument and typical kinetic results for the forward reaction are reported in Fig. 5. The observed pseudo-first-order rate constant increases linearly with increasing [Mn(II)]. In addition, similar results are obtained in the presence of Co(II),although the kinetic data are of a poorer quality since smaller absorbance changes occur under such conditions due to the effective back reaction. No experimental data could be measured at the lower Mn(II) concentration in the presence of added Co(II). The data in Fig. 5 support the expected rate law (7) for the overall reaction in (4), and result in $k_f = 64.8 \pm 0.7$ and $k_r = (3.7 \pm 0.2) \times 10^3$ M^{-1} s^{-1} at 22 °C.

TABLE 1. Experimental data for the estimation of K

$[N_3^-]$ (M)	$E^{\circ\prime}(Mn^{III}/Mn^{II})$ (V)	$E^{\circ\prime}(Co^{III}/Co^{II})$ (V)	$K \times 10^2$
0.100	0.5873	0.4972	2.89
0.200	0.5380	0.4467	2.76
0.300	0.5091	0.4172	2.70
0.400	0.4886	0.3962	2.65
0.500	0.4727	0.3800	2.62
1.00	0.4230	0.3295	2.49
1.50	0.3945	0.2999	2.43
1.75	0.3836	0.2887	2.40
2.00	0.3740	0.2790	2.39

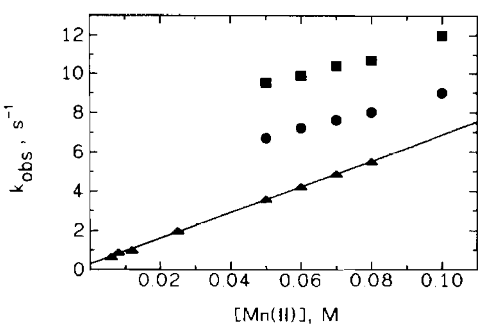

Fig. 5. k_{obs} as a function of [Mn(II)] for the reaction Co(III) + Mn(II) → Co(II) + Mn(III). Conditions: 3×10^{-5} M Co(III), 1.0 M N_3^-, 0.01 M HN_3 and 0 (▲), 0.75×10^{-3} (●), 1.5×10^{-3} (■) M Co(II). Temperature = 22 °C; ionic strength = 2.0 M ($NaClO_4$).

$$k_{obs} = k_f[Mn(II)] + k_r[Co(II)] \qquad (7)$$

Efforts to measure k_r directly, i.e. in the reaction of Mn(III) with Co(II), revealed unexpected complications. This reaction was studied at different Mn(II) concentrations, and the results are summarized in Fig. 6. On increasing the [Mn(II)], the intercept of the k_{obs} versus [Co(II)] plot increases in agreement with that expected on the basis of eqn. (7). However, although the slope of such plots should be independent of the [Mn(II)], they decrease with increasing [Mn(II)]. This means that there is presumably an interaction between the excess Mn(II) and the electrochemically produced Mn(III) prior to the kinetic experiments that decreases the fraction of Mn(III) available for the redox reaction with Co(II), i.e. the reverse reaction in (4). Such an interaction would predict an inverse dependence of k_r on the Mn(II) concentration as observed in the kinetic experiments. From the values of k_f and k_r it follows that K ($= k_f/k_r$) = 0.0175, which is in reasonable agreement with the thermodynamically determined value.

The results of this study clearly demonstrate how the addition of Mn(III/II) to a Co(III/II) solution in the presence of azide can affect the chemistry of the system. They also assist the interpretation of the catalytic role of these species during the sulfite

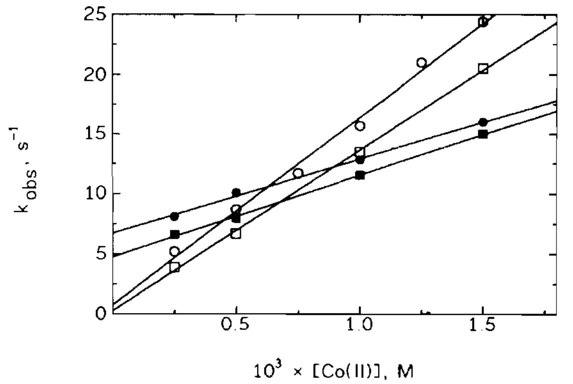

Fig. 6. k_{obs} as a function of [Co(II)] for the reaction Mn(III) + Co(II) → Mn(II) + Co(III). Conditions: 1×10^{-4} M Mn(III), 1.0 M N_3^-, 0.01 M HN_3 and 0.05 (■), 0.10 (●), 0.025 (□), 0.040 (○) M Mn(II). Temperature = 22 °C, ionic strength = 2.0 M ($NaClO_4$).

catalyzed autoxidation of Co(II) [3, 7]. For a typical [Mn(II)]:[Co(II)] ratio of 2:1 at 0.5 M azide the reported value of K predicts the formation of at least 5% Mn(III) that can rapidly undergo a redox reaction with S(IV) oxides. The details of this process will be reported in a forthcoming paper [8].

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