Occurrence of a Manganese(III) Intermediate in the $[MnO_4]^-$–SO_2 Redox Reaction†

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Evidence for a manganese(III) intermediate, previously implicated in the $[MnO_4]^-$–SO_2 electron-transfer process, has been obtained by conducting the reaction in the presence of F^-. A combination of *in situ* EPR and electronic absorption spectroscopies was used to follow the reaction course and physico-chemical techniques were used to ascertain the identity of the isolated manganese(III) products. The evidence suggests that in the presence of F^- manganese(VII) is directly reduced to manganese(III) and thence to manganese(II).

It is a text book[1] story that manganese(VII) (*cf.* MnO_4^-) is reduced to manganese(II) by SO_2 in an aqueous medium. Owing to its high sensitivity the reaction serves as a very useful test for the two reagents. As manganese is capable of exhibiting a wide spectrum of oxidation states, there exists a finite possibility of involvement of an intermediate oxidation level in the $[MnO_4]^-$–SO_2 redox process. Indeed DeThomas and Purdy[2] conjectured the involvement of a manganese(III) intermediate in such a reaction more than three decades ago. However, no convincing evidence was available in this regard.

We have been interested in manganese(III) chemistry[3] for some time and it has been our argument that fluoride ion is an efficient stabilizer of this oxidation level of the metal. It is with this perception that we sought to demonstrate the involvement of manganese(III) in the $[MnO_4]^-$–SO_2 redox process. Our approach was to detect the reaction intermediate by *in situ* experimentation and also by product isolation and characterization. The *in situ* experiments were required in order to rule out the formation of divalent manganese prior to that of manganese(III). This was especially important because a rapid reduction of some of the $[MnO_4]^-$ to aquated Mn^{2+} followed by its reaction with $[MnO_4]^-$ leading to manganese(III) could be an alternative possibility.

The aim of this work is to provide evidence to support the view that in the presence of fluoride ions manganese(VII) is directly reduced to manganese(III) and thence to its divalent state.

Experimental

All the chemicals used were of reagent grade quality. Infrared spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. Reflectance spectra were recorded against MgO using a Carl Zeiss Jena VSU 2-P instrument. Magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. EPR spectra were recorded using a Varian E 109 X-band spectrometer with 100 KHz field modulator. Electronic absorption spectra of the reaction solutions were recorded on a Hitachi Model 330 UV/VIS/NIR spectrophotometer fitted with a thermostatted cell holder. The pH values of the reaction solutions were measured using a Systronics type 335 digital pH meter. Deionized water was used for all the experiments described below.

Reaction of SO_2(g) *with* $KMnO_4$ *in Aqueous Solution in the Presence of Fluoride* (F^-).—(*i*) *Isolation and characterization of reaction intermediates.* (*a*) *Reaction intermediate* $K_2[MnF_3(SO_4)]$. Potassium permanganate (1.0 g, 6.33 mmol) was thoroughly mixed with KHF_2 (0.98 g, 12.55 mmol), to give a Mn:F ratio of 1:4. The mixture was then dissolved in water (30 cm^3) and SO_2 gas was bubbled through the solution with constant stirring until a brown solid precipitated. The flow of SO_2 was continued whereupon the solid redissolved to give a clear solution from which a crystalline pink solid precipitated on further bubbling of SO_2. The pH of the reaction solution was found to be in the region 2–2.5 and the flow of SO_2 was stopped at this stage. The product obtained as above was filtered, washed with ethanol two or three times, and finally dried *in vacuo* over concentrated H_2SO_4. The product analysed as $K_2[MnF_3(SO_4)]$ (Found: F, 20.3; K, 27.55; Mn, 19.3; SO_4^{2-}, 33.65. Calc. for $F_3K_2MnO_4S$: F, 19.90; K, 27.30; Mn, 19.2; SO_4^{2-}, 33.55%). IR (cm^{-1}): 1230s, 1145s and 1030s (ν_3), 975s (ν_1), 680s, 635s and 605s (ν_4) (ν_1, ν_3 and ν_4 are all S–O modes) and 525s [ν(Mn–F)]. Reflectance spectrum (cm^{-1}): 13,700 ($^5B_{1g} \longrightarrow {}^5A_{1g}$), 18 200 ($^5B_{1g} \longrightarrow {}^5B_{2g}$) and 21 650 ($^5B_{1g} \longrightarrow {}^5E_g$). μ_{eff} (Gouy method): 4.1 μ_B at 290 K.

(*b*) *Reaction intermediate* $K_2[MnF_5]\cdot H_2O$. Potassium permanganate (1.0 g, 6.33 mmol) and KHF_2 (2.47 g, 31.64 mmol) were dissolved in water (30 cm^3) maintaining the ratio of Mn:F at 1:10. Gaseous sulfur dioxide was bubbled through the solution with stirring until a rose-pink solid precipitated. At this stage, the pH of the reaction solution was found to be in the region 2–2.5. The rose-pink product obtained was isolated by filtration followed by washing twice with ethanol and finally drying *in vacuo* over concentrated H_2SO_4. The product was identified as $K_2[MnF_5]\cdot H_2O$ (Found: F, 37.95; K, 31.55; Mn, 22.40. Calc. for $F_5K_2Mn\cdot H_2O$: F, 38.6; K, 31.75; Mn, 22.3%). IR (cm^{-1}): 615m [ν(Mn–F), ν_3], 565s [ν(Mn–F), ν_4], 3468s [ν(O–H)] and 1635m [δ(H–O–H)]. Reflectance spectrum (cm^{-1}): 12 000 ($^5B_{1g} \longrightarrow {}^5A_{1g}$), 18 500 ($^5B_{1g} \longrightarrow {}^5B_{2g}$) and 21 000 ($^5B_{1g} \longrightarrow {}^5E_g$). μ_{eff} (Gouy method): 3.2 μ_B at 300 K.

(*ii*) In situ *methods for detection of reaction intermediates.* (*a*) *EPR experiments.* The solution EPR experiments were conducted at room temperature. A solution of a mixture of $KMnO_4$ and KHF_2 in a molar ratio of 1:2 (Mn:F = 1:4) was prepared. The solution strength was maintained at 10^{-3} mol dm^{-3} with respect to $KMnO_4$.

A regulated flow of SO_2 gas was maintained by using a mechanical regulator and a microjet. The pH of the reaction solution was recorded with a direct-reading digital pH meter.

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† *Non-SI unit employed:* $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

The solution registered a pH of *ca.* 5.5 prior to the initiation of bubbling of SO_2 gas. The reactant gas was then slowly bubbled through the solution into which the electrodes of the pH meter were already dipped so that the pH could be recorded simultaneously with the progress of flow of the gas. The SO_2 gas flow was stopped at every 0.2 pH interval followed by withdrawing a small volume of the solution and recording its EPR spectrum.

(*b*) *Electronic absorption spectra.* A procedure similar to that above was performed except that electronic absorption spectra, instead of EPR spectra, were recorded at different pH values. The spectra were recorded at ambient temperature.

Elemental Analyses.—A Perkin-Elmer model 2380 atomic absorption spectrophotometer was used for the analysis of K and Mn. Sulfate and F^- were estimated following the methods described earlier.[4] The oxidation state of manganese was determined chemically by a method elaborated previously.[3]

Results and Discussion

It was perceived that Mn^{III}, if formed in the $[MnO_4]^-$–SO_2 reaction, could be trapped in aqueous solution by F^-. Accordingly, the $[MnO_4]^-$–SO_2 reactions were conducted with Mn:F ratios being maintained at 1:4 or 1:10. A general observation was the lowering of the pH of the solution upon bubbling of SO_2 gas through it. The reaction carried out with an Mn:F ratio of 1:4 indicated that the process involved three different stages: (*i*) formation of a brown solid **1** at pH 3–2.5 with the mother-liquor becoming practically colourless; (*ii*) complete dissolution of this brown species with concomitant precipitation of a pink solid **2** at pH 2.5–2; and finally (*iii*) dissolution of the pink product at pH < 2 accompanied by decolorization of the reaction solution. When an analogous reaction was conducted with an Mn:F ratio of 1:10, the reaction course was very similar except that at pH 3–2.5 a brown solution, rather than a brown solid, was observed, and at pH 2.5–2 a rose-pink product **3**, instead of the pink species **2**, was obtained.

In order to get an insight into the $[MnO_4]^-$–SO_2 redox process, it was considered important to isolate the products **1**–**3** and ascertain the oxidation level of the metal. The brown product **1** and the pink species **2** both analysed for fluoride, SO_4^{2-} and Mn, while **3** did not contain any sulfate. Since both F^- and SO_4^{2-} are redox innocuous species, there was no interference in the chemical determination of the oxidation state of manganese. The iodometrically estimated oxidation level was ascertained to be $+\textsc{iii}$ in each case. Although the product **1** did not comply with any stoichiometric formula, the Mn^{III}:F ratio was consistently $> 2:1$. The IR spectra suggested the occurrence of co-ordinated sulfate. The products **2** and **3** were identified as $K_2[MnF_3(SO_4)]$ and $K_2[MnF_5]\cdot H_2O$, respectively. As it was not the central theme of this work to provide new methodologies for the synthesis of these compounds, they are not discussed further; indeed there are already very good synthetic methods for the preparation of similar compounds.[4,5]

In situ *Methods for Detecting Reaction Intermediates in the* $[MnO_4]^-$–SO_2 *Redox Reactions.*—Although it is certainly plausible that manganese(III) is involved as an intermediate in the reaction under investigation, the results of the above experiments do not in themselves provide conclusive evidence. Thus, further experimentation involving *in situ* methods for detection of reaction intermediates was required.

In order to obtain *in situ* evidence, two different experimental techniques, *i.e.* EPR and electronic absorption spectroscopy were performed on the reaction solutions (see Experimental section). The stock solution (pH 5.5) was 10^{-3} mol dm^{-3} with respect to $[MnO_4]^-$ and KHF_2 was added to give a Mn:F ratio of 1:4. The EPR spectra of the solution upon treatment with SO_2 gas were recorded at pH intervals of 0.2. The solution was EPR silent until pH 1.7 when it displayed a six-line spectrum typical of divalent manganese.[6] The pattern remained unaltered down to pH 1.3, below which no measurement was made. The EPR results suggest that under the present experimental conditions manganese(II) is not formed until the reaction pH is brought down to less than 2. The formation of manganese(III) at pH > 2 is thus more likely.

To complement the EPR observations electronic absorption spectroscopic experiments were conducted on similar solutions. Spectra were recorded at pH values similar to those for the EPR experiments. The parent solution (pH 5.5) showed the spectrum of $KMnO_4$,[7] as expected, with the charge-transfer bands appearing at *ca.* 32 100, *ca.* 19 000 and *ca.* 18 300 cm^{-1}. Upon bubbling of SO_2 through the solution with concomitant lowering of pH, these charge-transfer bands gradually disappeared with the simultaneous appearance of new bands at *ca.* 20 700, *ca.* 18 000 and *ca.* 12 900 cm^{-1}. The spectrum obtained at pH 3.3 showed absorptions only at these values. This spectral pattern is typical of manganese(III)[3,8] attributable to the $^5B_{1g} \longrightarrow {}^5E_g$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5A_{1g}$ transitions, respectively. The spectrum remained virtually unaffected until pH 2.1. Further lowering of the pH (to *ca.* 2) of the solution by reaction with SO_2 gas however led to the disappearance of the spectrum and the solution displayed virtually no absorption bands in agreement[9] with the formation of Mn^{II}. A combination of EPR and electronic absorption spectroscopic results thus provides strong evidence for the occurrence of a manganese(III) intermediate in the $[MnO_4]^-$–SO_2 redox process.

In conclusion, the results of this investigation serve to favour the suggestion that, in the presence of fluoride ion, Mn^{VII} is directly reduced to Mn^{III} and thence to Mn^{II}.

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