Inorganica Chimica Acta, 134 (1987) 187–189

Kinetics and Mechanism of the Oxidation of Dimethyl Sulfoxide by Permanganate Ion

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(Received May 7, 1987)

Manganese(III) has been detected as a short-lived intermediate in the permanganate oxidation of various unsaturated organic compounds [1–8] in acidic solutions. In such systems, Mn(III) subsequently disappears via reaction with the organic intermediates (hydroxy and/or oxo compounds). It may also form relatively stable complexes with carboxylate type ligands (substrates). In the absence of stabilizing ligands, disproportionation is observed, which can be generally represented as:

$$2\,Mn^{3+} \xrightleftharpoons{2H_2O} MnO_2 + Mn^{2+} + 4H^+ \qquad (1)$$

In the presence of added pyrophosphate, forming a stable complex with Mn^{3+}, disproportionation is suppressed and pyrophosphatomanganese(III) behaves as a stable product (it is a much less reactive oxidant than Mn_{aq}^{3+} or $MnOH^{2+}$). This is a useful diagnostic test for the formation of Mn(III) intermediates [5, 6].

Dimethylsulfoxide undergoes rapid oxidation by permanganate ion to dimethylsulfone. The oxidation of DMSO complexed in $[Co(NH_3)_5(DMSO)]^{3+}$ has been studied kinetically in acidic solution [8]. The formation of MnO_2 in this process was ascribed to the disproportionation of manganate(V) and manganate(VI) intermediates, which, however, have not been detected.

We have undertaken this study to check whether manganese(III) might perhaps be the source of the MnO_2 product in DMSO oxidation, as well as to extend our work on sulfite oxidation by MnO_4^- [7] to sulfur-containing organic compounds. Also, it is of interest to carry out mechanistic studies in alkaline solutions, where little information of this kind is available.

Results

Stoichiometry

Acidic solutions

The permanganate ion oxidation of DMSO in 0.05–1.0 M aqueous $HClO_4$ results in the formation of MnO_2. Its precipitation may be delayed depending on the reactant concentration and solution composition. If sodium pyrophosphate is added in at least a 3-fold excess relative to the concentration of MnO_4^-, no MnO_2 is formed. Instead, a cherry-red solution is obtained, whose spectrum is identical with the known spectrum of the pyrophosphato–manganese(III) complex. This fact proves that manganese(III) is an intermediate of the reaction, and MnO_2 is formed via its disproportionation. The measurements aimed at determining the stoichiometry and kinetics of the reaction in acidic solution have been carried out in the presence of a 5-fold excess of pyrophosphate, which makes manganese(III) the product of MnO_4^- reduction on the time-scale of these experiments.

The following experiments have been performed to establish the stoichiometry of oxidation. Equimolar amounts of DMSO and MnO_4^- (4×10^{-4} mol) were reacted in 0.10 M $HClO_4$. After the reaction, the residual oxidation power of the solution was determined iodometrically. The results show that 2.0 oxidation equivalents are consumed per mole DMSO.

When the reaction was run using a 5-fold excess of DMSO, iodometry showed that 20% of the permanganate oxidation power was retained, *i.e.* all the MnO_4^- was converted to Mn(III).

Thus the overall stoichiometric equation in acidic solution is

$$2DMSO + MnO_4^- + 4H^+ \xrightarrow[pyr]{} 2DMSO_2 + Mn(pyr)_3{}^{3+} + 2H_2O \qquad (1)$$

where $DMSO_2$ is dimethylsulfone, and pyr is pyrophosphate(2–) ion.

Alkaline solutions

The stoichiometry in alkaline aqueous solution has been determined by reacting 6×10^{-4} mol $KMnO_4$ and 4×10^{-4} mol DMSO in 0.25 M NaOH. The unreacted MnO_4^- was quenched with excess KI. After acidification, the iodine was titrated with standard thiosulfate. According to the results, 2 oxidation equivalents were consumed per mole DMSO. In a 5-fold excess of DMSO all of the added MnO_4^- was consumed but 80% of the initial oxidation titre was retained in the form of manganate-

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0020-1693/87/$3.50

(VI). The overall stoichiometry in alkaline media is therefore:

$$\mathrm{DMSO} + 2\mathrm{MnO_4}^- + 2\mathrm{OH}^- \longrightarrow \mathrm{DMSO_2} + 2\mathrm{MnO_4}^{2-} + \mathrm{H_2O} \qquad (2)$$

The product dimethylsulfone has also been determined by gas chromatography (OV-17, 140 °C). Its amount agreed to within ±10% with that required by the stoichiometric equations.

Kinetic Measurements

The disappearance of MnO_4^- was followed by the stopped-flow spectrophotometric technique [4]. Under pseudo first order conditions (excess DMSO), the stopped-flow traces recorded at 540 nm gave excellent linear log $(A - A_\infty)$ *versus* time plots in both acidic and alkaline solutions. The apparent first order rate constant is proportional to the DMSO concentration in both media. The rate constants are listed in Tables I and II. During the kinetic runs there was no MnO_2 formation: excess pyrophosphate in acidic solution stabilized manganese(III), and NaOH concentrations of 0.1 M or higher were sufficient to stabilize manganese(VI) for several minutes.

In acidic solutions, the kinetic law has the form:

$$-\frac{d[\mathrm{MnO_4}^-]}{dt} = k^{a}_{obs}[\mathrm{MnO_4}^-] = k_{acid}[\mathrm{DMSO}][\mathrm{MnO_4}^-] \qquad (3)$$

k^{a}_{obs} is independent of the acid concentration in the range between 1.0 M $HClO_4$ and pH 4.0. The kinetic results give $k_{acid} = 102 \pm 5\ M^{-1}\ s^{-1}$ in perfect agreement with the rate constant reported by de Oliveira *et al.* [8].

TABLE I. Apparent Second Order Rate Constants for the Oxidation of DMSO by MnO_4^- in Acidic Media[a]

[DMSO] × 10^2 (M)	[$HClO_4$] (M)	k_{acid} ($M^{-1}\ s^{-1}$)
1.0	0.1	110
2.5	0.1	104
5.0	0.1	102
10.0	0.1	99
20.0	0.1	100
30.0	0.1	103
5.0	0.05	100
5.0	0.30	110
5.0	0.50	104
5.0	1.00	104
5.0	0.10	102
5.0	pH 2.2[b]	106
5.0	pH 4.0[c]	102

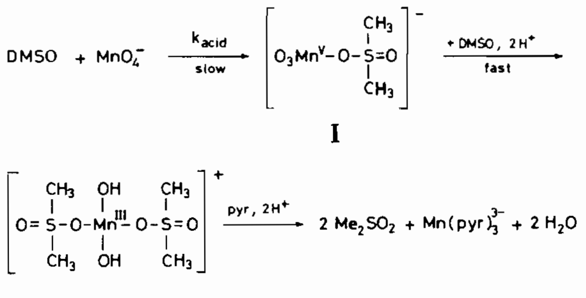
[a] $T = 25$ °C; $I = 1.0$ M with $NaClO_4$; $[MnO_4^-]_0 = 1.0 \times 10^{-3}$ M; $[Na_2H_2P_2O_7]_0 = 5.0 \times 10^{-3}$ M; average of 3 runs reproducible to within 5%. [b] Chloroacetic acid buffer. [c] Succinic acid buffer.

TABLE II. Apparent Second Order Rate Constants for the Oxidation of DMSO by MnO_4^- in Alkaline Media[a]

[DMSO] × 10^2 (M)	[NaOH] (M)	k_{base} ($M^{-1}\ s^{-1}$)
1.0	0.25	240
2.5	0.25	264
5.0	0.25	258
10.0	0.25	250
15.0	0.25	264
5.0	0.10	214
5.0	0.50	296
5.0	0.75	320
5.0	1.00	340
5.0	0.10	202[b]

[a] $T = 25$ °C; $I = 1.0$ M with $NaClO_4$; $[MnO_4]_0 = 1.0 \times 10^{-3}$ M; average of 3 runs reproducible to within 5%. [b] Ionic strength 0.1 M.

The following reaction mechanism is consistent with the available data in acidic solution:

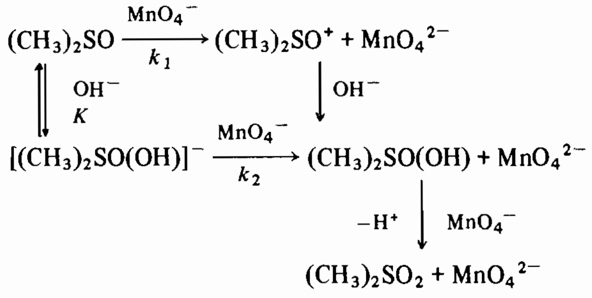


I

II

in which the rate-determining step is the attack of MnO_4^- at the S atom of DMSO. The resulting manganate(V) ester (**I**) rapidly reacts with a second DMSO molecule, to afford a symmetrical manganese(III) complex (**II**), which is then converted to the more stable pyrophosphato complex $Mn(pyr)_3^{3-}$.

de Oliveira *et al.* [8] also suggested a bridged dinuclear complex as intermediate with a structure similar to I. However, they propose that the intermediate decomposes to Mn(V) and Mn(VI). The manganese(III) product observed by us and the validity of stoichiometric eqn. (1), require the formation of intermediate **II**, ensuring utilization of 4 oxidation equivalents per MnO_4^- ion. Apparently, **I** is sufficiently protected against disproportionation to seek out a second DMSO molecule for O-transfer oxidation. This is a remarkable situation in view of the instability of manganate(V) in acidic solution. It resembles the behaviour of the intermediates in the



Scheme 1.

permanganate oxidation of acetylenic and olefinic derivatives, where the only detectable transient is also manganese(III).

In alkaline solutions, the kinetic results listed in Table II show that the rate law is

$$-\frac{d[MnO_4]}{dt} = k^b{}_{obs}[MnO_4^-]$$

$$= k_{base}[DMSO][MnO_4^-] \qquad (5)$$

and $k^b{}_{obs}$ is distinctly dependent on the NaOH concentration.The observed behaviour is consistent with the mechanism given by Scheme 1, involving two reactive species, *viz.* DMSO and its adduct with hydroxide ion. The rate-determining steps are electron transfer from each reactant to MnO_4^-, followed by rapid addition of an OH^- ion and/or electron transfer to a second MnO_4^-. Assuming rapid establishment of equilibrium (6) relative to subsequent oxidation, the following expression is obtained for $k^b{}_{obs}$:

$$k^b{}_{obs} = 2[DMSO]_0 \frac{k_1 + k_2K[OH^-]}{1 + K[OH^-]} \qquad (7)$$

Rate law (7) was fitted to the experimental data given in Table II by means of a least-squares procedure. An excellent fit afforded the following values:

$k_1 = 85 \pm 4\ M^{-1}\ s^{-1}$

$k_2 = 210 \pm 10\ M^{-1}\ s^{-1}$

$K = 2.00 \pm 0.04\ M^{-1}$

Under the conditions used, $K[OH^-]$ varies between 0.2 and 2.0, which means that *ca.* 16% to 66% of DMSO must be present as $[(CH_3)_2SO(OH)]^-$. The 2.5 times higher reactivity of the latter species is apparently due to its enhanced ability to transfer an electron owing to the net negative charge. The value of k_1 is in fair agreement with that of the rate constant in acidic solution.

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