Kinetics of Oxidation of Dimethyl Sulphoxide by Tervalent Manganese

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Summary Kinetic evidence is presented for the reversible formation of a radical ion from Me_2SO on oxidation by Mn^{3+}, which initiates polymerisation of acrylonitrile that is terminated by the oxidant.

OXIDATION of Me_2SO by one-electron oxidants has not been investigated, while the formation of the sulphone on treatment with permanganate and dichromate is well known.[1,2] Oxidation of diphenyl sulphoxide to the sulphone by Cr^{6+} has been shown to proceed through the radical ion followed by oxygen atom transfer.[3] Radical ions have been generated from heterocyclic sulphides and sulphoxides and their u.v. and e.s.r. spectra recorded.[4] We have used the system Me_2SO–Mn^{3+} as a redox initiator for vinyl polymerisation and report some features of the oxidation which leads to the radical ion.

Tervalent manganese stock solutions were prepared by anodic oxidation.[5] Me_2SO and acrylonitrile were purified by repeated distillation under reduced pressure and nitrogen, middle fractions being collected and stored over Linde molecular sieves. Details of the polymerisation procedure have been given before.[6] Under nitrogen, in the temperature range 40—45° and in 1—2 M-H_2SO_4 the oxidation is moderately fast, with 15—35% of the oxidant being consumed in 1 hr. Up to 45% conversion of monomer (M) into polymer could be achieved in this period ($[M] = 0{\cdot}6012$ M, $[Me_2SO] = 1{\cdot}4157$ M $[Mn^{3+}] = 3{\cdot}748 \times 10^{-3}$ M, and $[Mn^{2+}] = 0{\cdot}074$ M at 45°). The oxidation was first order in $[Mn^{3+}]$ but was retarded by $[Mn^{2+}]$ (Table: Expts. 1—3). Rates increased with $[Me_2SO]$ but became independent of substrate at high concentrations, indicating complex formation, the data yielding Lineweaver–Burk plots (Figure). Further increase in $[Me_2SO]$ decreased the rate. Reciprocal rates were partly proportional to $[Mn^{2+}]$ (Figure). The rates were unaffected by acidity or ionic strength. Polymerisation was not observed in the absence of either Me_2SO or Mn^{3+}. Rates($-$d[Mn^{3+}]/d*t*) were partly proportional to monomer concentration, first-order in [Mn^{3+}], and showed the same variation with [Me_2SO] as in oxidation (Table: Expts. 4—9). Polymerisation rates ($-$d[M]/d*t*) were first-order in [Me_2SO], second-order in monomer, and independent of [Mn^{3+}] at constant [Mn^{2+}] (Table: Expts. 4—9). The data in the Figure obtained in the absence of acrylonitrile indicate that the retardation by Mn^{2+} is not due to competitive complex formation which requires a common intercept for such plots at different Mn^{2+} concentrations. Participation by Mn^{4+} or the reversible oxidation of an initial complex by more Mn^{3+} can lead to retardation by Mn^{2+} with second-order kinetics in Mn^{3+}.[7] Recently, oxidation of maleic acid by Mn^{3+} has been shown to be first-order in each reactant while being retarded by Mn^{2+} and H^+.[8] The reversible formation of a radical like $CH_3{\cdot}SO{\cdot}CH_2{\cdot}$ requires that the rates be retarded by Mn^{2+} as well as H^+. The following scheme is consistent with our data, Mn^{3+} representing an aquated ion pair.

TABLE

Expt. No.	[Mn^{3+}] × 10^3 (M)	[Me_2SO] (M)	[Monomer] (M)	$-$d[Mn^{3+}]/d*t* × 10^7 mole/l/sec.	($-$d[Mn^{3+}]/d*t*)/[Mn^{3+}] = k_{obs} × 10^5 sec^{-1} [Mn^{2+} = 0·134M	[Mn^{2+}] = 0·35M	$-$d[M]/d*t* × 10^5 mole/l/sec.
1.	1·453	0·8494	Nil	—	4·662	2·935	—
2.	4·359	0·8494	Nil	—	4·368	2·758	—
3.	8·718	0·8494	Nil	—	4·556	2·819	—
4.	1·355	1·4157	0·5010	1·532	—	—	3·128
5.	2·710	1·4157	0·5010	2·830	—	—	3·152
6.	4·000	0·2359	0·5010	1·514	—	—	0·4792
7.	4·000	0·9436	0·5010	2·914	—	—	1·981
8.	3·748	1·4157	0·2004	5·304	—	—	0·9224
9.	3·748	1·4157	0·5010	7·082	—	—	5·4510

All data with 2 M-H_2SO_4; Temperature 45° for 8 and 9, all others at 40°. 4—5:[Mn^{2+}] = 0·126 M; 6—7: [Mn^{2+}] = 0·0894 M; 8—9: [Mn^{2+}] = 0·074 M.

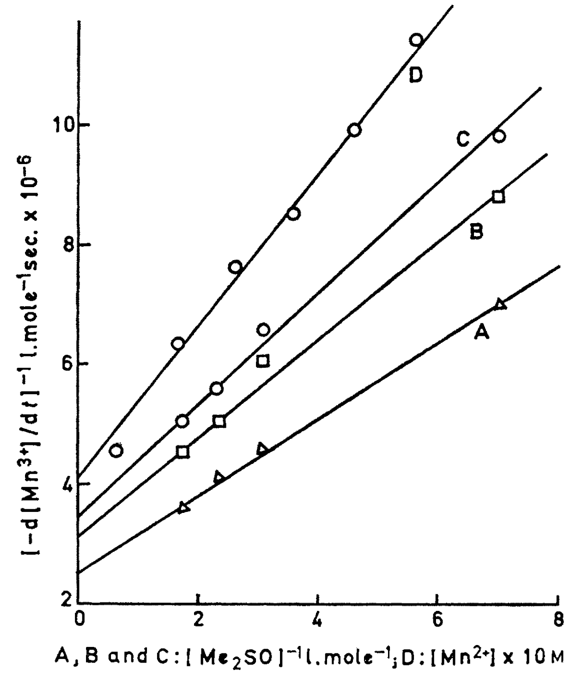
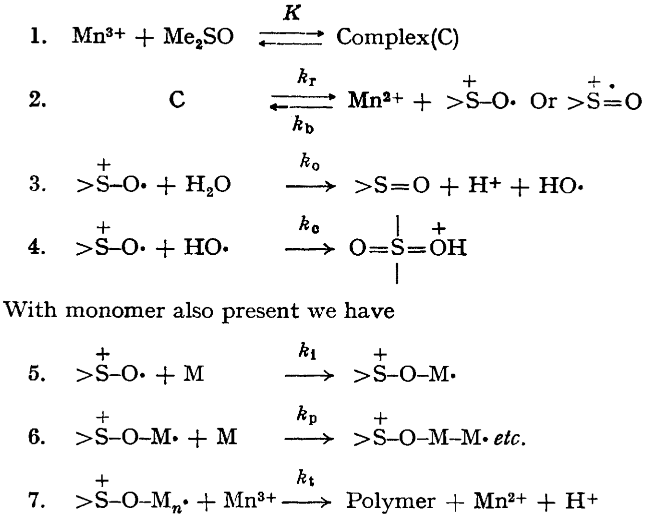


FIGURE A, B, and C: *Rate*$^{-1}$ *against* [Me_2SO]$^{-1}$ *at different* Mn^{2+} *concentrations.* [Mn^{2+}] = 5·9 × 10^{-2}M (A), 1·1 × 10^{-1} M (B), *and* 1·59 × 10^{-1} M (C) *at* 40° in 2 M-acid *with* [Mn^{3+}] = 5·135 × 10^{-3} M. D: *Rate*$^{-1}$ *against* [Mn^{2+}] *at* 40° *with* [Mn^{3+}] = 4·359 × 10^{-3} M *and* [Me_2SO] = 8·492 × 10^{-1} M in 2 M-acid.



$$1.\quad Mn^{3+} + Me_2SO \overset{K}{\rightleftharpoons} \text{Complex(C)}$$

$$2.\quad C \underset{k_b}{\overset{k_r}{\rightleftharpoons}} Mn^{2+} + {>}\overset{+}{S}{-}O{\cdot} \text{ Or } {>}\overset{+\,\cdot}{S}{=}O$$

$$3.\quad {>}\overset{+}{S}{-}O{\cdot} + H_2O \xrightarrow{k_o} {>}S{=}O + H^+ + HO{\cdot}$$

$$4.\quad {>}\overset{+}{S}{-}O{\cdot} + HO{\cdot} \xrightarrow{k_c} O{=}\overset{|}{\underset{|}{S}}{=}\overset{+}{O}H$$

With monomer also present we have

$$5.\quad {>}\overset{+}{S}{-}O{\cdot} + M \xrightarrow{k_i} {>}\overset{+}{S}{-}O{-}M{\cdot}$$

$$6.\quad {>}\overset{+}{S}{-}O{-}M{\cdot} + M \xrightarrow{k_p} {>}\overset{+}{S}{-}O{-}M{-}M{\cdot}\ \textit{etc.}$$

$$7.\quad {>}\overset{+}{S}{-}O{-}M_n{\cdot} + Mn^{3+} \xrightarrow{k_t} \text{Polymer} + Mn^{2+} + H^+$$

Step 3 is one mode of reaction of radical ions derived from sulphides and sulphoxides,[4] while termination of growing radicals by Mn^{3+} (step 7) appears to be important only at high temperatures.[9] Initiation of polymerisation by HO· radicals and the oxidation of the radical ion to a dication by Mn^{3+} must be ruled out on the basis of the kinetics. The i.r. spectrum of the polymer (KBr disc) shows a strong band at 1072 cm^{-1} due to the sulphoxide end-group.[10] Combination of HO· radicals to give H_2O_2 which can rapidly oxidise the sulphoxide or react with more Mn^{3+} cannot be ruled out, but this will not alter the kinetics. In solutions containing 1·2 × 10^{-2} M-Mn^{3+}, 1·5 × 10^{-1} M-Mn^{2+}, and 5 × 10—^{2} M-Me_2SO in 3M-acid there was 65% consumption of Mn^{3+} and 6—8% consumption of Me_2SO after prolonged oxidation at 45°, the sulphoxide being estimated by conversion into the sulphone.[2] Since we are restricted to low concentrations of the reactants this is not very conclusive. We have used other oxidising agents, *e.g.* Ce^{4+}

and Co^{3+}, with Me_2SO. The Co^{3+} reaction, though extremely fast, shows the same kinetic features (at 10°) as the Mn^{3+} oxidation, including complex formation and retardation by Co^{2+}. This means that the redox potential of the couple radical ion–Me_2SO is at least equal to that of the Co^{3+}–Co^{2+} couple in sulphuric acid. On the other hand, Ce^{4+} is a very poor oxidant for Me_2SO as compared with Mn^{3+}. The decrease in rates at very high $[Me_2SO]$ may be a medium effect, or it may be due to the formation of higher complexes which are less reactive. Such complexes have been prepared from manganic acetate.[11] The scheme outlined leads to the following kinetic expressions which are applicable to our data.

$$-\mathrm{d}[\mathrm{Mn}^{3+}]/\mathrm{d}t = \frac{2k_{\mathrm{o}}k_{\mathrm{r}}K[\mathrm{Mn}^{3+}]_{\mathrm{T}}[\mathrm{Me_2SO}]}{(k_{\mathrm{b}}[\mathrm{Mn}^{2+}] + 2k_{\mathrm{o}})(1 + K[\mathrm{Me_2SO}])}$$

for the oxidation, $[Mn^{3+}]_T$ representing total manganese in the tervalent state regardless of species and

$$-\mathrm{d}[\mathrm{Mn}^{3+}]/\mathrm{d}t = \frac{2\mathrm{k}_{\mathrm{r}}K\ \mathrm{Mn}^{3+}]_{\mathrm{T}}[\mathrm{Me_2SO}](k_{\mathrm{o}} + k_{1}[\mathrm{M}])}{(k_{\mathrm{b}}[\mathrm{Mn}^{2+}] + 2k_{0} + k_{1}[\mathrm{M}])(1 + K[\mathrm{Me_2SO}])}$$

for the polymerisation. Rates of polymerisation would be given by

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = \frac{k_{\mathrm{p}}k_{1}k_{\mathrm{r}}K[\mathrm{Me_2SO}][\mathrm{M}]^2}{(k_{\mathrm{b}}[\mathrm{Mn}^{2+}] + 2k_{\mathrm{o}} + k_{1}[\mathrm{M}])k_{\mathrm{t}}}$$

and chain lengths by '*n*' $= \dfrac{k_{\mathrm{p}}[\mathrm{M}](1 + K[\mathrm{Me_2SO}])}{k_{\mathrm{t}}[\mathrm{Mn}^{3+}]_{\mathrm{T}}}$

Some rate parameters calculated using the above equations at 40° are given below.

Oxidation:	Polymerisation:
$k_b/k_o = 15{\cdot}05$ l.mole^{-1}	$k_p/k_t = 1{\cdot}561$ (from rates)
$k_r = 1{\cdot}294 \times 10^{-4}$ sec.$^{-1}$	$k_p/k_t = 1{\cdot}71$ (from chain lengths)
$K = 2{\cdot}57$ l. mole^{-1}	$k_1/k_o = 1{\cdot}12$ l. mole^{-1}

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