Inorganica Chimica Acta, 221 (1994) 25–30

The decomposition of peroxomonosulfate induced by manganese(II) in acid solution

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(Received December 20, 1993)

Abstract

The rate law for the manganese(II)-induced decomposition of peroxomonosulfate ion, $HOOSO_3^-$, is

$$-\frac{d[HOOSO_3^-]}{dt}=k_{Mn}\frac{[HOOSO_3^-]^{1/2}[Mn^{2+}]^{3/2}}{[H^+]^{1/2}}$$

with rate constants $k_{Mn}=(5.1\pm0.3)\times10^{-3}$ and $(9.7\pm0.2)\times10^{-3}$ $M^{-1/2}$ s^{-1} at 50 °C in H_2SO_4 and $HClO_4$ media, respectively. The rate constant is sensitive to the nature and concentration of the anion. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are 31 ± 2 kJ mol^{-1} and -194 ± 5 J mol^{-1} K^{-1}, respectively, in 1 M H_2SO_4. The presence of manganese(III) as an intermediate and as a minor product is confirmed. Peroxodisulfate, a minor product presumably from chain termination, has been used to estimate the chain length. On the basis of all the data, a mechanism quite different from most metal-induced peroxomonosulfate decompositions is postulated and some consequences and complications are elaborated.

Key words: Kinetics and mechanism; Manganese complexes; Peroxo sulfate complexes

Introduction

In the course of our study of the chain lengths and mechanism of metal-induced decompositions of peroxomonosulfate [1], it became appropriate to reinvestigate induction by manganese(II). The study by Beltrán and Ferrús [2], although incomplete, showed a rate law which did not fit the type common to many $HOOSO_3^-$ decompositions**.

The reaction of peroxomonosulfate ion, $HOOSO_3^-$, with Mn^{2+} can lead to higher metal oxidation states (e.g. Mn^{3+}, MnO_2) or to peroxide decomposition depending on the acidity of the medium [3, 4]. In acetate buffer, the product is manganese(IV) oxide [4], whereas in 1.25 M H_2SO_4 peroxide decomposition is the major reaction with small amounts of Mn^{3+} being detectable [2]. Using the competing acceptor method, it was established that the sulfate radical anion, SO_4^-, is formed during the reaction [5]. The coupled decomposition of $HOOSO_3^-$ and HOOH has a manganese-induced mechanism which has not yet been resolved [6].

We have confirmed the results of Beltrán and Ferrús [2], completed the rate law, established that peroxodisulfate is a product, and estimated the chain length. A mechanism is proposed.

Experimental

Chemicals

The triple salt ($2KHSO_5\cdot KHSO_4\cdot K_2SO_4$) made by Interox (CUROX) was employed as source of $HOOSO_3^-$; no peroxodisulfate was detectable. Manganese(II) solutions were prepared using $MnSO_4\cdot H_2O$ (Fisher ACS Reagent) and deionized water containing a few drops of 6 M H_2SO_4 to prevent hydrolysis and air oxidation of Mn(II). Acids were reagent grade and used as received.

Rate measurements

Aliquots of reaction solutions were withdrawn at intervals and added to ice-cold NaI solution to quench the reaction; $HOOSO_3^-$ reacts quantitatively with I^-

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**It is assumed that the predominant peroxide species in these acid solutions has one proton rather than two. This is reasonable if, as expected, the first ionization of H_2SO_5 is at least as acidic as that of H_2SO_4.

0020-1693/94/$07.00
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to form I_2. Although Mn(III) and Mn(IV) react with I^-, no correction was necessary.

The concentration of $S_2O_8^{2-}$ formed in the reaction was usually determined at the time when the reaction was near completion. Aliquots of the reaction solution were analyzed iodometrically promptly at 0 °C and after 40 min at room temperature under CO_2 blanket. The $S_2O_8^{2-}$ concentration of the reaction solution was determined by the difference of the titers. Peroxomonosulfate reacts quickly at 0 °C, while $S_2O_8^{2-}$ reacts very slowly at this temperature.

Results

Rate law

The rate law reported by Beltrán and Ferrús [2] was

$$-\frac{d[HOOSO_3]}{dt}=k[HOOSO_3^-]^{1/2}[Mn^{2+}]^{3/2}$$

We have found that plots of $[HOOSO_3^-]^{1/2}$ against time were linear over 90% of reaction, indicating one-half order in peroxide; twice the slope of these plots, defined as k_{obs}, does not depend significantly on peroxide concentration. When log k_{obs} was plotted against log $[Mn^{2+}]_0$, slopes of 1.48 and 1.53 were obtained in aqueous H_2SO_4 and $HClO_4$ media, respectively, indicating three-halves order in manganese(II), in agreement with the earlier work. A summary of some kinetic runs is presented in Table 1.

It can be seen that the rate is also dependent on acidity both in H_2SO_4 (runs 3 and 7–11) and in $HClO_4$ (runs 15 and 19–22). Plots of log k against the Hammett acidity function H_0 [7] gave slopes of 0.57 and 0.52 in H_2SO_4 and $HClO_4$, respectively. We interpret these values to indicate inverse one-half order in acid. The apparent overall rate constant then is $k=k_{bs}[Mn^{2+}]^{-3/2}(\log H_0)^{-1/2}$.

Given that H_0 values are based on results at variable ionic strength, we have not held ionic strength constant. The rates could be studied only over a limited range of acidity because the reaction is very slow at high acidity and colloidal MnO_2 is formed at low acidity.

Anion dependence

The rate constant for H_2SO_4 medium is about half that for $HClO_4$. Inspection of the data shows that the rate constant decreases as the acid concentration increases for H_2SO_4, but not $HClO_4$, media. This dependence of rate on H_2SO_4 concentration is presumed to arise from sulfate complexation of the manganese cations. It has been shown [8] that the rates of manganese redox reactions are dependent on the nature of the anion.

Activation parameters

Runs 23–26, covering the temperature range 25–50 °C, lead to $\Delta H^{\ddagger}=31\pm2$ kJ mol^{-1} and $\Delta S^{\ddagger}=-194\pm5$ J mol^{-1} K^{-1} in 1 M H_2SO_4.

Peroxodisulfate formation

It was found that $S_2O_8^{2-}$ is generated by the decomposition reaction. This peroxide is known to be produced by two termination steps:

$$2SO_4^- \longrightarrow S_2O_8^{2-}$$

and

$$2{}^{\cdot}OOSO_3^- \longrightarrow O_2+S_2O_8^{2-}$$

Either way an apparent chain length, L_c, can be defined as

$$L_c=-\frac{\Delta[HOOSO_3^-]}{\Delta[S_2O_8^{2-}]}$$

Values of L_c are given in Table 1. The variation in L_c is striking: it decreases with increasing $[Mn^{2+}]$ and increases with increasing acidity.

Peroxodisulfate hydrolyzes slowly in acid solution at 50 °C and apparently it also slowly oxidizes Mn^{2+} (see below). Thus $[S_2O_8^{2-}]$ passes through a maximum at about the time that $HOOSO_3^-$ is consumed.

Manganese(III) build-up

As shown in Fig. 1(a), the concentration of Mn(III) rises during the first few minutes and then almost levels off, thus showing that Mn(III) is an intermediate, but when $HOOSO_3^-$ is nearly spent the Mn(III) concentration rises rapidly. It has been found that, while $HOOSO_3^-$ is decomposing, a plot of Mn(III) concentration against $[HOOSO_3^-]^{-1/2}$ is linear as shown in Fig. 1(b).

Discussion

The rate law for the manganese(II)-induced decomposition of $HOOSO_3^-$ is

$$-\frac{d[HOOSO_3^-]}{dt}=k_{Mn}\frac{[HOOSO_3^-]^{1/2}[Mn^{2+}]^{3/2}}{[H^+]^{1/2}}$$

The half-integral orders and the fact that the sum of orders for Mn^{2+} and $HOOSO_3^-$ is two suggests a free radical chain mechanism with bimolecular initiation. An induction period was observed in some runs suggesting the build-up of one or more intermediates.

We propose the mechanism:

$$MnOH^{2+} \overset{K_2}{\rightleftharpoons} MnO^+ + H^+ \quad \text{(fast)}$$

TABLE 1. Manganese-induced decomposition rates

Run No.	[Mn(II)] (M)	[PMS] (M)	[HX] (M)	Temp. (°C)	$t_{1/2}$ (min)	L_c	$10^5\ k_{obs}$ ($M^{1/2}\ s^{-1}$)	$10^3\ k$ ($M^{1/2}\ s^{-1}$)
1	0.050	0.134	1.50[a]	23	497	(17)	0.74	1.26
2	0.050	0.134	1.50[a]	50	120	53	2.95	5.03
3	0.075	0.134	1.50[a]	50	66.8	33	5.45	5.07
4	0.100	0.134	1.50[a]	50	45.1	33	8.52	5.14
5	0.125	0.134	1.50[a]	50	32.5	(22)	11.84	5.11
6	0.025	0.134	1.50[a]	50	312	57	1.11	5.33
7	0.075	0.134	2.025[a]	50	98.8	44	3.55	4.62
8	0.075	0.134	0.90[a]	50	37.1	(20)	9.80	5.91
9	0.075	0.134	1.20[a]	50	50.4	29	7.13	5.39
10	0.075	0.134	1.80[a]	50	81.8	52	4.38	4.95
11	0.075	0.134	1.50[a,c]	50	68.6	23	5.24	4.88
12	0.050	0.120	1.50[b]	50	54.0	27	6.80	11.20
14	0.025	0.107	1.50[b]	50	152	51	2.03	9.46
15	0.050	0.107	1.50[b]	50	54.5	40	5.88	9.66
16	0.075	0.107	1.50[b]	50	30.1	34	10.97	9.85
17	0.100	0.107	1.50[b]	50	19.6	29	17.41	10.14
18	0.125	0.107	1.50[b]	50	14.8	(20)	23.66	9.60
19	0.050	0.107	2.50[b]	50	91.7	48	3.36	9.60
20	0.050	0.107	2.00[b]	50	70.6	31	4.47	9.79
21	0.050	0.107	1.00[b]	50	40.2	25	8.20	9.43
22	0.050	0.107	0.50[b]	50	25.3	(23)	13.67	9.92
23	0.100	0.128	1.00[a]	25	89.5	13	4.92	2.10
24	0.100	0.128	1.00[a]	31.5	70.0	12	6.34	2.70
25	0.100	0.128	1.00[a]	41	45.5	15	9.17	3.91
26	0.100	0.128	1.00[a]	50	29.4	16	13.94	5.95

[a] H_2SO_4. [b] $HClO_4$. [c] Plus 0.1 M H_3PO_4.

$$Mn^{3+} + H_2O \overset{K_3}{\rightleftharpoons} MnOH^{2+} + H^+ \quad \text{(fast)}$$

$$Mn^{2+} + H_2O \overset{K_1}{\rightleftharpoons} MnOH^+ + H_+ \quad \text{(fast)}$$

$$MnOH^+ + HOOSO_3^- \xrightarrow{k_1} MnO^+ + H_2O + SO_4^- \quad (1)$$

$$SO_4^- + Mn^{2+} \xrightarrow{k_2} SO_4^{2-} + Mn^{3+} \quad (2)$$

$$MnOH^{2+} + HOOSO_3^- \xrightarrow{k_3} MnO^{2+} + H_2O + SO_4^- \quad (3)$$

$$2MnO^{2+} \xrightarrow{k_4} 2Mn^{2+} + O_2 \quad (4)$$

$$2SO_4^- \xrightarrow{k_5} S_2O_8^{2-} \quad (5)$$

$$S_2O_8^{2-} + Mn^{2+} \xrightarrow{k_6} Mn^{3+} + SO_4^{2-} + SO_4^- \quad (6)$$

$$S_2O_8^{2-} + H_2O \xrightarrow{k_7} HOOSO_3^- + HSO_4^- \quad (7)$$

K_1 is small (*c.* 2×10^{-11} [9]) so that Mn(II) exists predominantly as Mn^{2+}. Mn(III) is more acidic, $K_3=0.93$ [8], but Mn^{3+} is the dominant form in our more acidic solutions.

We have written Mn(IV) as MnO^{2+} for mechanistic simplicity. At lower acidities (e.g. in acetate buffer), manganese dioxide is a product of the reaction of Mn^{2+} and $HOOSO_3^-$. However, given the extremely low solubility of MnO_2 and the absence of precipitation or turbidity during our experiments, the concentration of Mn(IV) must be very small, suggesting that step (4) of the above mechanism is fast. Since the Mn^{3+} concentration is also small, in the order of 0.1 mM when a significant amount of peroxomonosulfate remains, the concentration of Mn^{2+} apparently remains essentially constant during the reaction.

Step (7) is a known acid-catalyzed reaction; the rate constant k_7 ranges from 2.5×10^{-5} s^{-1} (0.5 M $HClO_4$) to 11.5×10^{-5} s^{-1} (2 M $HClO_4$) at 50 °C [10]. This step is relatively slow on the time scale of the peroxomonosulfate decomposition reaction, but it has a significant effect, particularly at low [Mn^{2+}] and high acidity.

Since the dimerization of sulfate radical anion is very rapid*, the concentration of SO_4^- remains very low and the steady-state approximation is justified. Spectrophotometric monitoring of the reaction shows that Mn^{3+} quickly reaches a concentration which changes only slowly during the consumption of peroxomonosulfate. Late in the reaction, the Mn^{3+} concentration rises sharply, but the steady-state approximation appears to be valid up to *c.* 80% completion.

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*The rate constant 2 k_5 has values reported from 7.5×10^8 to 3.6×10^9 M^{-1} s^{-1} [11].

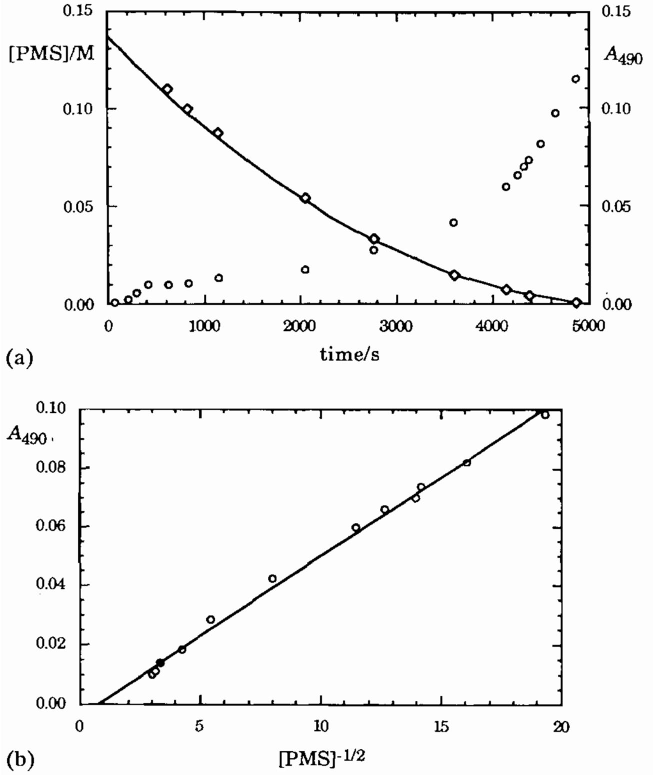


Fig. 1. Mn(II)-catalyzed decomposition of PMS in aqueous acid solution (kinetic run 26). Plot (a) shows that the absorbance at 490 nm, proportional to [Mn(III)], increases while PMS decomposes during the reaction; plot (b) shows the dependence of Mn(III) formation on the concentration of PMS.

Application of the steady-state approximation to SO_4^- and to Mn^{3+} gives the following expressions for the concentration of these species:

$$[SO_4^-]=\left\{\frac{[Mn^{2+}]}{k_5}\left(k_1'[HOOSO_3^-]+k_6[S_2O_8^{2-}]\right)\right\}^{1/2}$$

$$[Mn^{3+}]=\frac{[Mn^{2+}]}{k_3'}\left(k_1'+k_2\frac{[SO_4^-]}{[HOOSO_3^-]}+k_6\frac{[S_2O_8^{2-}]}{[HOOSO_3^-]}\right)$$

where $k_1'=k_1K_1/[H^+]$ and $k_3'=k_3K_3/[H^+]$. Substitution of these expressions into the rate of disappearance of peroxomonosulfate gives

$$-\frac{d[HOOSO_3^-]}{dt}=2k_1'[HOOSO_3^-][Mn^{2+}]+k_6[S_2O_8^{2-}][Mn^{2+}]+\frac{k_2[Mn^{2+}]^{3/2}}{k_5^{1/2}}\left(k_1'[HOOSO_3^-]+k_6[S_2O_8^{2-}]\right)^{1/2}-k_7[S_2O_8^{2-}]$$

Since k_1' is small, the first term is negligible; early in the reaction when $[S_2O_8^{2-}]$ is small, this rate law reduces to

$$-\frac{d[HOOSO_3^-]}{dt}=k_2\left(\frac{k_1'}{k_5}\right)^{1/2}[HOOSO_3^-]^{1/2}[Mn^{2+}]^{3/2}$$

which matches the empirical result with

$$k_{exp}=k_2\left(\frac{k_1'}{k_5}\right)^{1/2}[H^+]^{1/2}=k_2\left(\frac{k_1K_1}{k_5}\right)^{1/2}$$

Substituting the steady-state expression for $[SO_4^-]$ into that for $[Mn^{3+}]$ and neglecting terms in k_1' and $[S_2O_8^{2-}]$, we obtain

$$[Mn^{3+}]=\frac{k_2}{k_3'}\left(\frac{k_1'}{k_5}\right)^{1/2}\frac{[Mn^{2+}]^{3/2}}{[HOOSO_3^-]^{1/2}}$$

The absorbance at 490 nm was followed versus time for kinetic runs 2, 4 and 26; plots of absorbance versus $[HOOSO_3^-]^{-1/2}$ gave straight lines as shown in Fig. 1(b). Assuming $\epsilon=114\ M^{-1}\ cm^{-1}$ [2], the slope of these plots can be combined with k_{exp} to compute k_3', giving $k_3K_3=4.4\pm0.9\ s^{-1}$.

Late in the reaction, when $[HOOSO_3^-]\rightarrow 0$, the steady-state approximation for Mn^{3+} is no longer valid. With small $[HOOSO_3^-]$, Mn^{3+} is no longer consumed as fast as it is formed and the Mn^{3+} concentration begins to grow through step (6) of the mechanism. As shown in Fig. 1(a), the growth in $[Mn^{3+}]$ is nearly linear in time when the main reaction is nearly complete. Assuming that $d[Mn^{3+}]/dt=k_6[Mn^{2+}][S_2O_8^{2-}]$ and that $[S_2O_8^{2-}]\gg[Mn^{3+}]$, we can estimate k_6 from the slope of the linear region with $\epsilon=114\ M^{-1}\ cm^{-1}$ and the analytical value of $[S_2O_8^{2-}]$ at the completion of reaction. This analysis gives $k_6=(9.6\pm0.5)\times10^{-4}\ M^{-1}\ s^{-1}$ (average of three runs). It should be noted that the rate of step (6) is comparable to the rate of acid hydrolysis of peroxodisulfate, $k_7=7.5\times10^{-5}\ s^{-1}$ in 1.5 M $HClO_4$ at 50 °C [10].

The mechanism can be used as the basis for a computer simulation of the kinetics using the Macintosh program, STELLA [12]. In the simulations, the SO_4^- concentration was computed using the steady-state approximation

$$[SO_4^-]=\frac{k_2[Mn^{2+}]}{4k_5}\left\{-1+\left[1+\frac{8k_5[HOOSO_3^-]}{k_2^2[Mn^{2+}]}\times\left(k_1'+\frac{k_3'[Mn^{3+}]}{[Mn^{2+}]}+\frac{k_6[S_2O_8^{2-}]}{[HOOSO_3^-]}\right)\right]^{1/2}\right\}$$

but all other concentrations were handled explicitly. All simulations took $k_5=5\times10^8\ M^{-1}\ s^{-1}$ and (when the step was included) $k_6=1\times10^{-3}\ M^{-1}\ s^{-1}$. Simulations confirmed that the experimental rate constant is reasonably well expressed by $k_{exp}=k_2(k_1K_1/k_5)^{1/2}$ as derived above using the steady-state approximation.

The concentration of Mn^{3+} during the reaction was found to be close to that computed from the steady-state approximation.

As expected, simulations showed that the yield of $S_2O_8^{2-}$ is critically dependent on the ratio k_1'/k_2; this ratio was adjusted to match the experimental $S_2O_8^{2-}$ concentration at the completion of the reaction. Together with k_{exp}, we then have estimates of k_1' and k_2. The final fitted rate constants are given in Table 2 and a typical simulation, showing reactants, products and intermediates, is shown in Fig. 2.

The experimental values of the apparent chain length, L_c, shown in Table 1 are widely variable, but in general L_c is longer at high acidity, at low $[Mn^{2+}]$, and at high temperature. The source of these systematic variations is, we believe, understandable. As noted above, peroxodisulfate is consumed by two reactions, reaction with Mn^{2+} to produce SO_4^{2-} and acid hydrolysis to produce sulfate and an acid-dependent mixture of peroxomonosulfate and oxygen. The latter reaction is approximately first-order in H^+ and has an activation energy of 102 kJ mol^{-1} [13]. Thus as the acidity increases, the reaction of $HOOSO_3^-$ is slower and hydrolysis faster, so that the yield of peroxodisulfate decreases and the apparent chain length increases. The effect of Mn^{2+} concentration is a balance between two effects: at high Mn^{2+}, the reaction of $S_2O_8^{2-}$ with Mn^{2+} decreases $S_2O_8^{2-}$, but the $HOOSO_3^-$ reaction is faster so that there is less time for $S_2O_8^{2-}$ consumption. At low Mn^{2+}, there is less consumption of $S_2O_8^{2-}$ by reaction with Mn^{2+}, but more time is available for hydrolysis. The activation energy for the decomposition of $HOOSO_3^-$ is 33 kJ mol^{-1} compared with 102 kJ mol^{-1} for the hydrolysis reaction; thus much less hydrolysis occurs at 25 °C, even though the reaction time is increased.

TABLE 2. Rate and equilibrium constants

Symbol	Value	Ref.
k_{Mn} (H_2SO_4 medium)	$(5.1\pm0.3)\times10^{-3}$ $M^{-1/2}$ s^{-1}	a,b
k_{Mn} ($HClO_4$ medium)	$(9.7\pm0.2)\times10^{-3}$ $M^{-1/2}$ s^{-1}	a
K_1	2×10^{-11}	9
K_3	0.93	8
k_1	4×10^{-4} M^{-1} s^{-1}	a
k_2	2×10^{3} M^{-1} s^{-1}	a
k_3	1 M^{-1} s^{-1}	a
k_3K_3	0.9 s^{-1} (4.4 ± 0.9 s^{-1})	a
k_5	5×10^{8} M^{-1} s^{-1}	11
k_6	1×10^{-3} M^{-1} s^{-1}	a
k_7 (range)	$(2.5–11.5)\times10^{-5}$ s^{-1}	10
k_7 (average)	7.5×10^{-5} s^{-1}	a

[a]This work. [b]The data of Beltrán and Ferrús [2] give $k_{Mn}=3.2\times10^{-3}$ $M^{-1/2}$ s^{-1}.

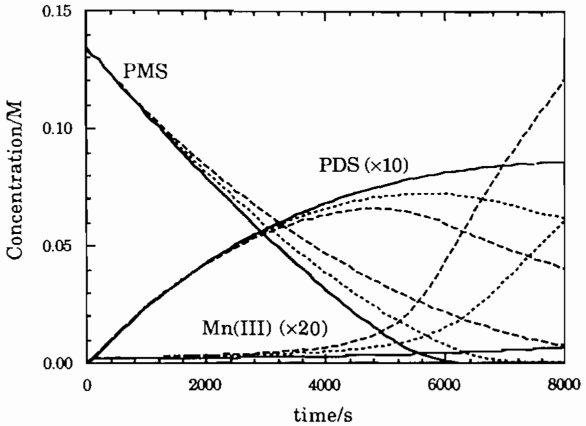
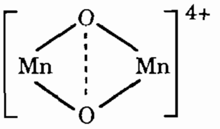


Fig. 2. Computer simulation of Mn^{2+} catalyzed decomposition of PMS. $[PMS]_0=0.133$ M, $[H_2SO_4]=1.5$ M, $[Mn^{2+}]_0=0.10$ M, $t=50$ °C; $k_1=2\times10^{-4}$ M^{-1} s^{-1}, $k_2=3180$ M^{-1} s^{-1}, $k_3=2$ M^{-1} s^{-1}, $k_5=5\times10^{8}$ M^{-1} s^{-1}, $k_6=0.0$ (——), 0.001 (·····), and 0.002 (– – –) M^{-1} s^{-1}.

Under some conditions (50 °C, 1.5 M H_2SO_4, 0.025 M Mn^{2+}), the half-time for $HOOSO_3^-$ decomposition is about twice as long as that of $S_2O_8^{2-}$ hydrolysis; obviously, there was considerable loss of $S_2O_8^{2-}$ before the run was complete. Under conditions which minimize loss of $S_2O_8^{2-}$ – high $[Mn^{2+}]$, low temperature, and low acidity – some hydrolysis may still occur, but it appears that the true chain length is best approximated by the L_c values for these runs, shown in parentheses in Table 1, giving $L_c\approx15–20$.

The production of dioxygen from water is presumed to be keyed to two adjacent manganese(IV) atoms [14]. A transition state configuration



is consistent with our kinetics.

It has already been shown that hydrolysis of $S_2O_8^{2-}$

$$S_2O_8^{2-}+H_2O \xrightarrow{H^+} HOOSO_3^- + HSO_4^-$$

can occur under the conditions where $HOOSO_3^-$ decomposes. This regenerates some $HOOSO_3^-$ and the regeneration would be most important when $HOOSO_3^-$ has decreased. $S_2O_8^{2-}$ brings in another complication. It can oxidize Mn^{2+} slowly [15], although to our knowledge a careful study of this reaction has not been made.

Acknowledgement

We thank Solvay Interox for continued support of peroxide chemistry.

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