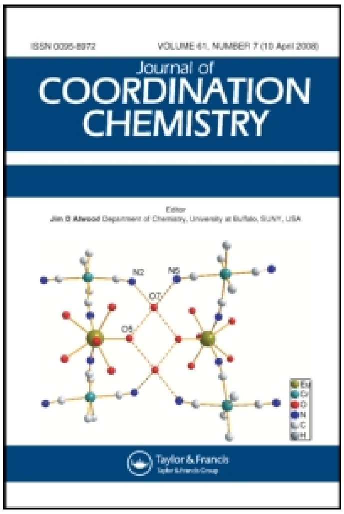

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

DECOMPOSITION KINETICS OF SODIUM PERBORATE CATALYZED BY ETHYLENEDIAMINETETRA-ACETATOMANGANESE(III)

Samy S. Anis[a]; Mohamed A. Mansour[a]
[a] Chemistry Department, Faculty of Science, Ain-Shams University, Abbassia, Cairo, Egypt

To cite this Article Anis, Samy S. and Mansour, Mohamed A.(1999) 'DECOMPOSITION KINETICS OF SODIUM PERBORATE CATALYZED BY ETHYLENEDIAMINETETRA-ACETATOMANGANESE(III)', Journal of Coordination Chemistry, 46: 3, 257 — 263
To link to this Article: DOI: 10.1080/00958979908048470
URL: http://dx.doi.org/10.1080/00958979908048470

J. Coord. Chem., 1999, Vol. 46, pp. 257–263
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

DECOMPOSITION KINETICS OF SODIUM PERBORATE CATALYZED BY ETHYLENEDIAMINETETRA-ACETATOMANGANESE(III)

SAMY S. ANIS* and MOHAMED A. MANSOUR

Chemistry Department, Faculty of Science,
Ain-Shams University, Abbassia, Cairo, Egypt

(Received 23 September 1997)

The decomposition of sodium perborate in the presence of ethylenediaminetetraacetatomanganese(III) was studied in aqueous solution over the pH range 8.3–10.8 at 50–65°C. The reaction was shown to exhibit second-order kinetics, first-order in each of the reactants. The rate law is

$$-\frac{d[BO_3^-]}{dt} = \left\{k_1 + \frac{k_2K}{[H^+]}\right\} [Mn(III)Y^-][BO_3^-]$$

where Y denotes the form of the ligand. Values of k_1 and k_2 were determined at various temperatures. Corresponding activation parameters are $\Delta H_1^* = 36.7\,kJ\,mol^{-1}$, $\Delta S_1^* = -182\,J\,K^{-1}\,mol^{-1}$, $\Delta H_2^* = 32.8\,kJ\,mol^{-1}$, $\Delta S_2^* = -194\,J\,K^{-1}\,mol^{-1}$. Comparison is made with hydrogen peroxide decomposition by manganese complexes.

Keywords: Manganese(III); complexes; perborate; peroxide; kinetics

INTRODUCTION

The presence of the manganese(III) ion in biological redox reactions has become increasingly apparent in recent years. It is known that manganese ions are required for the photosynethetic evolution of dioxygen from green plant chloroplasts.[1] A manganese metalloenzyme, superoxide dismutase, is responsible for the disproportionation of superoxide anion to molecular

---

* Corresponding author.

oxygen and hydrogen peroxide in procaryotes and in the mitochondria of eucaryotes.[2] The results of electron spin resonance and magnetic susceptibility[3] and electron absorption spectroscopy[2] suggest that the enzyme contains mangnese(III) in its resting state. The protein has also been the subject of nuclear magnetic resonance[4] examination of its mechanism of catalysis. Manganese complexes in oxidation state three have been prepared and characterized owing to the relative instability of the manganese(III) ion.[5] Complexes of manganese(III) are generally more stable because their formation constants are greater than the formation constants of the comparable manganese(II) complexes. Manganese(III) complexes are therefore much poorer oxidizing agents and are not subject to disproportionation. The solid manganese(III) EDTA complex has been prepared and characterized by Yoshino *et al.*,[6] as $K[Mn(H_2O)EDTA].H_2O$.

Disproportionation of H_2O_2 in the presence of manganese polyaminocarboxylates was reported by Jones and Hamm,[7] where the reaction of the Mn(III) CyDTA[†] complex with H_2O_2 was studied in the pH range 2–4 and found to be first order in $[H_2O_2]$, second order in [Mn(III)-CyDTA] and inversely dependent on $[H^+]$. The mechanism suggested involves fast formation of a peroxo intermediate followed by the slow decomposition of these species.

In the catalytic decomposition of H_2O_2 by the Mn(III) ENTMP complex[‡] as studied by Rizkalla *et al.*,[8] the reaction was followed over a pH range of 9–11 and found to be first order in both $[H_2O_2]$ and [Mn(III)-ENTMP] and inversely dependent on $[H^+]$. The mechanism suggested involves peroxide substitution in the inner sphere of the metal ion as the rate determining step.

The investigation reported in this paper concerns the catalytic decomposition of perborate ion by the Mn(III) EDTA complex and the mechanism of decomposition. We compare the results obtained with those for hydrogen peroxide decomposition.

EXPERIMENTAL

Ethylenediaminetetraacetic acid (H_4Y), potassium permanganate, sodium perborate tetrahydrate and ethanol were of B.D.H. Analar grade.

[†] CyDTA: 1,2-diaminocyclohexanetetraaceto.

[‡] ENTMP: ethylenediaminetetra(methylenephosphonato).

The solid complex was prepared as described by Yoshino *et al.*[6] In the method used, six grams of finely powdered potassium permanganate were added to a mixed solution of 40 cm^3 of water and 10 cm^3 of ethanol. The mixture was shaken and then carefully warmed. After vigorous reaction had ended, the mixture was further warmed to expell excess ethanol and aldehyde. To the mixture of manganese dioxide and potassium hydroxide so obtained, a stoichiometric amount of EDTA (H_4Y) was added with vigorous stirring. A reaction took place, evolving carbon dioxide, and a deep red solution was obtained. After filtration, an equal volume of cold ethanol was added to the filtrate. The mixture was allowed to stand for 3–4 h in a cold, dark place. The precipitated crystals were then filtered off with a glass fibre filter and washed with absolute alcohol and then ether. Finally they were dried in air in a cold, dark place, and red crystalline solid complex was obtained. Carbonate-free sodium hydroxide was used in all experiments to adjust pH. The hydrogen ion concentration was determined using a Radiometer pH-meter (model M62) fitted with a combined glass-calomel electrode. Spectroscopic measurements were obtained using a Unicam SP1800 spectrophotometer. The reaction was thermostatted to the proper temperature and the reaction initiated by addition of precalculated amount of sodium perborate. Aliquots were removed periodically and quenched by KI/H_2SO_4 mixture. The liberated iodine equivalent to the residual perborate and Mn(III) contents was then determined iodometrically.[9] Ionic strength was adjusted to 0.2 M with potassium nitrate.

RESULTS AND DISCUSSION

The electronic spectrum of $K[Mn(H_2O)EDTA].H_2O$, which has a distorted octahedral structure,[6] displays a band maximum at 500 nm. Addition of perborate produces an intermediate with λ_{max} at 415 and 610 nm. The rate of perborate decomposition was studied under *pseudo*-first order conditions with excess perborate. Logarithmic plots of the residual perborate contents as a function of time were found to be linear up to a degree of completion of 75% or more. At a fixed condition of pH, temperature and perborate concentration, the observed rate constant is directly proportional to the manganese complex concentration, which suggests a first order dependency on the catalyst concentration. The dependency of pH of the decomposition reaction was studied between 50°C and 65°C at fixed concentrations of perborate and manganese complex. The pH profile for the reaction suggests that one of the reactants is involved in acid–base equilibria in this pH range.

$[\mathrm{Mn(III)EDTA}]^- \overset{K}{\rightleftharpoons} [\mathrm{Mn(III)EDTA(OH)}]^{2-} + \mathrm{H}^+ \qquad \mathrm{p}K = 5.3$[6]

At higher alkalinity, the catalytic sensitivity is markedly retarded. Similar observations were reported by Francis *et al.*[10] for the decomposition of H_2O_2 catalyzed by $[\mathrm{Fe(III)EDTA}]^-$; they attributed the decrease in rate constant at higher alkalinity to the formation of the inactive dihydroxy complex. A summary of all observed rate constants obtained under various reaction conditions together with calculated rate constants are listed in Table I. Addition of perborate ion to the reaction mixture is accompanied by subsequent change in colour depending on the pH of the medium, attributed to the formation and breakdown of a mixed ligand complex.

The course of the colour change is pink → blue → yellow → pale brown → brown ppt. Hamm and Suwyn[11] attributed the change in colour from pink to yellow in the catalytic decomposition of H_2O_2 by Mn(III)

TABLE I Observed and calculated rate constants for the decomposition of perborate in the presence ethylenediaminetetraacetatomanganese complex; [perborate] = 0.15 M, I = 0.20 M

Temp. (°C)	*pH*	[*MnEDTA*] × 10^3 (M)	$k_{obs.} \times 10^4$ (s^{-1})	$k_{cal.} \times 10^4$ (s^{-1})
50	8.30	17.60	2.50	2.45
50	8.60	17.60	3.04	2.79
50	8.80	17.60	3.50	3.19
50	9.10	17.60	4.50	4.27
50	9.40	17.60	5.83	6.43
50	9.50	17.60	6.33	7.55
50	9.65	17.60	5.10	
50	9.80	17.60	2.83	
50	10.00	17.60	2.03	
58	8.35	17.60	3.33	3.02
58	8.80	17.60	4.17	4.00
58	9.20	17.60	6.75	6.30
58	9.40	17.60	8.82	8.36
58	9.60	17.60	10.67	11.80
58	9.80	17.60	9.17	
58	10.25	17.60	6.50	
58	10.80	17.60	5.75	
58	8.80	4.50	1.01	
58	8.80	8.95	2.01	
58	8.80	13.50	3.19	
65	8.60	17.60	4.98	5.22
65	9.10	17.60	7.01	8.06
65	9.20	17.60	7.92	9.13
65	9.35	17.60	9.90	11.28
65	9.50	17.60	14.12	
65	9.95	17.60	12.83	
65	10.20	17.60	11.83	

CyDTA to the formation of the monohydroxo complex (pK = 8.11). At higher pH, the formation of the unstable, intense yellow-brown solution was attributed to the formation of an oxo-Mn(IV) complex.[12] In strongly alkaline medium, the oxo-Mn(IV) species undergoes further hydrolysis leading to the formation of colloidal MnO_2, which, in turn, reduces the catalytic activity as evidenced by kinetic observations.

Trans-1,2-diaminocyclohexane tetraacetic acid (CyDTA) has been reported to form metal complexes which are more stable than analogous EDTA complexes.[13] The greater stability of the *trans*-CyDTA complexes has been explained on the basis of the rigidity of the cyclohexane ring by Day and Reiley.[14] The inflexibility of the cyclohexane ring makes it more difficult to move either of the acetate arms away from the metal ion. In reactions in which ligand substitution is involved in the rate determining step, it has been reported that $[Mn(III)EDTA]^-$ reacts faster than $[Mn(III)CyDTA]^-$ (substitution of carboxylate by other ions or groups). This difference in reactivity is anticipated for ligand substitution on the basis of values of the formation constants of both complexes (the specific rate constant for the decomposition for $[Mn(111)EDTA]^-$ is $1.20 \times 10^{-5} s^{-1}$ while for $[Mn(III)CyDTA]^-$ it is $0.65 \times 10^{-5} s^{-1}$ at 25°C and pH = 4).[11] Poh and Stewart[15] indicate that a convenient pathway for the reaction of $[Mn(111)CyDTA]^-$ with methanol to produce formaldehyde might be ligand substitution (methanol for carboxylate). Therefore, a ligand substitution mechanism was assumed in which the perborate ion substitutes one of the carboxylate arms bound to the manganese atom in the rate determining step.

The similarities of enthalpies of activation for both the acid-dependent and acid-independent pathways suggest that bond breaking and bond formation processes take place through a common entering $[HOOB{-}(OH)_3]^-$ and leaving (coordinated $-COO^-$) group. Based on the above observations, the mechanism of the catalytic process can be represented as shown below.

$$[Mn(111)Y]^- \overset{K}{\rightleftharpoons} [Mn(111)Y(OH)]^{2-} + H^+$$

$$BO_3^- + 2H_2O \rightarrow [HOO-B(OH)_3]^-$$

$$[Mn(111)Y]^- + [HOO-B(OH)_3]^- \xrightarrow[\text{slow}]{k_1} [Mn(111)Y-HOOB(OH)_3]^- + X$$

$$[Mn(111)Y(OH)]^{2-} + [HOO-B(OH)_3]$$
$$\xrightarrow[\text{slow}]{k_2} [Mn(111)Y(OH)-HOOB(OH)_3]^{2-} + X$$

$$[\mathrm{Mn(111)Y.HOO-B(OH)_3}]^- \xrightarrow[\text{fast}]{X} [\mathrm{Mn(IV)Y(O)}]^{2-} + \mathrm{OH}^\bullet + \mathrm{H_3BO_3}$$

$$[\mathrm{Mn(111)Y(OH)HOOB(OH)_3}]^{2-}$$
$$\xrightarrow[\text{fast}]{X} [\mathrm{Mn(IV)Y(O)}]^{2-} + \mathrm{OH}^\bullet + \mathrm{OH}^- + \mathrm{H_3BO_3}$$

$$[\mathrm{Mn(IV)Y(O)}]^{2-} + \mathrm{OH}^\bullet \longrightarrow [\mathrm{Mn(III)Y}]^- + \mathrm{O_2} + \mathrm{H}^+$$

$$\mathrm{H}^+ + \mathrm{OH}^- \longrightarrow \mathrm{H_2O}$$

where $X = -\mathrm{COO}^-$

The kinetic expression for such a scheme is

$$k_{obs} = \left\{k_1 + \frac{k_2K}{[\mathrm{H}^+]}\right\}[\mathrm{Mn(III)Y}^-]$$

$$\text{where } [\mathrm{Mn(III)Y}^-] = \left\{\frac{\mathrm{H}^+]}{[\mathrm{H}^+] + K}\right\}[\mathrm{Mn(III)EDTA}]_T$$

and $[\mathrm{Mn(111)EDTA}]_T = [\mathrm{Mn(111)Y}^-] + [\mathrm{Mn(111)Y(OH)}^{-2}]$.

Values of k_1 and k_2 at various temperatures calculated from the intercepts and slopes of the linear relationships of k_{obs} *versus* $[\mathrm{H}^+]^{-1}$ are listed in Table II together with the enthalpies and entropies of activation which were calculated from Arrhenius plots.

The species $[\mathrm{Mn(III)Y}]^-$ and $[\mathrm{Mn(III)YOH}]^{2-}$ differ in their overall anionic charges as a result of substituting the coordinated water molecule by the negatively charged hydroxyl group; thus a marked enhancement of k_1 compared to k_2 values is due to electrostatic factors in which the higher negative charge of the hydroxo species renders the reaction rate slower.

Comparison of the reactivity of manganese complexes towards decomposition of hydrogen peroxide and perborate ion shows that the catalytic

TABLE II Summary of rate constants and activation parameters for the decomposition of perborate in the presence of the MnEDTA complex

Temp. (°C)	k_1 ($M^{-1}s^{-1}$)	$k_2 \times 10^3$ ($M^{-1}s^{-1}$)
50	11.93 ± 2.3	1.95 ± 0.20
58	17.05 ± 2.0	2.64 ± 0.25
65	22.16 ± 2.4	3.74 ± 0.27

$\Delta H_1^\ddagger = 36.7 \pm 0.9\,\mathrm{kJ\,mol^{-1}}$ $\Delta S_1^\ddagger = -182 \pm 10\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$\Delta H_2^\ddagger = 32.8 \pm 1.3\,\mathrm{kJ\,mol^{-1}}$ $\Delta S_2^\ddagger = -194 \pm 15\,\mathrm{J\,K^{-1}\,mol^{-1}}$

decomposition of hydrogen peroxide by $[MnENTMP]^{5-}$ {$k_o = 8.83\,M^{-1}\,s^{-1}$ at 40°C, pH = 9.1}[8] is much faster than that of perborate decomposition by $[MnEDTA]^-$ {$k_o = 0.026\ M^{-1}s^{-1}$ at 50°C, pH = 9.1} in spite of the higher negative charge on the MnENTMP complex (5 –) compared to the MnEDTA complex (1 –). This is due to steric effects, since the perborate ion has a large size compared to hydrogen peroxide. This conclusion was confirmed by the value of k_o for hydrogen peroxide decomposition by $[Mn(III)CyDTA]^-$ ($k_o = 2.30\,M^{-1}\,s^{-1}$ at 25°C, pH = 3)[7] in which metal ion-peroxo complexes are formed. The reaction is several orders of magnitude faster than that involving perborate decomposition by the $[Mn(III)EDTA]^-$ complex.

References

[1] G.M. Cheniae, *Ann. Rev. Plant Physiol.*, **21**, 467 (1970).
[2] S.M. McCord and I. Fridovich, *J. Biol. Chem.*, **244**, 6049 (1969).
[3] J.A. Fee, E. Shapiro and T. Mos, *J. Biol. Chem.*, **251**, 6157 (1976).
[4] J. Villafranca, F. Yost and I. Fridovich, *J. Biol. Chem.*, **249**, 3532 (1974).
[5] S. Gangopadhgay, M. Ali and P. Banerjee, *Coord. Chem. Rev.*, **135**, 399 (1994).
[6] Y. Yoshino, A. Ouchi, Y. Tsunoda and M. Kojima, *Can. J. Chem.*, **40**, 775 (1962).
[7] T.E. Jones and R.E. Hamm, *Inorg. Chem.*, **13**, 1940 (1974).
[8] E.N. Rizkalla, S. S. Anis and L.H. Khalil, *Polyhedron*, **6**, 403 (1987).
[9] A.I. Vogel, Text Book of Quantitative Inorganic Chemistry, 3rd ed., (Longman, London, 1966).
[10] K.C. Francis, D. Cusmmins and J. Oakes, *J. Chem. Soc. Dalton Trans.*, 493 (1985).
[11] R.E. Hamm and M.A. Suwyn, *Inorg. Chem.*, **6**, 139 (1967).
[12] J. Stein, J.P. Fackler, G.J. McClune, J.A. Fee and L.T. Chen, *Inorg. Chem.*, **18**, 3511 (1979).
[13] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 936 (1954).
[14] R.J. Day and C.N. Reilleg, *Anal. Chem.*, **37**, 1326 (1965).
[15] L. Poh and R. Stewart, *Can. J. Chem.*, **50**, 3432 (1972).