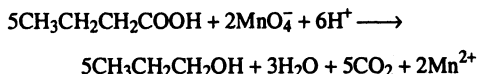


Micellar Catalysed Oxidative Decarboxylation of Butyric and Iso-Butyric Acids by Acidic Permanganate Ions

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A micellar catalyzed oxidative decarboxylation of butyric and isobutyric acid by permanganate ion in moderately concentrated acidic medium has been studied. The pre-micellar kinetics has been rationalised in the light of pseudo-phase model. The positive cooperativity index ($n = 2.09$) has been computed. The decarboxylation reactions are acid catalysed and, therefore, various hypotheses for the mechanism of acid catalysis were tested. Thus, the role of water molecule as proton abstracting agent is established. On addition of fluoride ions, a known complexing agent, there is a decrease in the reaction rate. The effects of variation of ionic strength and thermodynamic parameters have been computed. The stoichiometry for the reaction is:



On the basis of the various observations and product characterization a most plausible mechanism has been envisaged.

INTRODUCTION

A considerable amount of work on oxidative decarboxylation of various organic substrates by permanganate ion has been studied¹⁻⁸ but no information is available on the micellar catalyzed (sodium dodecyl sulfate) oxidation of butyric acid and isobutyric acid by permanganate. Therefore, the present study is undertaken.

EXPERIMENTAL

All chemicals used were of BDH or AnalaR. Potassium permanganate solution was prepared in doubly distilled water as given by Vogel⁹. The progress of the reaction was monitored by iodometric estimations of the reaction mixture at various time intervals.

RESULTS AND DISCUSSION

This has been observed that in the micellar catalyzed oxidative decarboxylation of butyric and iso-butyric acid the plot of $\log(a - x)$ versus time is a straight line. The variation of initial concentration of permanganate has practically no effect

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on the reaction velocity and the values of pseudo first order constants k_1 for both the substrates are found to be fairly constant. The order with respect to permanganate is thus confirmed to be one.

Dependence of rate on [substrate]: With the increase in the concentration of substrate the pseudo first order rate constants k_1 are found to be increased (Table-1). Plots of $\log k_1$ vs. \log [substrate] give straight lines with slopes equal to 0.99 and 1.04 for butyric and iso-butyric acid respectively. This confirms that the order of reaction with respect to each substrate is one. Further, plots of $1/k_1$ vs. 1 /[substrate] give straight lines passing through the origin [Fig. 1]. This confirms again that the order with respect to substrate is one and there is no kinetic evidence for intermediate complex formation between substrate and permanganate¹⁰.

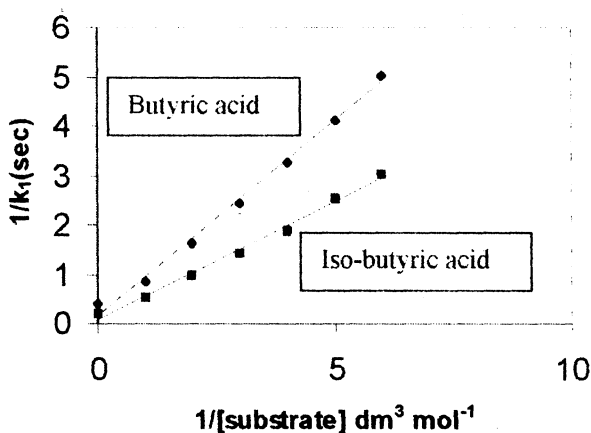


Fig. 1. (a) $1/k_1$ vs. 1 /[substrate]: $[KMnO_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[H_2SO_4] = 1.5 \text{ mol dm}^{-3}$; $[CH_3CH_2CH_2COOH] = 0.1 \text{ mol dm}^{-3}$; $[NaDS] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$; Temp. = 303 K

TABLE-1
VARIATION OF SUBSTRATE CONCENTRATION

$[KMnO_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[H_2SO_4] = 1.5 \text{ mol dm}^{-3}$; Temp. = 303 K;
 $[NaDS] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$

S.No.	[Substrate] (mol dm^{-3})	[Butyric acid] ($k_1 \times 10^4 \text{ sec}^{-1}$)	[isobutyric acid] ($k_1 \times 10^4 \text{ sec}^{-1}$)
1.	0.1	0.43	0.26
2.	0.2	0.74	0.45
3.	0.3	0.98	0.62
4.	0.4	1.58	1.10
5.	0.5	1.97	1.41
6.	0.6	2.58	1.62

Dependence of rate on surfactant concentration: The reaction has been found to be catalysed by addition of sodium dodecyl sulfate, an anionic surfactant (Table-2). The reaction rate increases with concentration from 1.0×10^{-4} to 6.0

$\times 10^{-4}$ M. The reported cmc of sodium dodecyl sulfate is 8.1×10^{-3} M at 25°C . Reports are available that the catalysis below cmc, *i.e.*, premicellar catalysis is also feasible¹¹. Micelles may be formed by assembling of amphiphilic molecules in water above a certain concentration (critical micellar concentration above cmc). Micelles acting as a kind of micro-reactors enhance the rate of reactions. The catalytic efficiency of micelles can be determined by the affinity of reactants toward the micelle and among themselves. Moreover, on account of their solubilisation capability micelles may increase the reactant concentration within the hydrophilic or hydrophobic areas and cause a favourable orientation of the reactants by polarity gradients. Ionic micelles can stabilize or inhibit polarized transition states within the aggregates and therefore enhance or slow down a reaction. In the present case the catalysis by NaDS before its cmc suggests that the substrate promotes micellisation of the anionic surfactant or that the small aggregates of the detergent exist below the cmc and that they catalyse the reaction. A similar substrate promoted micellisation has been observed in the deacylation of *p*-nitrophenyl benzoate¹². Also there is extensive evidence from other systems^{11, 13} that (i) external agents can promote micellisation, (ii) some aggregation of detergents occurs below cmc, and (iii) these small aggregates can be catalytically active¹⁴. The catalysis by sodium dodecyl sulfate has therefore been treated by a theme proposed by Piszpiwicz¹⁵. This scheme includes the decomposition of substrate-micelle complex into the free components, resulting in an equation of the form (1).

$$\log [k_{\text{obs}} - k_0/k_m - k_{\text{obs}}] = n \log [D] - \log K_D \quad (1)$$

From Eq. (1) the plot of $\log [k_{\text{obs}} - k_0/k_m - k_{\text{obs}}]$ vs. $n \log [D]$ should be linear with a slope = n , called the index of cooperativity. Values of n range from 1 to 6. In the present case, $n = 2.09$, indicating a positive cooperativity, *i.e.*, induced interaction of the additional substrate molecule due to the interaction of the micelle with the first substrate molecule.

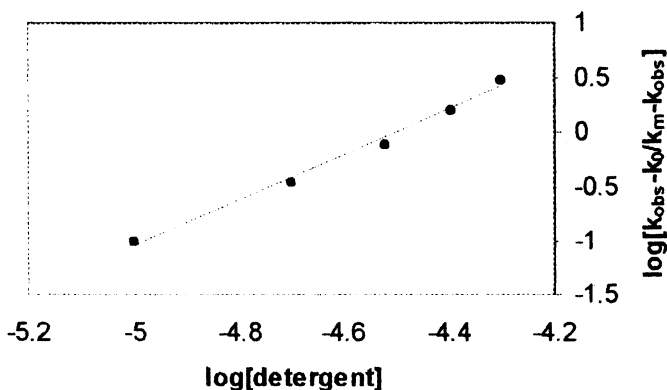


Fig. 2. Positive co-operativity: $[\text{KMnO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}] = 0.1 \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol dm}^{-3}$; Temp. = 303 K

TABLE-2
EFFECT OF VARIATION OF SURFACTANT CONCENTRATION

$[KMnO_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H_2SO_4] = 1.5 \text{ mol dm}^{-3}$; Temp. = 303 K

S.No.	$[NaDS] \times 10^4$ (mol dm^{-3})	[Butyric acid] ($k_1 \times 10^4 \text{ sec}^{-1}$)	[iso-butyric acid] ($k_1 \times 10^4 \text{ sec}^{-1}$)
1.	0.0	0.43	0.22
2.	1.0	0.85	0.52
3.	2.0	1.63	0.96
4.	3.0	2.45	1.42
5.	4.0	3.25	1.88
6.	5.0	4.12	2.54
7.	6.0	5.01	3.01

Effect of variation of sulfuric acid: To observe the effect of acid concentration on the reaction, the reactions were studied at different initial concentrations of sulphuric acid. In order to avoid complications from precipitation of MnO_2 reactions were carried out in strongly acidic medium. The MnO_4^- ion gets protonated in accordance with the equilibrium $MnO_4^- + H^+ \rightleftharpoons HMnO_4$ supported by the spectral studies suggesting that the $HMnO_4$ is one of the active oxidising species^{4(b), 16}. The rate of oxidation which is strictly proportional to the concentration of the substrate indicates that $HMnO_4$ oxidizes substrate directly¹⁷. The two Zucker-Hammet¹⁸ plots were found linear. This indicates that the reactions are acid catalyzed. However, none of the plots produce ideal slope values of unity [Table-3]. In view of these departures from the ideal slope values the Bunnett¹⁹ and Bunnett-Olsen's hypotheses²⁰ were tested. The slope values indicate that the water molecule should act as a proton abstracting agent in the rate determining step^{19-a}. The values of H_0 and $\log a_{H_2O}$ corresponding to given acid concentration have been taken from Paul and Long²¹ and Bunnett^{19-b} respectively.

TABLE-3
CORRELATION OF RATE WITH H_2SO_4 CONCENTRATION

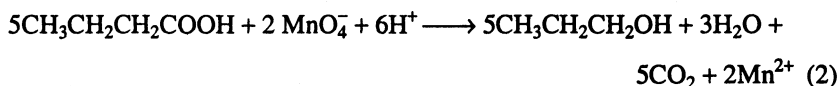
$[KMnO_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[CH_3CH_2CH_2COOH] = 0.1 \text{ mol dm}^{-3}$;
 $[NaDS] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$; Temp. = 303 K

Correlation	Slope values	
	[butyric acid]	[isobutyric acid]
(A) Zucker-Hammet plots		
1. H_0 vs $\log k_1$	0.62	0.70
2. $\log [\text{acid}]$ vs. $\log k_1$	1.57	1.89
(B) Bunnet plots		
$\log k - \log [\text{acid}]$ vs. $\log a_{H_2O}$	6.66	6.21
(C) Bunnet-Olsen plot (LFER)		
$\log k + H_0$ vs. $H_0 + \log [\text{acid}]$	1.06	1.08

Temperature and ionic strength variation: It has been observed that reactions follow the Arrhenius relationship. The values of entropy of activation which are less and negative suggest that these come under the category of slow reactions²² and it also suggests a bimolecular reaction in the rate determining step in the presence of water as a solvent and the involvement of proton transfer during the rate determining step for the acid catalyzed reactions²³. With the increase in the ionic strength by adding sodium sulfate there is an increase in the rate constant. Thus, positive salt effect indicates that there should be participation of neutral molecules in the rate determining step¹⁵.

Stoichiometry and Product Analysis

Experiments for the determination of stoichiometry of the reaction were carried out in the presence of excess of permanganate over [substrate]. After incubation for 48 h the excess permanganate was determined iodometrically. The observations indicate that five moles of butyric and isobutyric acid consume two moles of permanganate in the presence of the surfactant; the stoichiometry is thus represented as



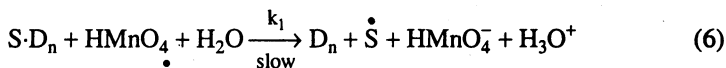
After ensuring the completion of reaction, the reaction mixture was separated by diethyl ether and concentrated. The product was identified as alcohol and carbon dioxide was identified by spot test²⁴. Similar products have been obtained in the oxidative decarboxylation and oxidation of butyric, iso-butyric and pyruvic acids by Kochi and Anderson²⁵.

Mechanism

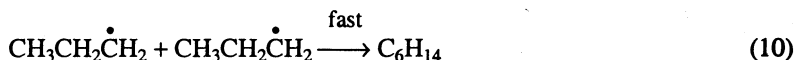
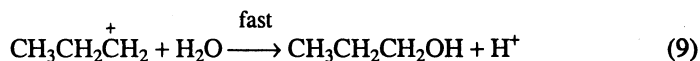
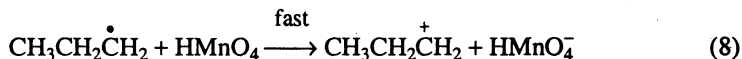
The physical basis for micellar catalysis involves several contributing factors. First, there is the effect of the micellar environment on the rate-controlling step in the reaction mechanism. The relative free energies of the reactant(s) and/or the transition state can be altered when the reaction takes place in the micellar phase instead of the bulk water. This concept is reminiscent of catalysis by an enzyme, and many initial studies of rates in micellar systems focussed on this possibility. However, further studies have shown that this effect is often rather small and cannot account for the very large rate changes in many micellar systems. A more important consideration is the localization of the reacting species in the relatively small volume of the micelles compared to the bulk solution. This leads to a large increase in the effective concentration and the observed rate (in terms of moles per unit time per litre of the entire solution) increases accordingly. The partitioning (*i.e.*, equilibrium distribution) of the reactants between the aqueous and micellar phases worked well for organic substrates.

On the basis of experimental results and various findings the following reaction mechanism has been suggested for the first stage. The presence of free radicals as intermediates has been confirmed by the induced reduction of mercuric chloride²⁶. There is an evidence of protonation of MnO_4^- to HMnO_4 as shown in

Eq. (3). The aggregation of detergent molecules to form micelles is depicted in Eq. (4). The substrate (S) and micelle bind together to form $S \cdot D_n$ (Eq. (5)). This is followed by the slow reaction in which the substrate-micellar entity, $HMnO_4$ and water react producing a free radical and $HMnO_4^-$ species as shown in Eq. (6). The carboxylate free radical thus formed will undergo disproportionation into alkyl free radical and carbon dioxide in the subsequent fast step as depicted in Eq. (7). Eqs. (8), (9), (10) and (11) are the usual possible reactions of free radicals. A representative mechanism has been given below by taking butyric acid:



where S is $CH_3CH_2CH_2COO\dot{C}$



The ascertainment of role of water molecule as proton abstracting agent in the rate determining step is on the basis of the slope values obtained from Bunnet and Bunnet-Olsen plots. In case of oxidation by permanganate, catalysis by Mn(II) ions is expected [table not given]. In fact Mn(II) gets oxidized by permanganate into Mn(III). This Mn(III) accelerates the reaction rate, being a strong oxidising agent. In order to assess the validity of this view a few experiments were carried out with initially added Mn(II). The reaction rate increases with the increase in the Mn(II) concentration. Further, to ensure the presence and activity of Mn(III) as an intermediate oxidizing species, the effect of addition of fluoride ions was tested. A sharp decrease in the reaction rate causes reduction in concentration of Mn(III). However, even substantial addition of fluoride ions does not suppress the reaction completely, indicating unequivocally that Mn(VII) is the main oxidant and not the other intermediate manganese species.

The above mechanism leads us to give the rate expression as follows:

$$-d[MnO_4^-]/dt = k_{obs}[nD][\text{substrate}][MnO_4^-]$$

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REFERENCES

1. J.W. Ladbury and C.F. Cullies, *Chem. Rev.*, **58**, 403 (1958).
2. T.J. Kemp, in: C.H. Bamford and C.F.H. Tipper (Eds.), *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, Vol. 7, Chapter 4, p. 325 (1972).
3. K.B. Wiberg and R. Stewart, *J. Am. Chem. Soc.*, **77**, 178 (1955).
4. R. Stewart, in: K.B. Wiberg (Ed.), *Oxidation in Organic Chemistry*, Part A, Academic Press, New York: (a) p. 20, (b) p. 48 (1965).
5. J. Banerji, *Chem. Soc. Perkin Trans.*, **2**, 435 (1973).
6. E.G. Prout and C.M. Lownds, *Inorg. Nucl. Chem. Lett.*, 617 (1973).
7. A.Z. Moghaddam and G.J. Rees, *Fuel*, **63**, 653 (1984).
8. D.G. Lee and J.G. Perez-Benito, *Can. J. Chem.*, **63**, 1275 (1985).
9. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longmans Green, London, p. 282 (1964).
10. R.N. Mehrotra, *J. Chem. Soc. (B)*, 1123 (1968).
11. T.C. Bruice, J. Katzhendler and L. Fedor, *J. Am. Chem. Soc.*, **90**, 1333 (1968).
12. F.M. Menger and C.E. Portnoy, *J. Am. Chem. Soc.*, **90**, 1333 (1968).
13. P. Mukherjee and K.J. Myselus. *J. Am. Chem. Soc.*, **77**, 2937 (1955).
14. P.S. Raghavan, V.S. Shrinivasan and N. Venkatasubramanian, *Indian J. Chem.*, **21B**, 42 (1982).
15. Dennis Piszkiwicz, *J. Am. Chem. Soc.*, **99**, 1550 (1977).
16. R.S. Verma, M.J. Reddy and V.R. Shastri, *J. Chem. Soc., Perkin Trans.*, 469 (1976).
17. G.V. Bakore *et al.*, *Z. Phys. Chem. (Leipzig)*, **19**, 227 (1964).
18. L. Zucker and L.P. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939).
19. J.F. Bunnett, *J. Am. Chem. Soc.*, (a) **83**, 4968 (1961); (b) **83**, 4596 (1961).
20. J.F. Bunnett and F.P. Olsen, *Can. J. Chem.*: (a) **44**, 1899 (1966); (b) **44**, 1917 (1996).
21. M.A. Paul and F.A. Long, *Chem. Rev.*, **57**, 1 (1957).
22. S. Glasstone, *Recent Advances in General Chemistry*, J and A. Church Hill Ltd., p. 317 (1936).
23. Jenck, *Catalysis in Chemistry and Enzymology*, McGraw-Hill, New York, p. 608 (1969).
24. F. Feigl, *Spot Tests in Organic Chemistry*, Elsevier, Amsterdam-Oxford (1975).
25. J.M. Anderson and J.K. Kochi, *J. Am. Chem. Soc.*, **92**, 1651 (1970).
26. J.M. Malcolm and R.M. Noyes, *J. Am. Chem. Soc.*, **74**, 2769 (1952).

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