International Journal of Modern Science and Technology
http://www.ijmst.co/
Vol. 1, Issue 3, June 2016. Page 106-110.
ISSN: 2456-0235

Research Article

Kinetics and mechanism of oxidation of 5-(4'-bromophenyl)-5-oxopentanoic acid by acid permanganate

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Abstract

The manganese (II)-catalyzed oxidation of substituted δ-oxoacid by (δ-oxo acids) by acid permanganate, in aqueous acetic medium containing sulphuric acid, has been studied. The reaction is first order each in [oxoacid], [MnO4^{-}] and [acid], less than unity order in both [substrate] and [catalyst], and also shows solvent isotope effect of 0.60 (k c' H_2O)/k c' (DO)). At low [H^+] the reaction is zero order with respect to [MnO4^{-}]. Oxidation rate is not much affected by electron withdrawing substituents, although it is susceptible to electron demand at the seat of the reaction. The linear free-energy relationship is characterized by smooth curves in Hammett plots of log k versus σ. However, the plots are linear with excellent correlation coefficient at all the studied temperatures when Brown's σ^+ values are used. The reaction constant is negative and increase with decrease in temperature. The mechanism involving decomposition of the complex, formed by participation of the neighboring group of δ-oxo acid and intramolecular catalysis of Mn (II) is proposed, wherein, both the C-C bond-breaking and C-O bond-making in the oxidation are involved. However, these two processes are influenced in different ways by the electron withdrawing and electron releasing substituents. A π-complex formation between Mn(II) and –ene of the enol from of oxo acid is proposed. A mechanism consistent with the observed kinetics results has been reported.

Keywords: Kinetics, Reaction mechanisms, δ-oxoacid, Oxidation, Acid permanganate, Isokinetic relationships, Manganese.

Introduction

In 5-(4'-bromophenyl)-5-oxopentsnoic acid (δ-oxo acids), two carbon atoms separate the carbonyl and carboxyl groups and thus they behave both as oxocompounds as well as acids without the direct influence of the nevertheless, an intramolecular catalysis in the iodination of δ-oxo acid and the neighboring group participation in the hydrolysis of its ethyl ester have been reported. On the other hand, in acidic medium δ-oxo acids undergo enolization and hence, δ-oxo acids are attractive substrates in teams of their mechanistic aspects. Acid permanganate is a stable solid and can be easily handled as compared with liquid bromine and hypobromous acid solutions. The product of permanganate oxidation is bromine ion, which can be safely recycled, making permanganate oxidations environmentally benign compared to metal ion oxidations. In recent times, studies on the use of transition metal ions, either alone or as binary mixtures, as catalysts in many redox reactions have been gaining interest. Their ability to form both σ and π bonds with other moieties or ligands is one of the chief factors for imparting catalytic properties to transition metals as well as their complexes. Most of the d-black elements show characteristic inter-ligand migration reactions and such a process forms one of the most important types of reactions in homogeneous catalysis. Mn (II) has been used as a homogeneous catalyst in many redox reactions catalysis. Mn(II) has been used as homogeneous catalyst in many redox reactions and its efficiency as a catalyst can be visualized from the oxidation studies of various substrates involving different oxidants such as Cr (VI), Tl(III), V(V), Ce (IV) and Br (V). The mechanism of catalysis is quite complicated due to the formation of different intermediate complexes, free radical and different oxidation state of manganese. In view of the above literature the chemistry of manganese is of topical interest. Preliminary experiment results indicated that the reaction of δ-oxoacid with

Received: 17.06.2016; Received after Revision: 25.06.2016; Accepted: 25.06.2016; Published: 26.06.2016.

permanganate in acid medium, without a catalyst was sluggish, but the reaction became facile in the presence of a small amount of $MnSO_4$ catalyst. Therefore, in order to explore the mechanism of oxo-acid-permanganate reactions and also to study the catalytic action of Mn(II), the manganese present reaction in the presence of mercury (II), a bromocomplexing metal ion, some interesting results were obtained. One of the principal characteristics of the B-Z reaction is a pre-oscillatory period called the induction period and is nearly always present in a B-Z. However, the present reaction does not shown any induction period over a wide concentration range of permanganate, Mn(II), oxo acid and H_2SO_4. The kinetic behavior of the reactants and catalyst are entirely different form the earlier reports of Mn (II) – catalyzed oxidation reactions including B-Z reaction. The mechanism neither resembles catalysis by bromide anions nor that of Mn(II)-catalyzed oxidation of organic substrates with the oxidants. This prompted us to investigated thoroughly the hither to unreported kinetics and mechanism of Mn(II)-catalyzed oxidation of oxo acids by permanganate in acid medium [1-5].

In the present study we aim to investigated thoroughly the kinetics and mechanism of oxidation of substituted 5-(4'-bromophenyl)-5-oxopentsnoic acid by permanganate in sulphuric acid medium containing Hg (II) and Mn (II), and to identify the active species of the substrate, catalyst and oxidant and the oxidant products. We have also studied the catalytic efficiency of Mn(II) and evaluated the related kinetic and thermodynamic parameters of the reaction along reaction along with their linear free-energy and isokinetic relationships.

Materials and methods

The δ-oxoacid, namely 5-(4'-Bromophenyl)-5-oxopentanoic acid, was prepared by the Friedel-crafts acylation of bromobeneze with glutaric anhydride. All the chemicals used were Analar grade. Potassium permanganate was used as such and acetic acid was distilled over chromic oxide before use. Perchloric acid was used as source of H^+ ions and sodium perchlorate was added to maintain the ionic strength. Sodium fluoride was added as a complexing agent to suppress the autocatalysis in permanganate oxidations [6]. The kinetics of the reaction was followed titrimetrically by standard iodometric procedure. The reaction was followed under pseudo first order conditions, maintaining always the concentration of the substrate in excess.

Product Analysis

Under kinetic conditions δ-oxoacid, H^+ and permanganate were mixed together. After 48 hours the excess permanganate was removed by neutralization by the addition of sodium metabisulphite. After the neutralization the reaction mixture was extracted with ether. The ether layer was separated and evaporated. The product was identified by spectral and analytical data as p-bromo benzoic acid [7, 8].The product was further confirmed as one mole of δ-oxoacid required 3 moles of permanganate.

$$5Br\text{–}C_6H_4\text{–}CO\text{–}(CH_2)_3\text{–}CO_2H + 15MnO_4^- + 20H^+ \longrightarrow 5Br\text{–}C_6H_4\text{–}CO_2H + 20CO_2 + 25H_2O + 15Mn^{2+}$$

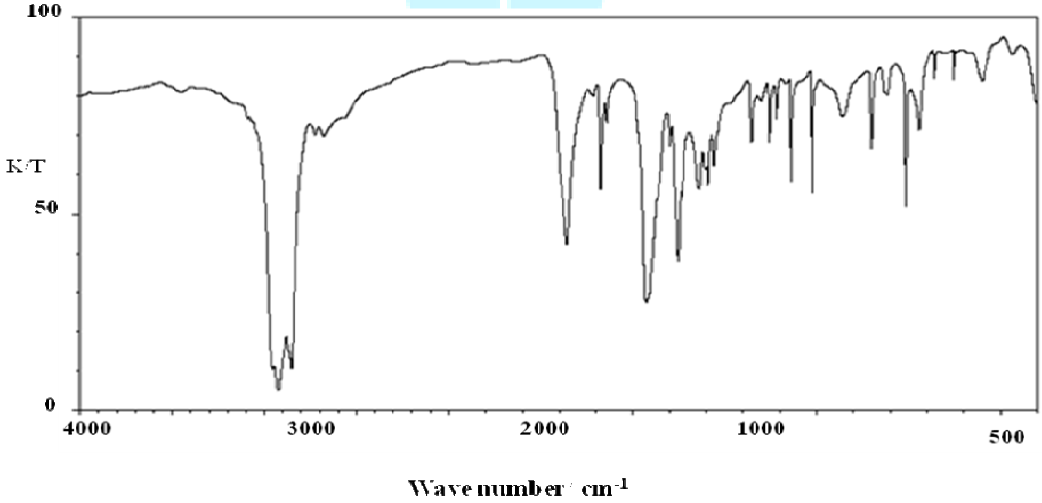


Fig. 1. FT-IR spectrum of 5-(4'-Bromophenyl)-5-oxopentanoic acid

Results and Discussion

Effect of reactants

The rate of oxidation was dependent on the first order with respect to the concentration of δ-oxoacid, H^+ and permanganate (Table 1).

Table 1. Oxidation of δ-oxoacid by acid permanganate at 35°C

10^2[oxoacid] / $mol\cdot dm^{-3}$	$10^3[KMnO_4]$ / $mol\cdot dm^{-3}$	$[H^+]$ / $mol\cdot dm^{-3}$	$10^5K'$ / s^{-1}
2.0	2.0	1.0	6.991
3.0	2.0	1.0	10.011
4.0	2.0	1.0	13.636
5.0	2.0	1.0	16.909
2.0	3.0	1.0	6.978
2.0	4.0	1.0	6.929
2.0	5.0	1.0	6.789
2.0	2.0	1.5	18.342
2.0	2.0	2.0	23.899
2.0[a]	2.0	1.0	7.772
2.0[b]	2.0	1.0	10.200
2.0[c]	2.0	1.0	12.612

$10^2[NaF] = 5.0\ mol\cdot dm^{-3}$, $10^2[NaClO_4] = 5.0\ mol\cdot dm^{-3}$, solvent – AcOH 30% V/V
[a]40% [b]50% and [c]60% V/V of Acetic acid

Mechanism and rate law

The reaction rate increases with increase in percentage of acetic acid. The reaction rate was not affected by the addition of acrylonitrile, hence the free radical path way was ruled out. The oxidation rate increases slightly with the increase in ionic strength of the medium. The protonation of permanganate ion leads to the formation of permanganic acid (PA) by addition of perchloric acid. The slowest and rate determining step involves the attack of permanganic acid on the enol form the δ-ketoacid. Thus the mechanism involves the two protons, one for the formation of $HMnO_4$ and another for the enolization of oxoacid (EA). The experimental results indicate that the reaction was first order with respect to $[MnO_4^-]$ at high mineral acid concentration and zero order dependence on $[MnO_4^-]$ at low $[H^+]$ (Table 2).

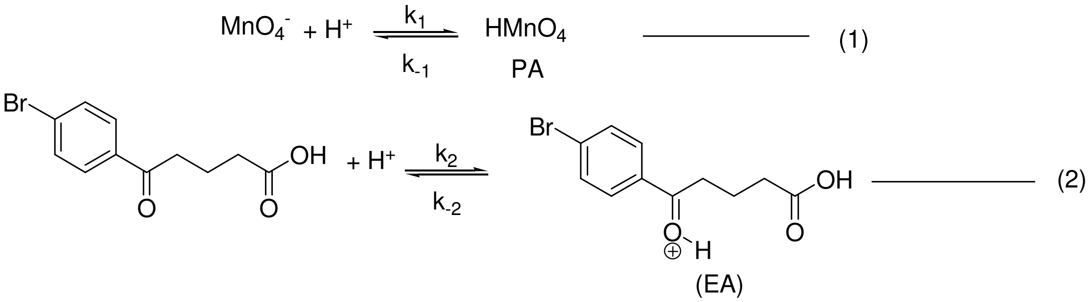
Table 2. Oxidation of δ-oxoacid by acid at low $[H^+]$

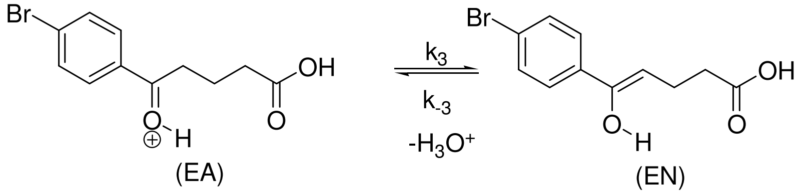
$10^3[KMnO_4]$ / $mol\cdot dm^{-3}$	10^3[zero order rate constant] / $mol\cdot dm^{-3}s^{-1}$
1.0	3.902
2.5	3.912
3.5	3.915
4.5	3.907

$10^2[NaF] = 5.0\ mol\cdot dm^{-3}$, $10^2[NaClO_4] = 5.0\ mol\cdot dm^{-3}$, 10^2[oxoacid] = $5.0\ mol\cdot dm^{-3}$, solvent – AcOH30% V/V, Temperature 35^0C, $10^2[H^+] = 5.0\ mol\cdot dm^{-3}$.

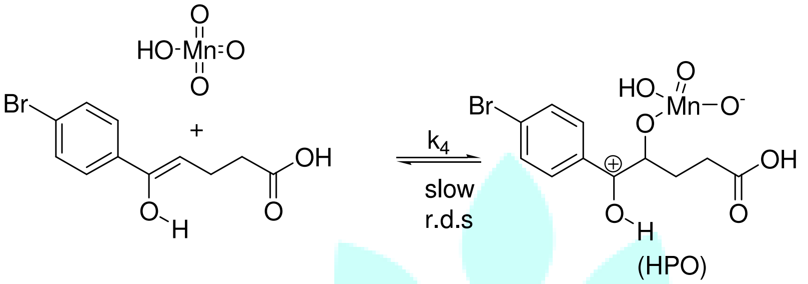
Thus under conditions of higher $[H^+]$, the enol removal is less rapid than its formation, but at lower $[H^+]$ the enol removal is faster than enol formation. This type of difference in order with respect to $[H^+]$ has been already reported [9,10]. Mn^{7+} is reduced to Mn^{5+} as hypomanganate ester (HPO) (step 4), which on hydrolysis followed by oxidation gives the acid. The formation of hypomanganate is believed to be a reaction intermediate in the acid medium permanganate oxidation of many organic and inorganic compounds [11-16].

Scheme





(3)



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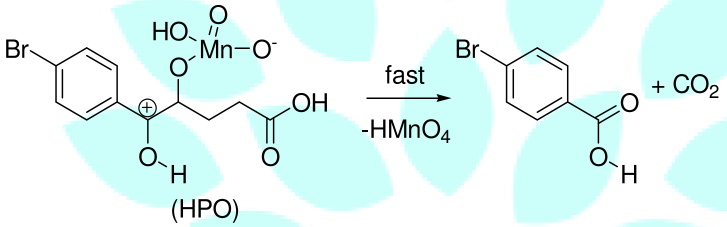

(5)

Rate law

$$\text{Rate} = -\frac{d[\mathrm{MnO_4^-}]}{dt} = \frac{k_2k_3k_4\,[\mathrm{H^+}][\mathrm{S}][\mathrm{HMnO_4}]}{(k_{-2}\,k_{-3})\,[\mathrm{H^+}] + k_4\,(k_{-2} + k_3)\,[\mathrm{HMnO_4}]}$$

at higher concentration of acid,

$$k_{-2}\,k_{-3}\,[\mathrm{H^+}] > k_4(k_{-2} + k_3)\,[\mathrm{HMnO_4}]$$

$$\text{Rate} = \frac{k_2k_3k_4\,[\mathrm{S}]\,[\mathrm{HMnO4}]}{k_{-2}\,k_{-3}} = \frac{k_2k_3k_4\,[\mathrm{S}]\,[\mathrm{HMnO_4^-}]}{k_{-2}\,k_{-3}\,[\mathrm{H^+}]}$$

where $K_a = \dfrac{[\mathrm{MnO_4^-}]\,[\mathrm{H^+}]}{[\mathrm{HMnO_4}]}$, S = δ-oxoacid

∴Observed rate at higher concentration of acid,

$$\text{Rate} = \frac{k_2k_3k_4}{k_{-2}\,k_{-3}\,k_a}$$

at lower acid concentration

$$k_4\,(k_{-2} + k_3)\,[\mathrm{HMnO_4}] > k_{-2}\,k_{-3}\,[\mathrm{H^+}]$$

$$\text{Rate} = \frac{k_2k_3k_4[\mathrm{S}][\mathrm{HMnO_4}][\mathrm{H^+}]}{k_4(k_{-2} + k_3)\,[\mathrm{HMnO_4}]} = \frac{k_2k_3}{(k_{-2} + k_3)}\,[\mathrm{S}][\mathrm{H^+}]$$

Conclusions

The reaction between δ-oxoacid by acid permanganate in aqueous acetic acid medium proceeds the protonation of permanganate ion and leads to the formation of permanganic acid (PA) by addition of perchloric acid. The slowest and rate determining step involves the attack of permanganic acid on the enol form the δ-ketoacid. Thus the mechanism involves the two protons, one for the formation of $HMnO_4$ and another for the enolization of oxoacid (EA). The reaction is first order with respect to [oxoacid], $[MnO^-_4]$ and $[H^+]$. At low $[H^+]$ the reaction is zero order with respect to $[MnO^-_4]$.

References

1. Ladbury JW, Cullis CP. Kinetics and mechanism of oxidation by permanganate. Chem Rev 58 (1958) 403-438.
2. Waters WA. Mechanisms of oxidation by compounds of chromium and manganese. Q Rev Chem Soc 12 (1958) 277-300.
3. Marigangaigh PN, Banerji KK. Kinetics and mechanisms of the oxidation of methyl aryl ketones. Austr J Chem 29 (1976) 1939-1945.
4. Sen PK, Mukhopadhyay G, Sen Gupta K K. Kinetics and mechanism of the oxidation of alkyl and aryl methyl ketones by permanganate ion in aqueous ethanoic acid. Transition Met Chem 23 (1998) 577-581.
5. Ballini R, Petrini M. Recent synthetic developments in the nitro to carbonyl conversion. Tetrahedron 60 (2004) 1017-1047.
6. Gardner KA, Kuehnert LL, Mayer JM. Hydrogen atom abstraction by permanganate: Oxidations of arylalkanes in organic solvents. Inorg Chem 36 (1997) 2069–2078.
7. Feigl F, Anger V. Spot tests in organic analysis. Elsevier, Amsterdam, (1975) 459.
8. Barter RM, Littler JS. Hydride ion transfer in oxidations of alcohols and ethers. J Chem Soc B (1967) 205-210.
9. Banerji KK. Kinetics and mechanism of the oxidation of substituted mandelic acids by acid permanganate. Tetrahedron 60 (1973) 1401-1403.
10. Morris DFC, Ritter TJ. Reduction of some iridium (iv) halogenocomplexes by benzene-1,4-diols in aqueous perchloric acid. Journal of the Less Common Metals 65(1979) 49-58.
11. Audsley AJ, Quick GR, Littler JS. Electron-transfer oxidation of organic compounds. Part 5. Oxidation of cyclohexanone by the tris-2,2′-bipyridylruthenium (III) cation. J Chem Soc Perkin Trans 2 (1980) 557-560.
12. Cotton FA, Wilkinson G. Advanced Inorganic Chemistry, Wiley Interscience, New York, (1988) 707.
13. Greenwood NN, Earnshaw A. Chemistry of the Elements, Pergamon Press, Oxford, (1984) 1222.
14. Muthukumaran B, Nagarajan S. Oxidation of 5-(4'-chlorophenyl)-5-oxopentanoic acid by acid permanganate. Oxidn Commun 19 (1996) 90.
15. Shree Devi S, Krishnamoorthy P, Muthukumaran B. Oxidation of 5-(4'-fluorophenyl)-5-oxopentanoic acid by acid permanganate. Oxidation communications, 37 (2014) 440-444.
16. Priya M, Elumalai M, Kiruthika S, Muthukumaran M. Influence of supporting materials for Pt-Ru binary catalyst in ethanol fuel cell. International Journal of Modern Science and Technology 1 (2016) 5-11.

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