Asian Journal of Chemistry Vol. 19, No. 1 (2007), 676–682

Reduction of Mn(III) in Pyrophosphate Medium by Diketones: Kinetics and Mechanism

B.L. HIRAN*, R.K. MALKANI, B.K. DANGARH† and B.K. AMB†
Chemical Kinetics Laboratory, Department of Chemistry
College of Science, M.L. Sukhadia University, Udaipur-313 001, India
Fax: (91)(294)423192 E-mail: hiranbl@rediffmail.com

Oxidation of acetyl acetone and benzoyl acetone by Mn(III) pyrophosphate has been investigated. Benzoyl acetone undergoes C-C cleavage while acetylacetone undergoes C-H cleavage. This has been confirmed by product study and supports the proposal that large negative entropy of activation is associated with C-H cleavage and large positive value is associated with C-C cleavage. The energy of activation observed for benzoyl acetone is 97.8 kJ mol^{-1} while for acetyl acetone 35.7 kJ mol^{-1}. Relevant mechanisms have been suggested which are consistent with the observed rate laws. In both these oxidations free radical intervention and Michaelis-Menten type of kinetics is observed. In similar conditions benzoyl acetone reacts faster than acetyl acetone. The reactions obey the rate law

$$\frac{1}{\text{Initial rate}} = \frac{[H_2P_2O_7^{2-}]/K}{k[\text{Mn(III)}][S]} + \frac{1}{k[\text{Mn(III)}]}$$

(K is complex formation constant between Mn (III) pyrophosphate and substrate.)

Key Words: **Kinetics, Oxidation, Diketones, Mn(III) pyrophosphate.**

INTRODUCTION

Except the report on the disproportionation of tris-pentanedione-Mn(III) in aqueous pentanedione under varying acidity[1], no report on the oxidation of diones by Mn(III) pyrophosphate has appeared till date. Mn(III) pyrophosphate is a selective oxidant. Oxidation of organic compounds by Mn(III) pyrophosphate has been reviewed[2]. This report deals with the oxidation of 1,3-diketones by Mn(III) pyrophosphate and is an extension of the work reported from this laboratory[3] on the oxidation of organic compounds by Mn(III) pyrophosphate.

EXPERIMENTAL

Mn(III) pyrophosphate was prepared by the method of Lingane and Karplus[3]. Purity of acetyl acetone (AA) (Merck) and benzoyl acetone (BA) (Fluka) was checked by their boiling points. All chemicals used were of analytical grade specification.

Substrate solution of acetyl acetone was prepared in distilled water while that of benzoyl acetone was prepared in 20% methanol and 80% water mixture (v/v) and their reactions with Mn(III) pyrophosphate were also carried out in 20% methanolic solution of distilled water (80% v/v). Solutions of substrates and oxidant were thermostated (±0.1° C) before mixing in glass-stoppered conical

---

†Government Post Graduate College, Neemuch, India.

flasks. Kinetics of the reduction of oxidant was followed iodometrically using precautions to avoid air-oxidation of iodide ions. For the initial 15–20% completion of the reaction linear plots of $(a - x)$ against t (eight points) were used to evaluate initial rates (Table-1). The order in Mn(III)-pyrophosphate is apparent from Table 1.

$$\text{Initial rate (graphical)} = 7.53 \times 10^{-7}\ \text{mol}^{-1}\ \text{dm}^{-3}\ \text{sec}^{-1}$$

Therefore, $$k_1 = \frac{7.53 \times 10^{-7}}{1.75 \times 10^{-3}} = 4.30 \times 10^{-4}\ \text{sec}^{-1}$$

Reactions carried out under nitrogen atmosphere revealed that the presence of air (oxygen) does not affect the rate. The reactions were, therefore, carried out without excluding air from solutions.

Induced polymerization of acrylonitrile (stabilizer free, *i.e.*, washed with dilute sodium hydroxide solution followed by distilled water) by reaction mixture in both the cases confirmed the free radical nature of the reactions.

Tables 2–6 collect the typical data obtained in these oxidations on the variation of the concentration of substrate [S], pyrophosphate [Py], Mn(II), solvent composition and hydrogen ions (pH) respectively. The representative data are for acetyl acetone.

Product Study

The product studies were made under kinetic conditions but with larger quantities of the reactants. After completion of the reactions between pH 2–4 and at 313 K the oxidized mixtures were neutralized with saturated solution of sodium bicarbonate and then extracted with chloroform. The chloroform extracts were dried over anhydrous sodium sulphate. These were, then, subjected to IR analysis using Perkin-Elmer IR spectrometer No. 783. Observation of group frequencies near 3500 cm^{-1} revealed the presence of —OH group. One of the oxidized products was hydroxy substrate in case of acetyl acetone.

The neutralized oxidized mixtures, after extraction with chloroform (as above) were acidified again and then extracted with chloroform. The chloroform extracts were then evaporated to dryness. In case of oxidation of benzoyl acetone a solid product was obtained. This was detected to be benzoic acid by IR spectral study and mixed melting point determination.

RESULTS AND DISCUSSION

The product study indicates that benzoyl acetone undergoes C—C bond cleavage to produce benzoic acid as one of the products of oxidation by Mn(III). The compound acetyl acetone yields only hydroxy substrate and thus undergoes C—H cleavage and no C—C bond cleavage products were detected in their oxidation products. A Michaelis-Menten type of kinetics is indicated [*cf.* Table-2]. Thus:

$$\begin{tikzcd} S + Mn(III\ (H_2P_2O_7)_3^{3-} \arrow[r, shift left, "K"] & \arrow[l, shift left] {[S\cdot Mn(III)(H_2P_2O_7)_2]^- + H_2P_2O_7^{2-}} \arrow[d, "\text{Slow}"', "k"] \\ & \text{Products} \end{tikzcd} \qquad (1)$$

and initial rates are given by the following expression:

$$\text{Initial rate} = \frac{k[S][Mn(III)[Py]_3}{[H_2P_2O_7^{2-}]/K + [S]} \tag{2}$$

$$\frac{1}{\text{Initial rate}} = \frac{[H_2P_2O_7^{2-}]/K}{k[Mn(III)(Py)_3]}\frac{1}{[S]} + \frac{1}{k[Mn(III)(Py)_3]} \tag{3}$$

TABLE-1
A TYPICAL RUN: OXIDATION OF ACETYL ACETONE BY Mn(III) PYROPHOSPHATE

$[AA] = 4.0 \times 10^{-3}$ mol dm^{-3}; $[\text{Pyrophosphate}]_T = 1.25 \times 10^{-2}$ mol dm^{-3}; pH = 3.0; $[Mn(III)(py)_3] = 1.75 \times 10^{-3}$ mol dm^{-3}; Temp. = 313 K

Time (min)	mL of hypo (N/1000) used	Time (min)	mL of hypo (N/1000) used
0	9.8	6	8.4
1	9.6	7	8.2
2	9.3	8	8.0
3	9.1	9	7.8
4	8.8	10	7.6
5	8.6	—	—

TABLE-2
EFFECT OF SUBSTRATE VARIATION ON INITIAL RATE

$[Mn(III)(py)_3] = 1.75 \times 10^{-3}$ mol dm^{-3}; $[\text{Pyrophosphate}]_T = 1.25 \times 10^{-2}$ mol dm^{-3}; pH = 3.0; Temp. = 313 K

1/[S]	Initial rate × 10^{-7} mol dm^{-3} sec^{-1}	
	Acetyl acetone	Benzoyl acetone
500	6.66	4.29
250	7.20	6.85
167	7.30	8.81
125	7.53	10.10
100	7.60	11.55
pH	**3.0**	**4.0**

TABLE-3
EFFECT OF PYROPHOSPHATE ON INITIAL RATE

$[Mn(III)(py)_3] = 1.75 \times 10^{-3}$ mol dm^{-3}; pH = 3.0; Temp. = 313 K

1/[S]	Initial rate × 10^{-7} mol dm^{-3} sec^{-1}	
	Acetyl acetone	Benzoyl acetone
7.25	7.14	6.85
22.25	6.24	3.40
37.25	5.56	2.25
52.25	5.01	1.72
67.25	4.60	1.38
pH	**3.0**	**4.0**

TABLE-4
EFFECT OF Mn(II) ION ON INITIAL RATE

$[\mathrm{Mn(III)(py)_3}] = 1.75 \times 10^{-3}$ mol dm^{-3}; [Substrate] = 4.0×10^{-3} mol dm^{-3}; $[\mathrm{Pyrophosphate}]_T = 1.25 \times 10^{-2}$ mol dm^{-3}; pH = 3.0; Temp. = 313 K

[Mn(II)] × 10^{-3} mol dm^{-3};	Initial rate × 10^{-7} mol dm^{-3} sec^{-1}	
	Acetyl acetone	Benzoyl acetone
0.0	7.14	20.65
1.0	5.26	15.60
2.0	4.11	12.40
3.0	5.50	10.47
4.0	3.00	8.93
pH	**3.0**	**4.0**

TABLE-5
EFFECT OF pH VARIATION ON INITIAL RATE

$[\mathrm{Mn(III)(py)_3}] = 1.75 \times 10^{-3}$ mol dm^{-3}; [Substrate] = 4.0×10^{-3} mol dm^{-3}; $[\mathrm{Pyrophosphate}]_T = 1.25 \times 10^{-2}$ mol dm^{-3}; Temp. = 313 K

pH	Initial rate × 10^{-7} mol dm^{-3} sec^{-1}	
	Acetyl acetone	Benzoyl acetone
1.8	—	—
2.0	49.92	543.35
2.2	31.67	346.78
2.4	20.85	245.55
2.6	14.13	154.93
2.8	9.59	105.37
3.0	7.14	60.26

A plot of 1/(Initial rate) *vs.* 1/[S] would be linear (eqn. 3) as has been observed in both the cases. Intercept/slope of these plots gave the values of $K/[\mathrm{H_2P_2O_7^{2-}}]$ to be 2845 for acetyl acetone and 268 for benzoyl acetone. Eqn. (3) also suggests that plots of 1/(Initial rate) against $[\mathrm{H_2P_2O_7^{2-}}]$ in [Pyrophosphate] variation, under otherwise identical conditions, would also be linear as observed (*cf.* Table-3) for a typical representation. This would also yield the values of K and serve as a check on these values obtained in substrate variation. The data are collected in Table-7. These values are comparable within experimental error. Santappa and coworkers[5] also suggested a complex formation between Mn(III) and unsaturated acids.

Addition of Mn(II) decreases the initial rate of oxidation. This is due to the reversible formation of Mn(II)-substrate complex, which reduces the concentration of free substrate. Levesley and Waters[6] have obtained similar results in the oxidation of tartaric acid and malic acid by Mn(III) pyrophosphate.

It has been observed that addition of acetic acid decreases the rate of oxidation in both the compounds studied. This is due to the formation of $[Mn(H_2P_2O_7]_2(CH_3COO)]^{2-}$ complex which is a poorer oxidant[3] compared to $[Mn(H_2P_2O_7)_3]^{3-}$. A representative data for acetylacetone has been given in Table-6.

$$[Mn(H_2P_2O_7)_3]^{3-} + CH_3COOH \overset{K'}{\rightleftharpoons} [Mn(H_2P_2O_7)_2(CH_3COO)]^{2-} + H_3P_2O_7^-$$

TABLE-6
EFFECT OF ACETIC ACID PERCENTAGE ON INITIAL RATE (REPRESENTATIVE DATA FOR ACETYLACETONE)

$[Mn(III)(py)_3] = 1.75 \times 10^{-3}$ mol dm^{-3}; [Substrate] = 4.0×10^{-3} mol dm^{-3}; $[Pyrophosphate]_T = 1.25 \times 10^{-2}$ mol dm^{-3}; pH = 3.0; Temp. = 313 K

Acetic acid (%, v/v)	Initial rate $\times 10^{-7}$ mol dm^{-3} sec^{-1}
0.0	7.14
10.0	6.29
20.0	5.43
30.0	4.50
40.0	3.97
50.0	2.70

Although the evaluation of extra thermodynamic parameters by way of temperature variation cannot be dissected and ascribed to any of the participating steps in the overall reaction, these overall values of $\Delta E_a^{\#}$ and $\Delta S^{\#}$ of these reactions (Table-8) do suggest that these values can be used to differentiate between C-H and C-C cleavage.

Bakore and Narain[7] have shown that a distinction can be made between systems involving C-H fission and those involving C-C fission in the oxidation of α-hydroxy acids by chromium(VI) on the basis of overall entropy of oxidation. Fairly large negative entropy of activation is associated with C-H fission in the rate-determining step. Bakore and Shanker[8] have shown that overall entropy of activation can also be used to distinguish between C-H fission and C-C fission in the oxidation of α-hydroxy acids by vanadium (V). Similar results have been obtained by Malkani *et al.*[3] The thermodynamic parameters obtained from the kinetic measurements in this investigation also support the view that in these oxidations a large negative entropy of activation is associated with C-H fission and that positive entropy of activation is associated with C-C fission.

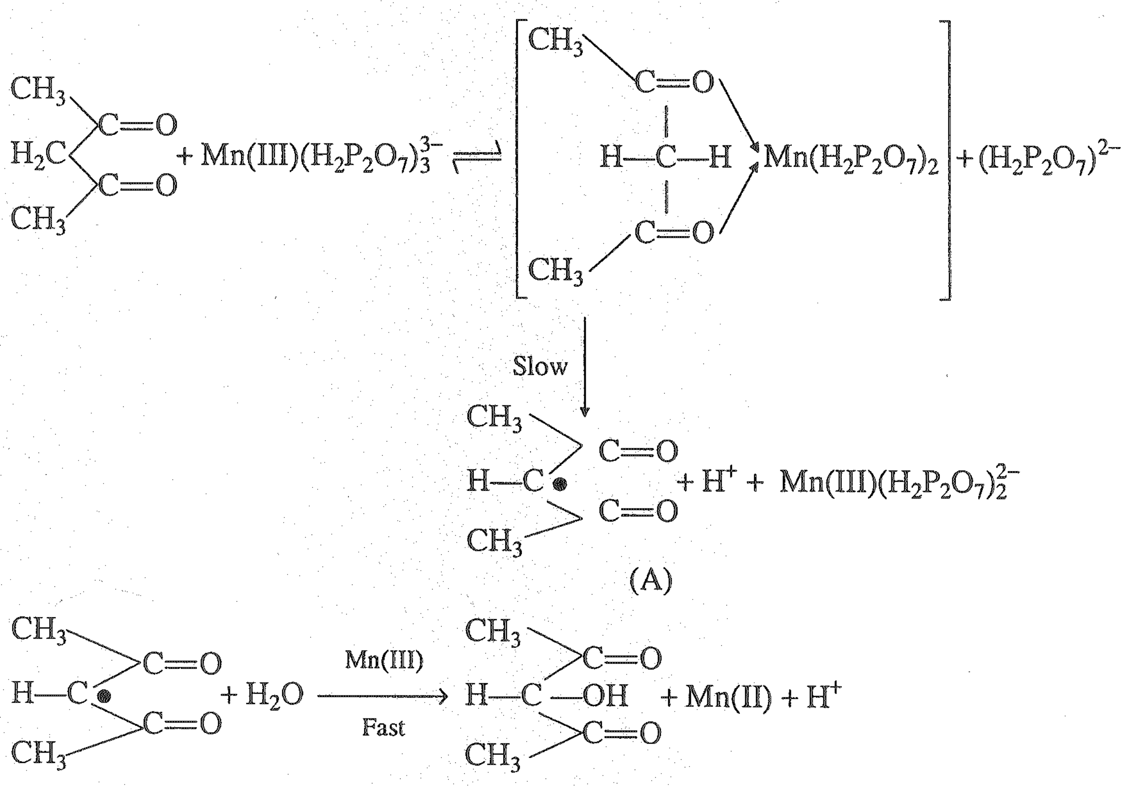
TABLE-7
OXIDATION OF 1,3-DIKETONES BY Mn(III) PYROPHOSPHATE

Substrate	K from substrate variation	K from pyrophosphate variation
Acetyl acetone	23.51	25.72
Benzoyl acetone	1.94	1.84

TABLE-8
THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF 1,3-DIKETONES BY Mn(III) PYROPHOSPHATE

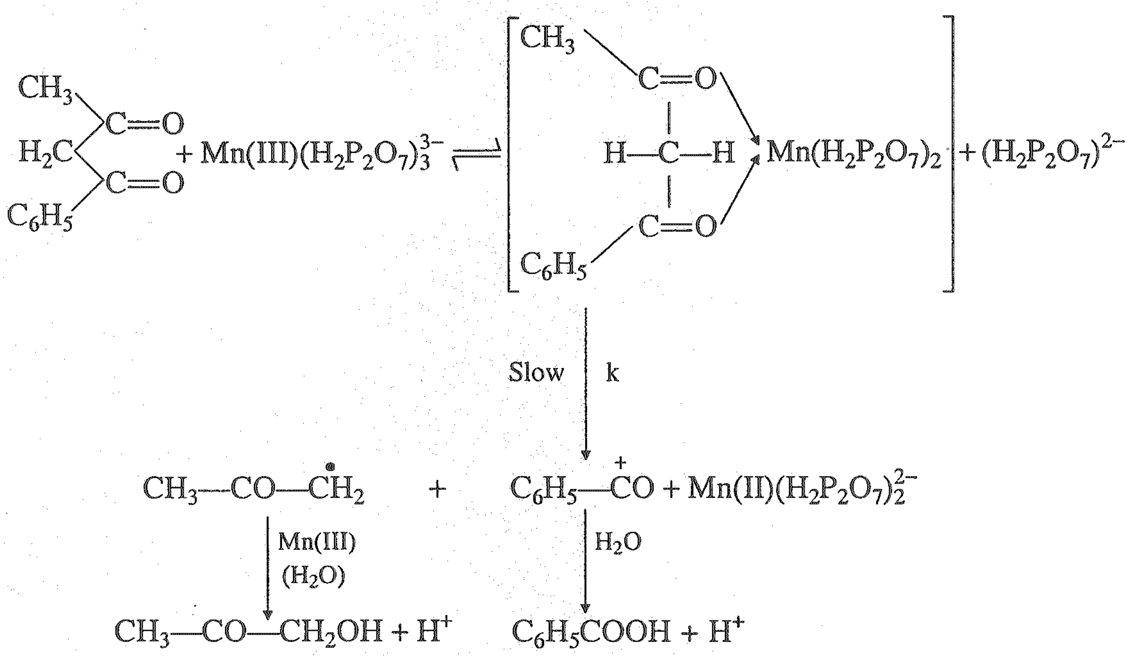
Substrate	$\Delta E_a^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J deg^{-1} mol^{-1})	$\Delta F^{\#}$ (kJ mol^{-1})
Acetyl acetone	35.7 ± 0.5	–142.1 ± 1.5	78.1
Benzoyl acetone	97.8 ± 1.5	–79.4 ± 0.8	74.0

Under kinetic conditions the product of oxidation in case of acetyl acetone is hydroxy acetyl acetone, while in case of benzoyl acetone, it is benzoic acid. The oxidized products were identified by their IR spectra. This indicates that two different reaction paths oxidize these two compounds. Oxidation of acetyl acetone involves C-H fission, while that of benzoyl acetone involves C-C fission. For C-H fission[9], the energy of activation is in the range of 21–33 kJ mol^{-1}. The energy of activation observed for acetyl acetone is 35.7 kJ mol^{-1}. On this basis, it would appear that oxidation of acetyl acetone proceeds to hydrogen abstraction, probably by the scheme given below:



The formation of radical (A) by the abstraction of H is further supported by the results of Snider *et al.*[10] The fact that energy of activation for these reactions is 35.7 kJ mol^{-1} and the entropy of activation is 142 J mol^{-1} K^{-1} suggests that C-H fission is involved in these oxidation reactions[7, 8].

In the case of benzoyl acetone the energy of activation is 97.8 k J mol^{-1}. The product of oxidation is benzoic acid. The oxidation probably follows the path:



The fact that energy of activation of the reaction is 97.8 kJ mol^{-1} and that the entropy of activation is positive suggests that C-C fission[7, 8] is involved in these oxidation reactions.

Stabilization of the intermediate and products of the oxidation (radical and carbocation) in the rate-limiting step is also in line with the mechanism. Balasubramanian *et al.*[11] also suggested free radical involvement in oxidation of anisic acid by Mn(III) acetate.

REFERENCES

1. G H. Cartledge, *J. Am. Chem. Soc.*, **73**, 4416 (1951).
2. W.A. Waters and J.S. Littler, in: K.B. Wiberg (Ed.), Oxidation in Organic Chemistry, Academic Press, New York (1965); E.V.S. Subramanyan, K.I. Bhat and B.E. Kumaraswamy, *Int. J. Chem. Kin.*, **33**, 449 (2001); K. Ishwar Bhat, B.S. Sherigera and I. Pinto, *Indian J. Chem.*, **33A**, 42 (1994).
3. R.K. Malkani, K.S. Suresh and G.V. Bakore, *J. Inorg. Nucl. Chem.*, **39**, 621 (1977); R.K. Malkani, K.S. Suresh and G.V. Bakore, *J. Indian Chem. Soc.*, **55**, 215 (LV) (1978).
4. J.J. Lingane and Karplus, *Ind. Eng. Chem. Anal.*, **18**, 191 (1946).
5. R. Devarajan, P. Elayperumal, T. Balakrishanan and M. Santappa, *Indian J. Chem.*, **18A**, 488 (1979).
6. P. Lavesley and W.A. Waters, *J. Chem. Soc.*, 217 (1953).
7. G.V. Bakore and S. Narain, *J. Chem. Soc.*, 3419 (1963).
8. G.V. Bakore and R. Shanker, *Can. J. Chem.*, **14**, 1717 (1966).
9. C. Walling, Free Radicals in Solutions, John Wiley & Sons, New York (1957).
10. B. Snider, J.J. Patricia and A.K. Steven, *J. Org. Chem.*, **53**, 1988 (1988).
11. V. Balasubramanian, S. Muthukumaran, A. Loganayangi and N. Karthikeyan, *Asian J. Chem.*, **13**, 1279 (2001).

(*Received*: 13 February 2006; *Accepted*: 30 June 2006) AJC-4995