BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2027—2029 (1970)

A Kinetic Investigation of Oxidation of Ethyl Methyl Ketone by Manganese(III) Sulphate

K. K. BANERJI, P. NATH and G. V. BAKORE[*1]

Department of Chemistry, University of Jodhpur, Jodhpur, India

(Received September 10, 1969)

The oxidation of ethyl methyl ketone with manganese(III) sulphate has been studied. The main product of oxidation is acetaldehyde. The reaction is first order with respect to each manganese(III) and the ketone. The rate of oxidation is independent of acidity and is not affected by changes in solvent composition. Addition of manganese(II) also does not affect the rate. The energy of activation, the entropy of activation and free energy of activation at 35°C have values 20.5 kcal/mol, −3.50 e.u. and 21.6 kcal/mol respectively. The rate of enolisation, measured by bromination method, is less than that of oxidation under similar conditions. A mechanism involving an attack directly on the ketone by manganese(III) sulphate-complex has been suggested.

Ketones were shown to be oxidised by manganic pyrophosphate *via* their enolic form.[1] Littler,[2] however, observed that manganese(III) sulphate oxidizes cyclohexanone at a rate faster than its enolisation and suggested that oxidation of ketones does not necessarily proceed through enolisation. Oxidation of aliphatic ketones by manganese(III) has not received adequate attention and, therefore, this investigation was taken up.

Experimental

Materials. B.D.H. ethyl methyl ketone was used after fractionation. Acetic acid (B.D.H., 99.5%) was distilled over chromic acid before use. All other chemicals used were chemically pure.

Manganese(III). Sulphate was prepared by the method described by Vogel.[3] Manganese(III) solutions were standardized iodometrically.

Kinetic Measurements. Unless otherwise stated the solvent used was 20% acetic acid - 80% water (*v*/*v*). Sufficient excess of manganese(II) was added to prevent disproportionation and subsequent hydrolysis of manganese(III).

Throughout the investigation the concentration of the ketone was kept in sufficiently large excess to ensure that the rate of reduction of manganese(III) is proportional to the oxidation of the ketone itself and not to the rate of destruction of any reactive intermediate.

Reaction mixtures were prepared by mixing all reagents except the ketone, in requisite quantities and were brought to the thermostatic temperature (±0.03°C). Reaction was started by adding the ketone rapidly.

Reactions were followed by quenching aliquots, withdrawn at fixed intervals of time, in slight excess of ferrous ammonium sulphate and estimating the residual iron(II) by titrating it against standardized cerium(IV) solution using ferroin as an indicator. From this the amounts of manganese(III) left in the reaction mixture at different time intervals were calculated.

Rates of Enolisation. Enolisation rates were measured by bromination method.

The rates of bromination was followed by adding bromine to a thermostated solution of the ketone in acetic acid containing sulphuric acid. Aliquots were withdrawn at fixed intervals of time, acidity adjusted by sodium bicarbonate and bromine left unreacted was determined iodometrically.

Results

Product Analysis. Completely reduced reaction mixtures gave a blue colour with solution of morpholine and sodium nitroprusside[4] indicating that acetaldehyde is the main product of oxidation.

Rate Laws. When ketone is in excess the rate of disappearance of manganese(III) follows first order rate laws. The rate constant is independent of the initial concentration of the oxidant (Table 1). Thus the order with respect to manganese(III) is one. The order with respect to the ketone is also one (Table 2).

Under the conditions of constant ionic strength the rate of oxidation is practically independent of hydrogen ion concentration (Table 3).

Effect of Manganese(II). Addition of manganous sulphate does not affect the rate of oxidation

---

[*1] Present address: Department of Chemistry, University of Udaipur, Udaipur, India.

1) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, **1955**, 497.

2) J. S. Littler, *ibid.*, **1962**, 832.

3) A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis," Longmans Green & Co. Ltd., London (1964), p. 327.

4) F. Fiegl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., Amsterdam (1956), p. 33.

Table 1. Variation of rate with concentration of Mn(III)

[Ketone]: 4.42×10^{-2}M, [Mn(II)]: 0.20M, [H_2SO_4]: 2.0M Temperature 35°C

$[\mathrm{Mn(III)}]\times10^3$ mol l^{-1}	2.10	3.15	4.20	6.30	8.40	10.5
$k_1\times10^3$ min^{-1}	10.6	10.8	11.0	11.0	10.8	11.0

Table 2. Variation of rate with concentration of the ketone

[Mn(III)]: 4.20×10^{-3}M, [Mn(II)]: 0.21M, [H_2SO_4]: 2.0M Temperature 35°C

$[\mathrm{Ketone}]\times10^2$ mol l^{-1}	2.21	4.42	8.84	11.1	13.3	17.7	22.1
$k_1\times10^3$ min^{-1}	5.53	11.0	22.0	27.7	32.8	44.3	54.9
$10\cdot k_1/[\mathrm{Ketone}]$	2.50	2.49	2.49	2.49	2.47	2.50	2.48

Table 3. Variation of rate with concentration of hydrogen ions

[Ketone]: 4.42×10^{-2}M, [Mn(III)]: 4.22×10^{-3}M, [Mn(II)]: 0.11M
[H_2SO_4+$NaHSO_4$]: 5.0M Temperature 35°C

[H_2SO_4] mol l^{-1}	2.0	2.5	3.0	3.5	4.0	4.5	5.0
$k_1\times10^3$ min^{-1}	11.0	11.0	10.0	11.0	11.5	11.0	10.2

Table 4. Variation of rate with solvent composition

[Ketone]: 4.42×10^{-2}M, [Mn(III)]: 4.15×10^{-3}M, [Mn(II)]: 0.11M, [H_2SO_4]: 2.0M
Temperature 35°C

Percentage of acetic acid	20.0	30.0	40.0	50.0	60.0
$k_1\times10^3$ min^{-1}	11.0	11.5	11.0	10.8	10.8

Table 5. Effect of bisulphate ion

[Ketone]: 4.42×10^{-2}M, [Mn(III)]: 4.20×10^{-2}M, [Mn(II)]: 0.11M, [H_2SO_4]: 2.0M
Temperature 35°C

[HSO_4^-] mol l^{-1}	2.0	2.5	3.0	4.0	4.5	5.0
$k_1\times10^3$ min^{-1}	11.0	11.0	10.8	10.6	10.4	10.4

Table 6. Effect of temperature

[Mn(III)]: 4.20×10^{-3}M, [Ketone]: 4.42×10^{-3}M, [Mn(II)]: 0.20M, [H_2SO_4]: 2.0M

Temperature °C	30	35	40	45
$k_1\times10^3$ min^{-1}	6.30	11.0	19.1	31.6
$k\times10^3$ l mol^{-1} sec^{-1}	2.38	4.15	7.20	11.9

of ethyl methyl ketone by manganese(III). Similar results were observed in the oxidation of cyclohexanone with manganese(III) sulphate.[5]

Similarly, change in the solvent composition caused by varying the proportion of glacial acetic acid in the solvent mixture, has no appreciable effect on the oxidation rate (Table 4).

Increase in the concentration of bisulphate ions also does not have any effect on the oxidation rate (Table 5).

Effect of Temperature. The reaction was studied at different temperatures between 30 to 45°C (Table 6). The specific rate constant, k, is defined as

$$k=\frac{k_1\ (\mathrm{min}^{-1})}{[\mathrm{ketone}]\times60}$$

The plot of $\log k$ against the inverse of temperature is a straight line. The Arrhenius equation is,

---

[5] T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, **1964**, 339.

TABLE 7. THERMODYNAMIC PARAMETERS

Temp. °C	$\Delta H^{\neq}$ kcal mol^{-1}	p$Z\times10^{-12}$ l mol^{-1} sec^{-1}	$\Delta S^{\neq}$ e.u.	$\Delta F^{\neq}$ at 35°C kcal mol^{-1}
30	20.5	1.72	−3.50	21.6
35		1.69		
40		1.72		
45		1.72		
	Average	1.71		

TABLE 8. RATES OF BROMINATION

Temperature 35°C

Percentage acetic acid	20.0	30.0	50.0	80.0
$k_2\times10^4$ l mol^{-1} sec^{-1}	3.92	4.17	4.56	12.3

therefore, valid for this reaction. The thermodynamic parameters were evaluated in the usual way (Table 7).

Rates of Bromination. The bromination of ethyl methyl ketone is of first order with respect to the ketone, first order with respect to hydrogen ion but zeroth order with respect to bromine. The rate of bromination divided by concentrations of ketone and hydrogen ions gives (k_2 l mol^{-1} sec^{-1}). Table 8 records the values of k_2 at different proportions of acetic acid-water.

The rate of bromination was studied at temperatures between 30 and 40°C and thermodynamic parameters were evaluated (Table 9).

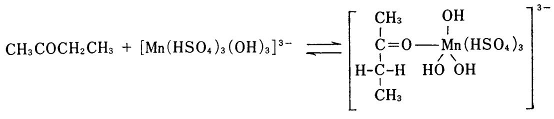
Discussion

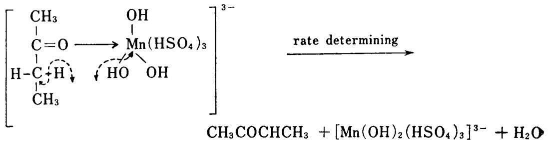
Manganese(II) is known to affect the rate of oxidation of several compounds,[5,6] where the oxidizing species is Mn(IV) and this has been attributed to its effect on the following equilibrium:

$$\mathrm{Mn(IV)} + \mathrm{Mn(II)} \rightleftharpoons 2\mathrm{Mn(III)}$$

Absence of any effect of manganese(II) on the rate of the oxidation suggests that in this case, Mn(III) is the only oxidizing species.

In sulphuric acid medium manganese(III) exists as a sulphato-complex. In stronger solutions of sulphuric acid, which are used to prepare Mn(III), sulphate ion exists as HSO_4^-. The coordination number of manganese(III) is probably six and hence the probable composition of sulphatocomplex could be $[Mn(HSO_4)_3(OH)_3]^{3-}$. Therefore, the oxidizing species is $[Mn(HSO_4)_3(OH)_3]^{3-}$.





$$CH_3COCHCH_3 \xrightarrow[\text{fast}]{\text{oxidation}} CH_3COOH + CH_3CHO$$

Enolisation of ethyl methyl ketone is an acid catalysed reaction, whereas the oxidation is independent of acidity. Had the enol form been involved in the oxidation, the rate expression would have included a term containing hydrogen ion concentration. Furthermore, the increase in the proportion of acetic acid in the solvent mixture decreases the dielectric constant of the medium and favours reactions involving protonation. Acid catalysed enolisation of ketone is such a reaction. No effect of the change in the solvent composition on the rate of the oxidation again suggests that enolisation is not the rate determining factor in this reaction.

The rate of enolisation of ethyl methyl ketone in 20% acetic acid solution at 35°C is 3.92×10^{-4} l mol^{-1} sec^{-1}, while the specific rate constant, k, for the oxidation under similar condition is 41.5×10^{-4} l mol^{-1} sec^{-1}. If enolisation was to precede oxidation, the rate of oxidation in the limit could be equal to the rate of enolisation, but could never exceed the rate of enolisation. This, therefore, clearly proves that oxidation of ethyl methyl ketone by manganese(III) sulphate proceeds by a direct attack on the keto- form.

The first step in the oxidation is the rapid, reversible formation of complex between the ketone and the manganese(III) sulphate complex, followed by the rate-determining step to give a radical which is then oxidized by several fast steps to acetaldehyde and acetic acid.

TABLE 9. EFFECT OF TEMPERATURE ON THE RATE OF BROMINATION

Solvent: 50% acetic acid-50% water (v/v)

Temp. °C	30	35	40	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ e.u.	$\Delta F^{\neq}$ at 30°C kcal mol^{-1}
$k_2\times10^4$ l mol^{-1} sec^{-1}	2.58	4.57	7.84	20.9	−6.4	22.9

---

[6] D. R. Rosseinsky, *ibid.*, **1963**, 1181.