Kinetics of the Oxidation of methyl *n*-propyl ketone by manganese(III) sulphate

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(Z. Naturforsch. 26 b, 30–31 [1971]; received 8 September 1970)

The oxidation of methyl *n*-propyl ketone by Mn(III) sulphate in aq. acetic acid is first order with respect to the ketone and Mn(III). The rate is independent of acidity and solvent composition. The activation parameters for oxidation and enolisation were evaluated. Oxidation is faster than enolisation under similar conditions. A mechanism involving an attack on the keto-form by Mn(III) is proposed.

Manganese(III) pyrophosphate oxidises cyclohexanone at a rate equal to the rate of enolisation and this supports the belief that ketones are oxidised via their enol form¹. LITTLER², however, observed that manganese(III) sulphate oxidises cyclohexanone at a rate faster than its enolisation and concluded that the keto-form is directly attacked. Oxidation of aliphatic ketones has not received much attention and hence this investigation was taken up.

Results

Product Analysis: The completely reduced reaction mixture gives a red-brown colour with ninhydrin in the presence of strong sulphuric acid. This indicates that propionaldehyde is the main oxidation product³.

Rate-laws: When the concentration of ketone is in excess, the rate at which Mn(III) disappears follows first order rate laws. Further the first order rate constant is independent of initial concentration of Mn(III) (Tab. 1). The oxidation rate varies linearly with the concentration of the ketone (Tab. 2). Variation in the concentration of sulphuric acid, at constant ionic strength, does not appreciably affect the rate oxidation (Tab. 3).

$10^3 [\text{Mn(III)}]$ (mol·l ⁻¹)	2.19	3.28	4.38	6.56	8.75	10.9
$10^4 k_1$ (sec ⁻¹)	1.33	1.44	1.44	1.54	1.33	1.44

Tab. 1. Oxidant dependence of reaction rate.
[Ketone]: 4.61×10^{-2} M [H₂SO₄] 4.0 M [Mn(II)] 0.22 M.

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¹ A. Y. DRUMMOND and W. A. WATERS, J. chem. Soc. [London] 1955, 397.

$10^2 [\text{Ketone}]$ (mol·l ⁻¹)	2.31	4.62	9.24	11.5	13.9	18.5
$10^5 k_1$ (sec ⁻¹)	7.20	14.4	28.9	36.0	43.3	57.8
$10^3 k_1$ / [Ketone]	3.12	3.12	3.13	3.13	3.11	3.12

Tab. 2. Substrate dependence of reaction rate.
[Mn(III)] 4.28×10^{-3} M [H₂SO₄] 2.0 M [Mn(II)] 0.21 M.

[H ₂ SO ₄] (mol·l ⁻¹)	2.0	2.5	3.0	3.5	4.0	5.0
$10^4 k_1$ (sec ⁻¹)	1.44	1.60	1.44	1.20	1.44	1.20

Tab. 3. Acidity dependence of reaction rate.
[Ketone] 4.62×10^{-2} M [Mn(III)] 4.28×10^{-3} M [Mn(II)] 0.11 M [H₂SO₄+NaHSO₄] 5.0 M.

Addition of Mn(II) sulphate (0.05–0.5 M) has no effect on the oxidation rate. Similarly changes in proportions of acetic acid (20–60%) in the solvent mixture have no effect.

Effect of temperature: Data in Tab. 4 summarize the effect of temperature on the rate of oxidation. The specific rate constant, k is obtained from the relation, $k = k_1/[\text{ketone}]$. A plot of log k against the inverse of temperature gave a straight line. The Arrhenius equation is, therefore, valid for this reaction.

Temp. (°C)	30	35	40	45	ΔH^* (kcal·mol ⁻¹)	ΔS^*
$10^3 k$ (l·mol ⁻¹ ·sec ⁻¹)	1.80	3.12	5.38	8.98	21.0	-4.1 e.u.

Tab. 4. Effect of temperature.
[Mn(III)] 4.28×10^{-3} M [Mn(II)] 0.21 M [H₂SO₄] 2.0 M.

² J. S. LITTLER, J. chem. Soc. [London] 1962, 832.

³ F. FEIGL, "Spot Tests in Organic Analysis", Elsevier, Amsterdam 1966, p. 591.

Rate of Enolisation: The rates of enolisation were obtained by the bromination method. The bromination of methyl *n*-propyl ketone is first order with respect to the ketone and hydrogen ions but zero order to bromine. The rate of bromination increases with the proportion of acetic acid in the solvent mixture (Tab. 5). The rates of bromination were obtained at different temperatures (Tab. 6).

Acetic acid [%]	20	30	50	80
$10^4 k_2$ ($l \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$)	3.31	3.96	5.20	11.1

Tab. 5. Rate of bromination, Temp. 35 °C.

Solvent	50% acetic acid			ΔH^*	ΔS^*
Temp. [°C]	30	35	40	(kcal·mol ⁻¹) (e. u.)	
$10^4 k_2$ ($l \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$)	2.28	4.00	6.76	20.5	-8.1

Tab. 6. Effect of temperature on bromination rate.

Discussion

Absence of any effect of Mn(II) on the oxidation rate indicates that Mn(III) is the only active species. Mn(II) retards the oxidation effected by Mn(IV) due to the following equilibrium ^{4, 5}.

The kinetics of the oxidation and enolisation of methyl *n*-propyl ketone are quite different. Whereas enolisation is an acid catalysed reaction and is favoured by increase in the proportion of acetic acid in solvent, the oxidation is independent of these variations. The rate of enolisation of methyl

n-propyl ketone in 20% acetic acid solution, at 35 °C is $3.31 \times 10^{-4} l \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$, while the specific rate constant, k , for oxidation under similar condition is $31.2 \times 10^{-4} l \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$. If enolisation were to precede oxidation, the oxidation rate in the limit could be equal to the rate of enolisation, but could never have exceeded it. This, therefore, clearly shows that oxidation of methyl *n*-propyl ketone by Mn(III) sulphate proceeds by a direct attack on the keto-form.

Experimental

Materials. Methyl *n*-propyl ketone (B.D.H.) was used after fractionation. Acetic acid (99.5%, B.D.H.) was distilled over chromic acid. All other chemicals used were chemically pure.

Manganese(III) sulphate was prepared as described by VOGEL ⁶.

Kinetic measurement. Reactions were carried out at 35 °C (± 0.05 °C) and in 20% acetic acid solvent unless mentioned otherwise. Concentration of the ketone was always in large excess to that of Mn(III). A sufficiently large excess of Mn(II) is added to prevent disproportionation of Mn(III) to Mn(IV). The reaction was followed by quenching aliquotes, withdrawn at known intervals of time in slight excess of Fe(II) and titrating the residual Fe(II) against Ce(IV).

⁴ T. J. KEMP and W. A. WATERS, J. chem. Soc. [London] 1964, 339.

⁵ D. R. ROSSEINSKY, J. chem. Soc. [London] 1963, 1181.

⁶ A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longmans Green & Co., London 1964, p. 327.