Kinetics & Mechanism of Acid Permanganate Oxidation of Cyclohexanone

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The oxidation of cyclohexanone by acid permanganate is of first order each with respect to cyclohexanone, the oxidant and the hydrogen ion. The increase in [acetic acid] increases the rate sharply. The reaction exhibits a primary isotope effect $k_{D}/k_{H} = 3.35$ and a solvent isotope effect $k_{D_{2}O}/k_{H_{2}O} = 5.5$ at 25°. The oxidation is much slower than the acid-catalysed enolization. The magnitude of the solvent isotope effect suggests that oxidation proceeds through the enol intermediate. Tentative mechanisms have been proposed.

LITTLER reported that acid permanganate oxidation of cyclohexanone is of zero order with respect to cyclohexanone, the oxidant and the hydrogen ion. Some preliminary studies (unpublished results), however, showed that the oxidation of aliphatic ketones exhibits a first order dependence on permanganate in acid conditions. Hence, it was considered worthwhile to reinvestigate the oxidation of cyclohexanone more thoroughly. To our surprise, the results obtained are quite different from those reported by Littler.

Materials and Methods

Cyclohexanone (Fluka) was purified through the preparation of its bisulphite adduct. Perchloric acid (Baker, 60%) was used as a source of hydrogen ions. Acetic acid (BDH, analar) was distilled over chromic oxide before use. 2,2,6,6-Tetradeutero-cyclohexanone was prepared by the method of Best et al. All other reagents used were of AR grade.

Kinetic measurements — The reactions were carried out at a constant temperature (±0.1°). The kinetic data are reported in Tables 1 and 2. Aliquots of the reaction mixture were quenched with excess of FeSO$_4$ solution and back titrated with standardized KMnO$_4$. The data on isotope effect were obtained spectrophotometrically at 532 nm. The rate constants reported are the mean values of duplicate runs and are reproducible within ±4%. The rate of enolization was measured by the bromination method.

Results

The acid permanganate oxidation of cyclohexanone is autocatalytic. Such a phenomenon is well known in peroxynitrate oxidation and is attributed to the reactions of Mn(III)/Mn(IV). To suppress these reactions, a large excess of NaF was added to each reaction mixture.

Identification of the oxidation product — The oxidation of cyclohexanone (0.1M) by acid KMnO$_4$ (0.001M) in the presence of HClO$_4$ (1.0M) and NaF (0.05M) resulted in the formation of mainly cyclohexane-1,2-dione which was isolated as its Ni(II) dioxime complex (85% yield) and identified.

<table>
<thead>
<tr>
<th>$10^6$[KMnO$_4$]</th>
<th>$10^6$[Ketone]</th>
<th>$10^8$[$H^+$]</th>
<th>$k$</th>
<th>$10^6$ min$^{-1}$</th>
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</table>
Solvent isotope effect — The oxidation of cyclohexanone was carried out in 95% D₂O. The rate constants in D₂O and H₂O at 25° were 27·92 x 10⁻³ litre⁻² mole⁻¹ sec⁻¹ and 5·12 x 10⁻³ litre⁻² mole⁻¹ sec⁻¹, respectively. Thus the solvent isotope effect $k_{D,O}/k_{H,O} = 5·5$ at 25°.

Kinetic isotope effect — The oxidation rates of cyclohexanone and 2,2,6,6-tetradeteriocyclohexanone at 25° were $10^{10} = 5·12$ and $1·52$ litre⁻² mole⁻¹ sec⁻¹ respectively. Thus the kinetic isotope effect $k_{D,O}/k_{H,O}$ is 3·35 at 25°.

Effect of temperature — The effect of temperature on the reaction rate is given in Table 2. The specific rate constant ($k$) was obtained from the relation $k = k_1/[ketone][H^+]$ litre⁻² mole⁻¹ sec⁻¹.

Rates of bromination — The bromination of cyclohexanone and [cyclohexanone] and [H+] gives $k_2$ (litre mole⁻¹ sec⁻¹) for the forward reaction in Eq. (2). Activation parameters — The values of $\Delta H^+$ and $\Delta S^+$ for the oxidation and bromination of cyclohexanone were found to be 15·2 ± 0·5 and 12·2 ± 0·5 kcal mole⁻¹, and 19·3 ± 1·5 and 20·4 ± 1·5 kcal mole⁻¹ respectively.

Discussion

The observation of Littler¹ that the rate of oxidation of cyclohexanone is equal to its rate of enolization is not borne out by the present study. The results indicate that the rate of oxidation of cyclohexanone by permanganate is much slower than its rate of enolization, and hence the kinetic relations cannot show whether the ketone molecule or its enol form is attacked. However, it merely indicates that the transition state of the rate determining process involves the elements of a molecule of ketone and a molecule of permanganic acid. The active oxidizing species is likely to be permanganic acid (HMnO₄)₆⁷.

The primary isotope effect ($k_{H,D}/k_H = 3·35$) shows that the fission of an $\alpha$–C–H bond is rate controlling but this does not necessarily mean that the oxidation step involves the ketone form and not the enol form. The acid-catalysed enolization involves the reactions (1) and (2).

\[
\text{RCO.CH}_2\text{R}^+ + \text{H}_2\text{O}^+ \rightarrow \text{R}^+ \text{C(OH)}\text{CH}_2\text{R}^+ + \text{H}_2\text{O} \quad \quad (1) \\
\text{RC}^+\text{(OH)}\text{CH}_2\text{R}^+ + \text{H}_2\text{O} \rightarrow \text{R.C(OH)}\text{=CHR}^+ + \text{H}_2\text{O}^+ \quad \quad (2)
\]

The forward reaction in Eq. (2) is slow since it involves the fission of a C–H bond. Thus the formation of an enol should also exhibit the primary isotope effect.

A comparison of acid-base equilibria in water and D₂O indicates that for any proton-catalysed reaction the expected solvent isotope effect $k_{D,O}/k_{H,O}$ is about 2·0–2·5. This should favour the oxidation by HMnO₄ as the equilibrium (3) is shifted by D₂O so as to yield higher concentration of HMnO₄ than would be present in water.

\[
\text{MnO}_4^- + 2\text{H}_2\text{O}^+ \leftrightarrow \text{HMnO}_4^- + \text{H}_2\text{O} \quad \quad (3)
\]

However, the observed solvent isotope effect ($k_{D,O}/k_{H,O} = 5·5$) is almost double of that reported for any proton-catalysed reaction. This cannot be due to the participation of a second proton as any such protonation would have been revealed by kinetic measurements. The only other conclusion possible is that the pre-equilibrium involved in producing rate-determining reaction complex of the oxidation include two different acid-catalysed processes; viz. those represented by Eqs. (2) and (3). This is in agreement with the conclusion reached by Best et al.² in the chromic acid oxidation of cyclohexanone.

The rate laws obtained for the oxidation of cyclohexanone are similar to those for the oxidation of alcohols by acid permanganate. Since the per- manganic oxidation of alcohols involves formation of a carboxonium ion, the formation of such an intermediate is also likely in the case of enols (Mechanism 1).

Another possibility is that the attack on the enol is a concerted process (Mechanism 2) giving immediately an $\alpha$-ketomanganate ester (A) which is hydrolysed to give an $\alpha$-ketol and Mn(V) species.
References