

Kinetics & Mechanism of Acid Permanganate Oxidation of Cyclohexanone

MARIGANGAIAH, P. N. MATHUR & K. K. BANERJI
Department of Chemistry, University of Jodhpur, Jodhpur

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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 $k_H/k_D = 3.35$ and a solvent isotope effect $k_{D_2O}/k_{H_2O} = 5.5$ 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.

LITTLER¹ reported that acid permanganate oxidation of cyclohexanone is of zero order with respect to the oxidant. Some preliminary studies (unpublished results), however, showed that the oxidation of aliphatic ketones exhibits a first order dependence on permanganate in acid conditions.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. The results of such a study are reported in this paper. To our surprise, the results obtained are quite different from those reported by Littler¹.

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-Tetradeuterio-cyclohexanone was prepared by the method of Best *et al.*². All other reagents used were of AR grade.

Kinetic measurements — The reactions were carried out at a constant temperature ($\pm 0.1^\circ$). 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 $\pm 4\%$. The rate of enolization was measured by the bromination method³.

Results

The acid permanganate oxidation of cyclohexanone is autocatalytic. Such a phenomenon is well known in permanganate 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 mixture⁴.

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.

Rate laws — The reactions were studied under pseudo first order conditions by keeping a large excess of cyclohexanone over permanganate. Under these conditions, the oxidation of cyclohexanone by acid permanganate gave first order plots. We repeated carefully the experiments reported by Littler¹ but could not confirm his observations regarding the zero order dependence of the reaction rate on the oxidant. Further, the first order rate constant was independent of the initial [permanganate] thereby confirming that the oxidation is strictly of first order with respect to the oxidant. The oxidation was also first order with respect to cyclohexanone. Throughout the acidity range used, the reaction velocity was linearly dependent on the $[H^+]$ in solutions of constant ionic strength. Some representative rate data are given in Table 1.

Effect of varying solvent composition — The oxidation rate increased sharply with increasing [acetic acid]. This may be attributed to the lowering of dielectric constant of the medium⁵, which favours reactions involving protonation. Further, the enolization of the ketone is catalysed by acetic acid and this may also affect the rate of reaction. The values of k at 25° and $[NaF] = 0.05M$ were 8.28×10^{-2} , 9.89×10^{-2} , 17.9×10^{-2} and 22.1×10^{-2} litre² mole⁻² sec⁻¹ for 20, 30, 40, and 50% acetic acid respectively.

TABLE 1 — OXIDATION OF CYCLOHEXANONE BY ACID PERMANGANATE

$\{[NaF] = 0.05M; \text{solvent} = \text{acetic acid-water (20:80, v/v)}; \mu = 2.05M; (\text{temp.} = 25^\circ)\}$

$10^3 [KMnO_4]$ M	$10^3 [\text{Ketone}]$ M	$[H^+]$ M	$k_1 \times 10^3$ min ⁻¹
2.0	6.15	1.0	30.6
1.0	6.15	1.0	30.7
4.0	6.15	1.0	30.7
1.0	3.07	1.0	15.4
1.0	7.70	1.0	38.4
1.0	12.3	1.0	61.4
1.0	6.15	0.5	17.8
1.0	6.15	1.5	56.3
1.0	6.15	2.0	75.5

TABLE 2 — OXIDATION AND BROMINATION RATES OF CYCLOHEXANONE

{Solvent, acetic acid-water (20: 80, v/v)}

Temp. °K	Oxidation 10^3k (litre ² mole ⁻² sec ⁻¹)	Bromination 10^4k_2 (litre mole ⁻¹ sec ⁻¹)
293	5.20	7.33
298	8.26	10.9
303	12.4	15.8
308	18.7	22.8

Solvent isotope effect — The oxidation of cyclohexanone was carried out in 95% D₂O. The rate constants in D₂O and H₂O at 25° were 27.92×10^{-3} litre² mole⁻² sec⁻¹ and 5.12×10^{-3} litre² mole⁻² sec⁻¹, respectively. Thus the solvent isotope effect $k_{D_2O}/k_{H_2O} = 5.5$ at 25°.

Kinetic isotope effect — The oxidation rates of cyclohexanone and 2,2,6,6-tetradeuteriocyclohexanone at 25° were $10^3k = 5.12$ and 1.52 litre² mole⁻² sec⁻¹ respectively. Thus the kinetic isotope effect $k_H/k_D = 3.35$ 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 $k = k_1/[\text{ketone}][H^+]$ litre² mole⁻² sec⁻¹.

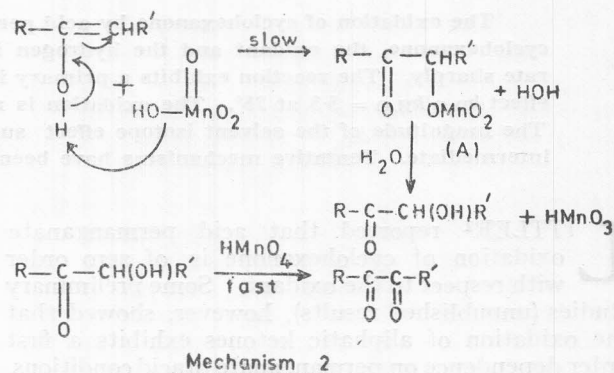
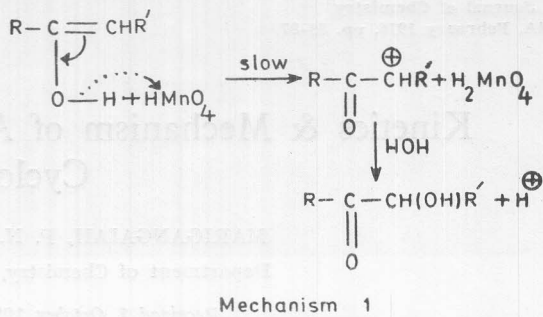
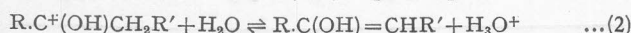
Rates of bromination — The bromination of cyclohexanone was found to be of first order each with respect to cyclohexanone and H⁺ ion, but independent of [bromine]. The rate of bromination divided by [cyclohexanone] and [H⁺] gives k_2 (litre mole⁻¹ sec⁻¹) (Table 2).

Activation parameters — The values of ΔH^\ddagger , ΔS^\ddagger and ΔF^\ddagger for the oxidation and bromination of cyclohexanone were found to be 15.2 ± 0.5 and 12.2 ± 0.5 kcal mole⁻¹, -13.3 ± 1.5 and -27.0 ± 1.5 e.u., and 19.3 ± 1.5 and 20.4 ± 1.5 kcal mole⁻¹ respectively.

Discussion

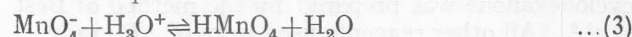
The observation of Littler¹ that the rate of oxidation of cyclohexanone is equal to its rate of enolization is not borne out by the present study. The results indicate that the rate of oxidation of cyclohexanone by permanganate is much slower than its rate of enolization, and hence the kinetic relations 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)^{6,7}.

The primary isotope effect ($k_H/k_D = 3.35$) shows that the fission of an α -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).



The forward reaction in Eq. (2) is slow since it involves the fission of a C-H bond⁸. Thus the formation of an enol should also exhibit the primary isotope effect.

A comparison of acid-base equilibria⁹ in water and D₂O indicates that for any proton-catalysed reaction the expected solvent isotope effect k_{D_2O}/k_{H_2O} 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.



However, the observed solvent isotope effect ($k_{D_2O}/k_{H_2O} = 5.5$) 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 permanganate¹⁰. Since the permanganate oxidation of alcohols involves formation of a carbonium ion^{4,10}, 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 α -ketomanganate ester (A) which is hydrolysed to give an α -ketol and Mn(V) species.

References

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The rate of reaction of cyclohexanone with permanganate in a weakly acidic medium was studied at various temperatures. The rate of reaction was found to be first order with respect to cyclohexanone and first order with respect to permanganate. The activation energy of the reaction was found to be 14.5 kcal/mole.

$$\ln k = \ln A - \frac{E_a}{RT}$$

where k = rate constant, A = pre-exponential factor, E_a = activation energy, R = gas constant, T = absolute temperature.

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Table I - Reaction Rate Constants (k) at different temperatures for the reaction of cyclohexanone with permanganate in a weakly acidic medium

Temperature (°C)	k (min ⁻¹)
25	0.012
30	0.018
35	0.025
40	0.035
45	0.050
50	0.070
55	0.100
60	0.140
65	0.190
70	0.260
75	0.350
80	0.480
85	0.650
90	0.880
95	1.200

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Materials and Methods

Cyclohexanone was prepared by a standard method. Permanganate was prepared by a standard method. The reaction was carried out in a weakly acidic medium at various temperatures. The rate of reaction was studied by measuring the change in optical density of the reaction mixture at different wavelengths.

Results and Discussion

The rate of reaction of cyclohexanone with permanganate in a weakly acidic medium was studied at various temperatures. The rate of reaction was found to be first order with respect to cyclohexanone and first order with respect to permanganate. The activation energy of the reaction was found to be 14.5 kcal/mole.