



Ru(III) AND Os(VIII) CATALYSED OXIDATION OF 4-METHYL CYCLOHEXANONE BY PERIODATE IN AQUEOUS ALKALINE MEDIUM

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ABSTRACT

Under identical conditions, the 4-methyl cyclohexanone was oxidized by periodate in the presence of Ru(III). The order of the reaction with respect to [Ru(III)], [ketone] and [periodate] are unity, fractional and zero, respectively. The effect of temperature was studied and kinetic parameters were evaluated. The probable mechanism has been proposed and rate law applied.

Key words: 4-Methyl cyclohexanone, Kinetics, Reaction mechanism.

INTRODUCTION

The activity of periodate as an oxidizing agent varies greatly as a function of pH and is capable of subtle control. In alkaline solution, it is less potent oxidant than in acidic medium. In alkaline medium, it is known to exist as different species involving multiple equilibria¹ and one needs to know the active form of the oxidant in the reaction. The reduction potential of $\text{IO}_4^-/\text{IO}_3^-$ couple is +1.6V and 0.70V in acid and alkaline media, respectively. Ruthenium (III) is known to be an efficient catalyst in several redox reactions, particularly in alkaline solutions^{2,3}.

Periodate is a clean and relatively selective reagent for the oxidative cleavage of organic compounds containing α -hydroxy, -oxo, amino or -carboxyl groups. There is extensive literature on the kinetics of the periodic acid oxidation of glycols⁴⁻⁷ but the kinetics of the periodate oxidation of amino alcohols^{8,9}, dicarbonyl compounds¹⁰, amino acids¹¹ and cyclic ketones¹² has received much less attention. Oxidation with periodate cause denaturation of proteins and inactivation of enzymes.

The mechanism of catalysis can be quite complicated due to the formation of different intermediate complexes, free radicals and different oxidation states of ruthenium.

EXPERIMENTAL

Materials and methods

4-Methyl cyclohexanone was of A.R. grade. [Ru(III)] solution was prepared by dissolving RuCl_3 in 0.20 mol dm^{-3} HCl and its concentration was determined.^{13,14} KOH and KCl were employed to maintain the

required alkalinity and ionic strength. A stock standard solution of Os(VIII) was prepared by dissolving OsO₄ in 0.50 mol dm⁻³ NaOH and the concentration was determined.

An aqueous solution containing cyclic ketone and requisite amount of base and metal ion were thermostated at the desired temperature. To this, a known concentration of pre equilibrated periodate was added and the progress of the reaction was followed by estimating unreacted periodate iodometrically at regular time intervals. The pH of the solution was maintained by KH₂PO₄.

RESULTS AND DISCUSSION

Ru(III)-catalysed oxidation

Under the conditions $[IO_4^-] \ll [ketone]$, the order in $[IO_4^-]$ and $[Ru(III)]$ were found to be zero and one respectively. The order in $[ketone]$ was fractional as evidenced by the slope. The rate increased with increase in $[OH^-]$. (Table 1, Fig. 1) The product of oxidation was carboxylic acid. The negligible effect of ionic strength might be due to the neutral molecules in the reaction.

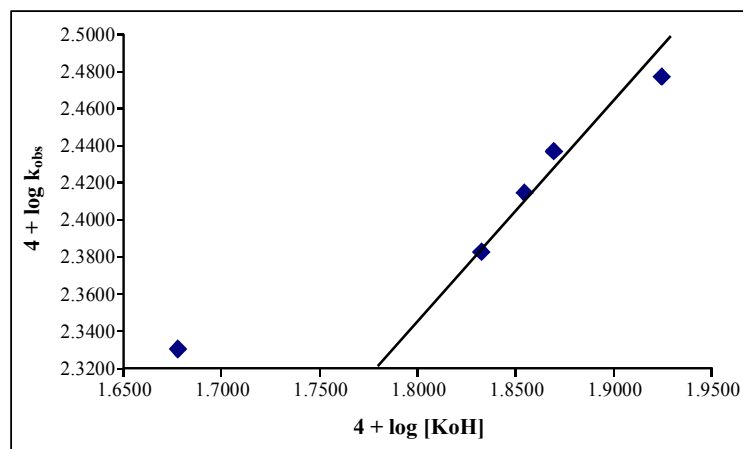


Fig. 1: $[Substrate] = 2.46 \times 10^{-3} \text{ mol dm}^{-3}$, $[Oxidant] = 7.40 \times 10^{-4} \text{ mol dm}^{-3}$, $[OH^-] = 4.90 \times 10^{-5} \text{ mol dm}^{-3}$, $[Ru(III)] = 1.23 \times 10^{-5} \text{ mol dm}^{-3}$, $[KCl] = 2.46 \times 10^{-2} \text{ mol dm}^{-3}$, Temp. 308.15 K

Table 1: Effect of concentration of $[OH^-]$ on oxidation of Ru (III) catalysed 4-methyl cyclohexanone $[Substrate] = 2.46 \times 10^{-3} \text{ mol dm}^{-3}$, $[Oxidant] = 7.40 \times 10^{-4} \text{ mol dm}^{-3}$, $[OH^-] = 4.90 \times 10^{-5} \text{ mol dm}^{-3}$, $[Ru(III)] = 1.23 \times 10^{-5} \text{ mol dm}^{-3}$, $[KCl] = 2.46 \times 10^{-2} \text{ mol dm}^{-3}$, Temp. 308.15 K

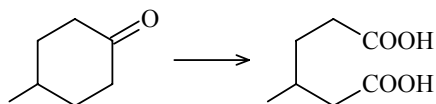
$[OH^-] \times 10^6 \text{ mol dm}^{-3}$	$k_{obs} \times 10^2 \text{ min}^{-1}$	$k_{obs} \times 10^3 \text{ sec}^{-1}$
9.52	1.37	2
8.33	1.36	2.26
7.14	1.67	2.78
4.76	1.79	2.29

The effect of temperature has been studied between the range of 288-308 K. From the plot of $\log K_{obs}$ vs. $1/T$, the energy of activation was calculated as 5.97 Kcal mol⁻¹.

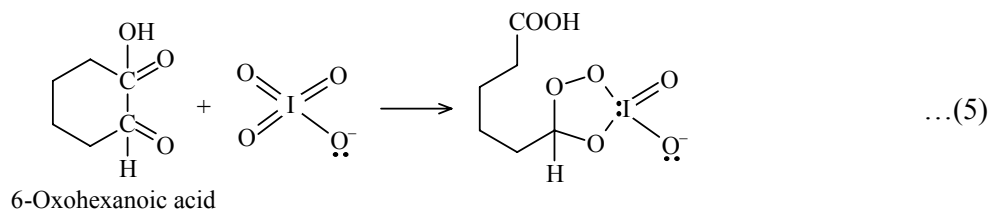
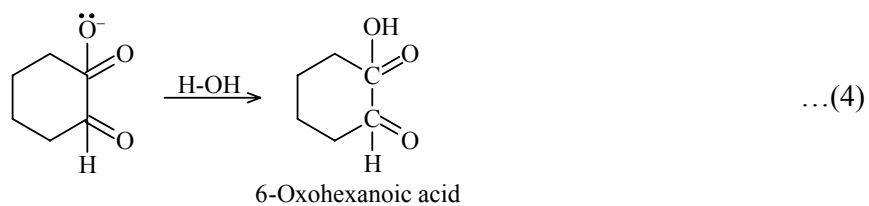
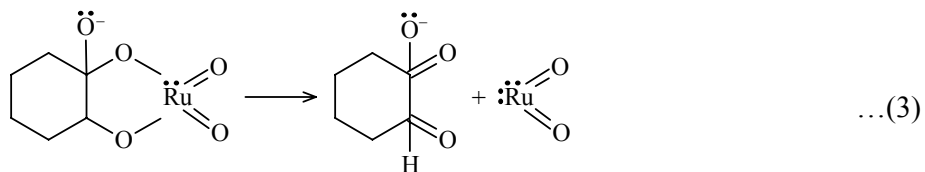
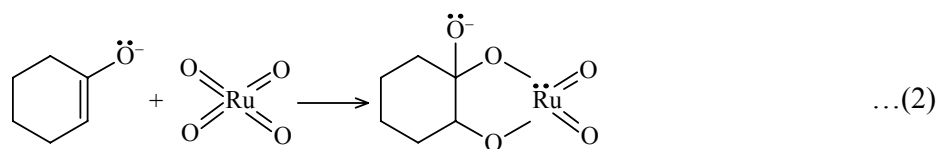
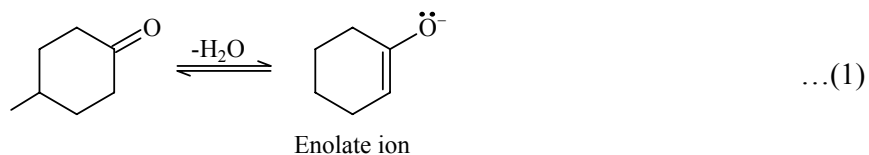
The negative values of the entropy of activation indicate the complex rigidity (Table 2).

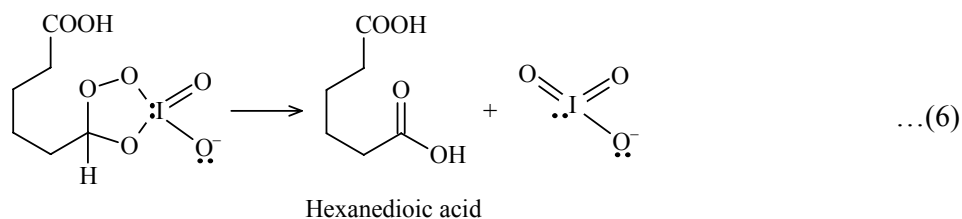
Table 2: Kinetic parameters [Substrate] = $2.46 \times 10^{-3} \text{ mol dm}^{-3}$, [Oxidant] = $7.40 \times 10^{-4} \text{ mol dm}^{-3}$, [OH⁻] = $4.9 \times 10^{-5} \text{ mol dm}^{-3}$, [Ru(III)] = $1.23 \times 10^{-5} \text{ mol dm}^{-3}$, [KCl] = $2.46 \times 10^{-2} \text{ mol dm}^{-3}$, Temp. 308.15 K

E _a (k cal mol ⁻¹)	Δ H [#] (k cal mol ⁻¹)	Δ S [#] (e.s.u.)	Δ G [#] (k cal mol ⁻¹)
5.98	3.5920	-57.02250	22.311000

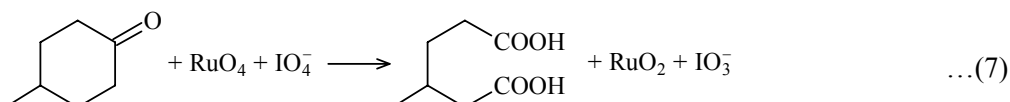
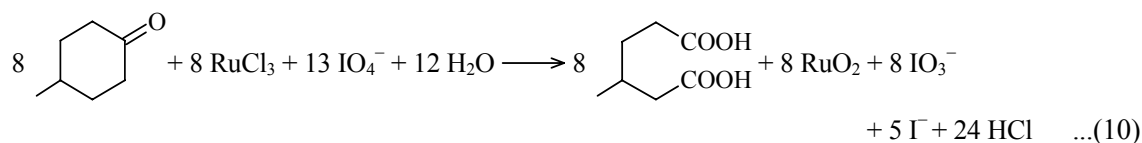
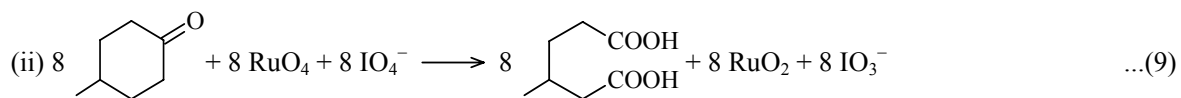
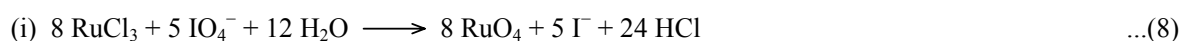


Mechanism:





(Scheme 1)

Overall reaction:**Stoichiometry of reaction**

Increase in rate with increase in $[\text{OH}^-]$ indicates that both the hydroxylated species of $[\text{Ru(III)}]^{15}$ and the enolate ion of the cyclic ketone are the reactive species in the reaction (Step I in scheme).

Since $[\text{OH}^-] \gg [\text{Ru(III)}]$, it is assumed that all $[\text{Ru(III)}]$ is present as hydroxylated species. The slow step involves the interaction of hydroxylated species of Ru (III) with the enolate ion resulting in the formation of Ru(I) and intermediate (II), probably a carbonium ion. Formation of an intermediate could be via a hydride ion transferred to Ru(III). Since the latter is known to be a good hydride ion obstructer.^{16,17} As very low concentration of Ru(III) was used, no kinetic evidence could be obtained for the formation of Ru(I). The intermediate carbonium ion is assumed to undergo oxidation by periodate to yield the final product. The catalyst Ru(III) is regenerated in a subsequent step. The rate law derived for the above mechanism is given by –

$$\frac{-d[\text{IO}_4^-]}{dt} = \frac{k_2 \cdot k_1 [\text{Cycloketone}][\text{OH}^-][\text{Ru(III)}]}{1 + k_1 [\text{Cycloketone}] + k_1 [\text{OH}^-]} \quad \dots(11)$$

Since K_1 (the enolisation constant) is very less and as a result, $K_1[\text{ketone}] + K_1[\text{OH}^-]$ is very small compared to one and hence, neglected. The resulting rate law satisfactorily explains all the observed kinetic results.

Os(VIII)-catalysed oxidation

In Os(VIII) catalysed oxidation also, the order in $[\text{IO}_4^-]$ and $[\text{Os(VIII)}]$ were found to be zero and one, respectively as in Ru(III)-catalysed reaction. Carboxylic acid was the product of oxidation. The enol,

which is the most likely species in alkaline medium is assumed to undergo hydroxylation by OsO₄¹⁸. The formation of the ester type complex between Os(VIII) and enolate ion is shown to be the rate controlling step. The rate law derived for the disappearance of periodate is given by equation-

$$\frac{-d[\text{IO}_4^-]}{dt} = K_0 = \frac{k_1 \cdot k_2 [\text{Ketone}][\text{OH}^-][\text{Ru(III)}]}{1 + k_1 [\text{Ketone}] + k_1 [\text{OH}^-]} \quad \dots(12)$$

This rate law satisfactorily explains all the kinetic features.

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