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Kinetics of oxidation of 3-methyl cyclohexanone by periodate catalysed by Ru(III) in alkaline medium

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ABSTRACT

Under identical conditions, the 3-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. The effect of temperature was studied and kinetic parameters were evaluated. The probable mechanism and rate law applied.

KEYWORDS

Cyclic ketones;
Kinetics;
Reaction mechanisms.

INTRODUCTION

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 glycols[1,2] but the kinetics of the periodate oxidation of amino alcohols[3], dicarbonyl compounds[4], amino acids[5] and cyclic ketones[6] has received much less attention. Oxidation with periodate cause denaturation of proteins and inactivation of enzymes.

In recent years, the transition metal ions such as Osmium, Ruthenium, and Palladium are used as catalyst[7]. The mechanism of catalysis depends on the nature of substrates, oxidants and other experimental conditions. The metal ions act as catalysts by one of these different paths such as the formation of the complexes with reactants or oxidation of substrates itself or through the formation of free radicals. Ruthenium and its chloro compounds have greater use in homogeneous catalysis[8-10]. However Ru(III) catalysed oxidation of 3-methyl cyclohexanone in alkaline medium has been studied herewith a discussion of mechanism.

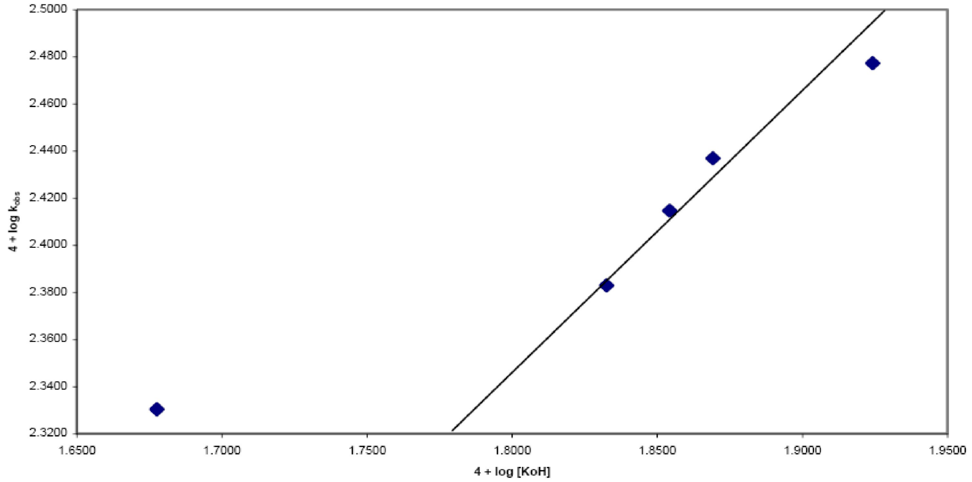
MATERIALS AND METHODS

3-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. KOH and KCl were employed to maintain the required alkalinity and ionic strength.

An aqueous solution containing cyclic ketone and requisite amount of base and metal ion were thermostated of the desired temperature. To this was added a known concentration of pre-equilibrated periodate and the progress of the reaction followed by estimating unreacted periodate iodometrically at regular time intervals. The pH of the solution was maintained by KH_2PO_4.

RESULTS AND DISCUSSION

Under the conditions $[IO_4^-]$ <<< [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, Figure 1). The product of oxidation was carboxylic acid. The negligible effect of ionic strength might be due to the neutral molecules in the reaction.



[Substrate] = 2.4569 x 10^{-3} mol dm^{-3}, [Oxidant] = 7.40 x 10^{-4} mol dm^{-3}, $[OH^-]$ = 4.9 x 10^{-5} mol dm^{-3}, [Ru(III)] = 1.23 x 10^{-5} mol dm^{-3}, [KCl] = 2.46 x 10^{-2} mol dm^{-3}, Temp.= 308 K

Figure 1

TABLE 1 : Effect of concentration of $[oH^-]$ on oxidation of Ru(III) catalysed 3-methyl cyclohexanone

Sr.No.	$[OH^-]$ mol dm^{-3}	log $[OH^-]$	k_{Obs} min.$^{-1}$	log k_{Obs}	4+log $[OH^-]$	4+log k_{Obs}
1	4.760E-03	-2.3224	0.02140	-1.670	1.6776	2.3304
2	6.800E-03	-2.1675	0.02415	-1.617	1.8325	2.3829
3	7.150E-03	-2.1457	0.02598	-1.585	1.8543	2.4146
4	7.400E-03	-2.1308	0.02735	-1.563	1.8692	2.4370
5	8.400E-03	-2.0757	0.03001	-1.523	1.9243	2.4773

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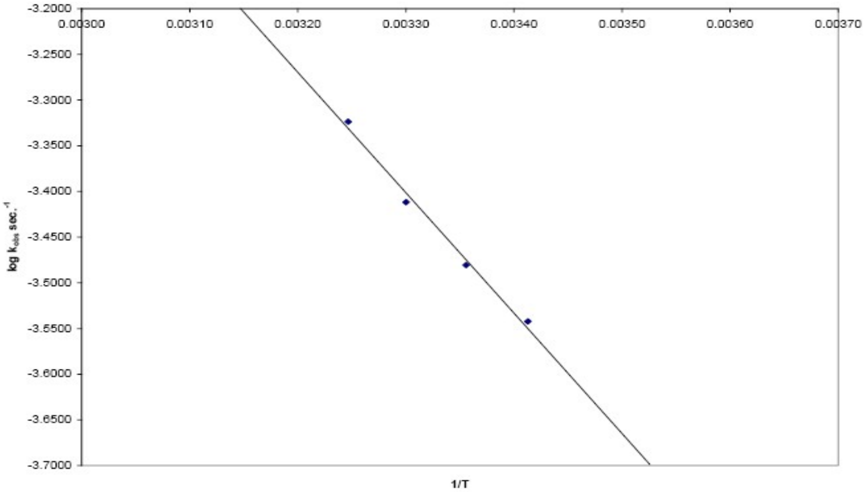

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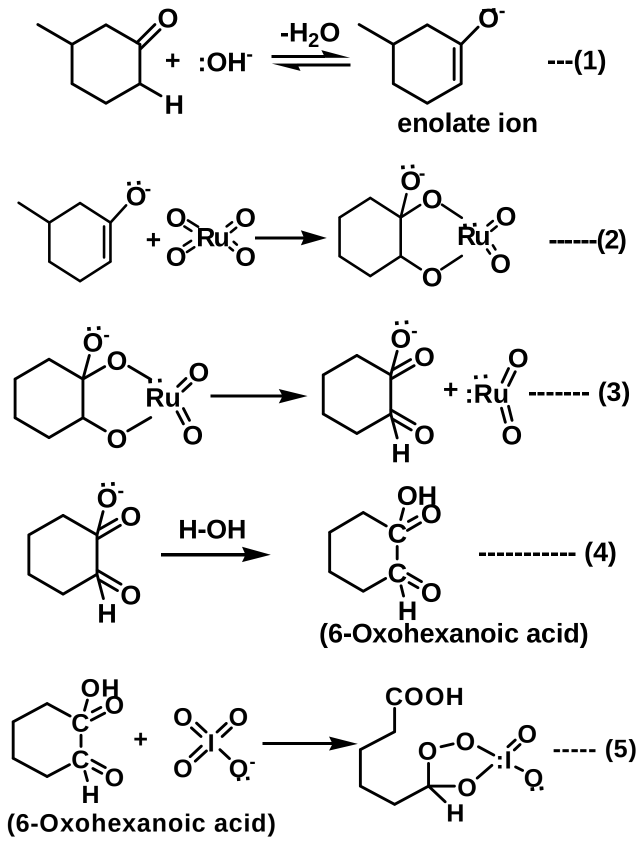
Figure 2

TABLE 2 : Kinetic parameters

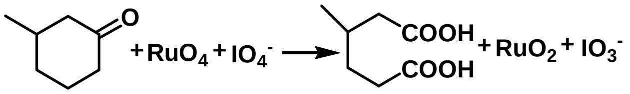
Ea k cal mol^{-1}	$\Delta H^{\#}$ Kcal mol^{-1}	$\Delta S^{\#}$ e.s.u.	$\Delta G^{\#}$ k cal mol^{-1}
5.98	3.5920	-57.02250	22.311000

[Substrate] = 2.4569 x 10^{-3} mol dm^{-3}, [Oxidant] = 7.40 x 10^{-4} mol dm^{-3}, [OH^-] = 4.9 x 10^{-5} mol dm^{-3}; [Ru(III)] = 1.23 x 10^{-5} mol dm^{-3}, [KCl] = 2.46 x 10^{-2} mol dm^{-3}, Temp. 308.15 K.

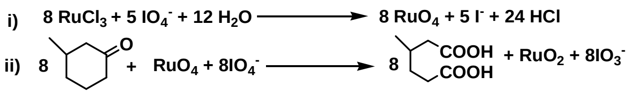


Scheme 1

Overall reaction route



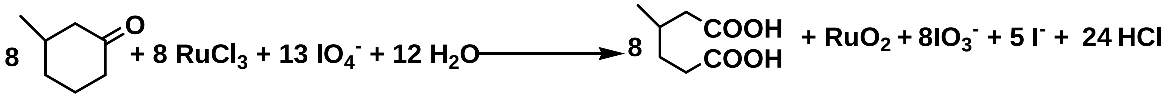
Stoichometry of reaction route



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

Since [OH^-] >>> [Ru(III)], it is assumed that all [Ru(III)] is present as hydroxylated species [Ru(III)]*. The slow step involves the interaction of hydoxylated species of Ru(III) with the enolate ion resulting in the formation of Ru(I) and intermediate(II) probably a carbonium ion. Formation of a intermediate could be via a hydride ion transferred to Ru(III). Since the latter is known to be a good hydride ion obstructer. As there is very low concentration of Ru(III) 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 -

$$\frac{-d\,[IO_4^-]}{dt} = \frac{k_2 \,.\, k_1 \,[\text{cycloketone}]\,[OH^-]\,[Ru(III)]}{1 + k_1\,[\text{cycloketone}] + k_1[OH^-]}$$



Since K_1 (the enolisation constant) is very less and hence K_1[ketone]+K_1[OH^-] is very small compared to one and hence neglected. The resulting rate law satisfactorily explains all the observed kinetic results.

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