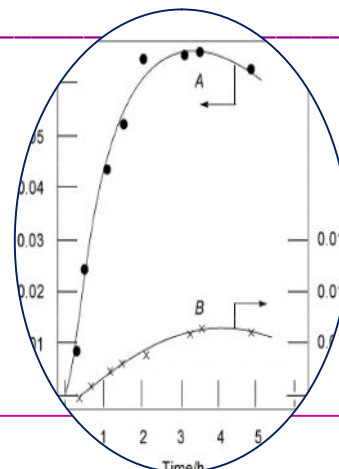_____

KINETICS AND MECHANISM OF OXIDATION OF 2-METHYL CYCLOHEXANONE BY VANADIUM (V)

Dr. Rajendra Swain
Assistant Professor, Department of Chemistry, Post Graduate Govt. College for Girls Sector-42, Chandigarh.

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ABSTRACT

The kinetics of the oxidation of 2-methyl cyclohexanone by V(V) in aqueous acetic acid medium have been investigated in the temperature range 40-55°C. The reaction exhibits first order with respect to both oxidant and substrate at constant $[H^+]$ and is catalysed by acid but the dependence in $[H^+]$ is complex. A suitable mechanism consistent with the observed kinetic data has been proposed and rate law derived. 2-Methyl adipic acid is the product. The reaction is not catalysed by anionic surfactant like sodium lauryl sulphate.

KEYWORD : oxidant and substrate at constant $[H^+]$, 2-Methyl adipic acid.

INTRODUCTION

It has been reported that 2-hydroxy cyclohexanone[1] has been oxidised by acid solutions of vanadium (V) with the formation of transient organic free radicals. Radicals[2] had been also detected in the oxidation of cyclohexanone by Littler and Waters. However there is no report in the literature as to the study of the mechanism of oxidation of 2-methyl cyclohexanone by V(V). To understand the redox processes in micellar media[3] it was considered worthwhile to extend the study to the oxidation of 2-methyl cyclohexanone by vanadium(V) which is the subject matter of this communication.

EXPERIMENTAL

2-Methyl cyclohexanone (BDH-England) was used as such after checking the purity. Since it was insoluble in aqueous medium, all the solutions of 2-methyl cyclohexanone were prepared in aqueous acetic acid (10% V/V). The oxidant namely vanadium (V) solution was estimated iodometrically.[4]

RESULT AND DISCUSSION
Dependence of Rate in Oxidant

As 2-methyl cyclohexanone was not soluble in aqueous medium, the reaction was carried out in of aqueous acetic acid (10% V/V) and kinetics recorded under pseudo-first order condition with respect to the

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oxidant. The order with respect to the V(V) is one as seen from constancy of pseudo-first order rate constants (k_ψ) up to at least 60% of the reaction and linearity of $\log[V(V)]_t$ versus time plots under different experimental conditions.

Effect of added salt:

To study the effect of ionic strength on the reaction rate pseudo-first order rate constants were measured in presence of $NaClO_4$ varying in the range 0.05-0.3M keeping other reactants constant. The pseudo-first order rate constants were collected in table-1. Constancy of the rate constant in different $NaClO_4$ concentrations shows that concentrations shows that ionic strength has no effect on the rate. Hence in subsequent experiments ionic strength was not maintained.

Dependence on Substrate:

Dependence on [2-methyl cyclohexanone] was ascertained by carrying out kinetics with varying [substrate] at constant acidity, oxidant and temperature-Pseudo-first order rate constants obtained in presence of different 2-methyl cyclohexanone concentrations are given in table-I. Plot of k_ψ versus [substrate] is perfectly linear passing through the origin as well as $k_\psi/[S]$ values are constant indicating unit dependence in the substrate.

Table-1

Pseudo-first order rate constants for the oxidation of 2-methyl cyclohexanone by V(V).

Temp. = 40^0C, Solvent = 10% HAC (V/V) 10^3 [V(V)] = 5.0mol.dm^3.

10^2 [Substrate] mol.dm^{-3}	10 [H$^+$] mol.dm^{-3}	10^2 [NaClO$_4$] mol.dm^{-3}	$10^2 k_\psi$ min^{-1}
5.0	3.90	---	4.49
		5.0	4.61
		10.0	5.01
		20.0	5.0
		30.0	5.71
5.0	18.0	---	10.0
		5.0	10.1
		10.0	10.1
		20.0	10.02
		30.0	10.15
2.5	13.2	---	4.15
5.0			8.75
7.5			11.3
10.0			17.3
12.5			20.5
15.0			24.5

Dependence of rate on acidity:

In the presence of varying [HClO$_4$] pseudo-first order rate constants were collected in the table-II. It is observed from the table that the reaction rate increases with the increase of the perchloric acid concentration and plot of k_ψ^{-1} versus [H$^+$]$^{-1}$ [Fig.I] is linear with positive intercept and positive slope. This suggests that protonation is involved in the pre-equilibrium step.

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Table-2

Pseudo-first order rate constants for the oxidation of 2-methyl cyclohexanone by V(V) is different solvent composition.

10^2 [2-methyl cyclohexanone] = 5.0 mol.dm^{-3}, 10^3 [V(V)] = 5.0 mol.dm^{-3} Temp. = 40^{0}C.

10[H$^+$]		10^3 k$_\psi$ min^{-1}	
mol.dm^{-3}	10% HAC	15%HAC	20% HAC
6.0	5.0	4.7	3.5
10.0	7.2	6.3	5.1
14.0	9.0	8.1	6.2
20.0	9.8	9.5	8.2

Effect of Temperature:

Arrhenius plots are linear and have been used to compute the thermodynamic parameters from the rate data measured over the temperature range 40 to 55°C. Energy and entropy of activation at 0.3(M) [H$^+$] are 30.0 ± 0.5Kjmol^{-1} and -230 $^\pm$ 10JK^{-1}mol^{-1} respectively.

Table-3

Pseudo-first order rate constants for the oxidation of 2-methyl cyclohexanone by V(V) at different temperature.

10^2[2-methyl cyclohexanone] = 5.0mol.dm^{-3}, 10^3 [V(V)] = 5.0 mol.dm^{-3}, solvent = 10% HAC (V/V).

10[H$^+$]	10^3K$_\psi$ min^{-1}	10^3K$_\psi$ min^{-1}	10^3K$_\psi$ min^{-1}	10^3K$_\psi$ min^{-1}
mol.dm^{-3}	40^{0}C	45^{0}C	50^{0}C	55^{0}C
6.0	5.0	6.4	8.9	11.0
10.0	7.2	9.0	12.9	17.5
14.0	9.0	12.0	18.4	23.2
20.0	9.8	14.5	20.5	26.4

[H$^+$]$^-$	k$_\psi$ $^{-1}$	k$_\psi$ $^{-1}$	k$_\psi$ $^{-1}$	k$_\psi$ $^{-1}$
	40^{0}C	45^{0}C	50^{0}C	55^{0}C
1.66	20.0	156.25	112.35	90.90
10.0	133.3	111.1	77.51	57.14
0.71	111.1	81.96	52.91	43.10
0.5	102.0	68.96	48.78	37.87
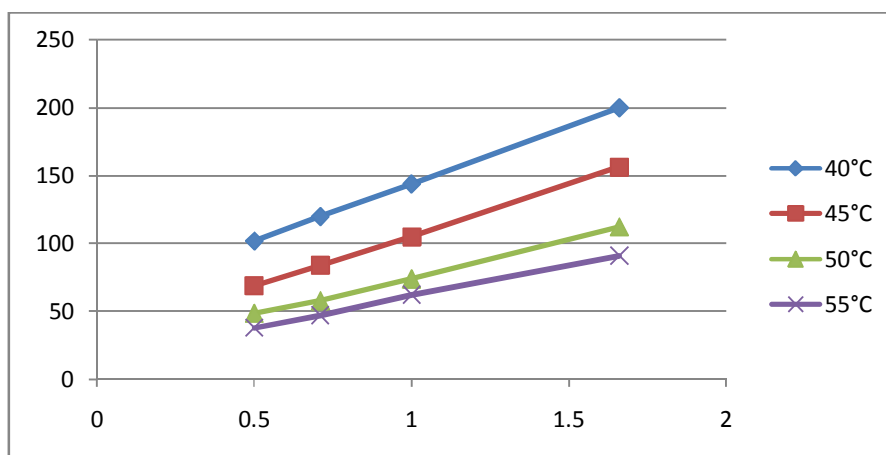
Graph-1, In X-axis [H$^+$]$^{-1}$ in Y-axis [k$_\psi$]$^{-1}$

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Effect of acrylamide on the reaction:

The reaction when carried out in the presence of acrylamide, no turbidity was observed. But the radical formation cannot be ruled out in oxidations by one electron oxidant probably the radical is oxidised much faster before the polymerisation occurs.

Effect of acetic acid:

Pseudo-first order rate constants were collected in presence of varying proportion of acetic acid in table-2. It is observed that the reaction is sensitive to the solvent composition. The rate decreases as the amount of acetic acid increases or on the other hand, rate decreases with decrease of dielectric constant with a polar like transition state[6] likely to be involved during the reaction.

Product Analysis:

2-Methyl cyclohexanone and excess of vanadium (V) solution in 0.3(M) HClO$_4$ were equilibrated for 24hrs. The mixture was treated with NaHCO$_3$ solution and was ether extracted to remove unreacted 2-methyl cylohexanone. The aqueous solution is again acidified and subjected to ether extraction. The ether layer was separated and evaporated slowly. Needles of 2-methyl adipic acid separated which was confirmed by its melting point (Lit value - 64°C).

Rate law and mechanism:

Extensive oxidation of 2-methyl cyclohexanone by V(V) is closely similar to the oxidations that can be affected by ceric and magnanic salts, which are also one electron abstracting agents[2,7]. Under various experimental conditions the acid catalysed reaction must be related to the structure of the oxidant but not to the organic substrate. Rossotti and Rossatti[9,10] have shown that V(V) exists mostly as VO$_2^+$ at PH<1. The acceleration of the reaction with increase in [H$^+$] in the case of many vanadium(V) oxidation has been explained by Waters *et al.* as due to the formation V(OH)$_3^{2+}$ according to the equilibrium.

$$VO_2^+ + H_3O^+ = V(OH)_3^{2+}$$
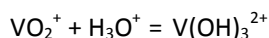
The oxidation product of 2-methyl cyclohexanone by V(V) in acid medium is 2-methyl adipic add which was ascertained by the product analysis. From the solvent isotope effect and dependence on acidity it has been well established that during the oxidation of cylohexanone the keto form of the cyclohexanone participates in the oxidation by one electron oxidants like V(V), Ce(IV), etc. The dependence in oxidant as well as acid was found to be first order. This together with negligible salt effect[5,6] indicates that the present reaction occurs between a neutral molecule and an Ion. This in turn suggests that the Keto form is involved. The dependence in acid suggests that the V(V) species in acid solution is governed by the following equilibrium :

$$VO_2^+ + H_3O^+ \overset{K_1}{\Rightarrow} [V(OH)_3]^{2+}$$
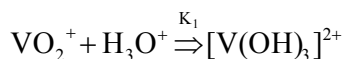
So [V(OH$_3$]$^{2+}$ is the active oxidant species involved in the rate limiting step. Thus the following steps are proposed for the oxidation of 2-methyl cyclohexanone by V(V) in aqueous acetic acid medium consistent with the observations the following steps are proposed

$$VO_2^+ + H_3O^+ \overset{K_1}{\Rightarrow} [V(OH)_3]^{2+} \qquad ...(1)$$

$$[V(OH)_3]^{2+} + S \xrightarrow{k_2} V(IV) + product \qquad ...(2)$$
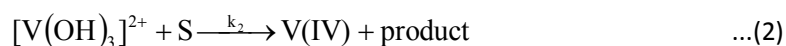
Rate is given by

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$$\frac{-d[V(V)]_t}{dt} = k_2[S][V(OH)_3]^{2+} \qquad \ldots(3)$$

But $[V(V)]_t = [VO_2^+] + [V(OH)_3]^{2+}$ ...(4)
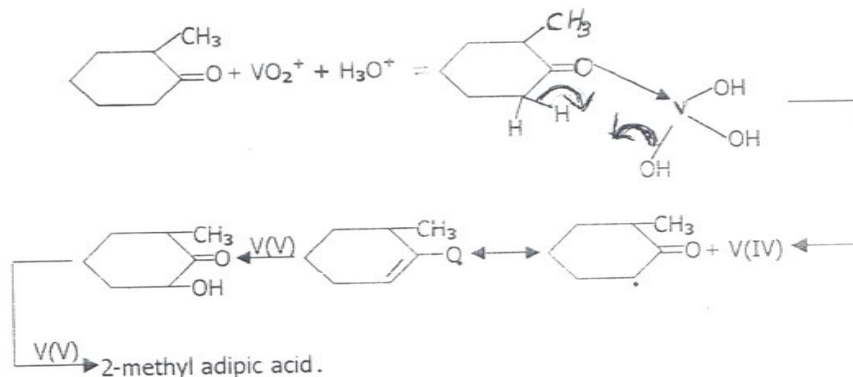
From equation (1)

$VO_2^+ = [V(OH)_3]^{2+} / K_1[H^+]$

By introducing VO_2^+ in equation (4) we get

$$[V(V)]_T = \frac{[V(OH)_3]^{2+}}{K_1[H^+]} + [V(OH)_3]^{2+}$$

$$= [V(OH)_3]^{2+} \left\{ \frac{1 + K_1[H^+]}{K_1[H^+]} \right\}$$

$$\text{Or, } [V(OH)_3]^{2+} = \frac{[V(V)]_T K_1[H^+]}{1 + K_1[H^+]} \qquad \ldots(5)$$

By substituting $[V(OH)_3]^{2+}$ in equation (3) we get

$$\text{Rate} = \frac{K_2 K_1 [S][V(V)]_T [H^+]}{1 + K_1[H^+]} \qquad \ldots(6)$$

The rate equation (6) explains the order in V(V), acid and substrate concentration. The observation appears to be consistent with the following scheme,

Although no complex has been detected its formation cannot be ruled out as the same may be very unstable and undergoes fast decomposition to products.

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