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EFFECT OF SODIUM LAURYL SULPHATE IN THE OXIDATION OF CYCLOPENTANONE BY VANADIUM (V)

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ABSTRACT

Oxidation of cyclopentanone by V(V) in aqueous perchloric acid medium has been studied both in presence and absence of sodium lauryl sulphate. The rate is first order in both cyclopentanone and V(V). The dependence in H^+ is unity. The oxidation is catalysed by SLS. The rate reaches maximum around the cmc and then decreases when the surfactant concentration further increases. The kinetic data have been rationalised by Berezin model indicating both the reactants are bound to the micellar phase. Cyclopentanone appears to be bound by hydrophobic interaction while V(V) species bound by hydrophilic forces.

KEYWORDS : *Oxidation of cyclopentanone , Berezin model , hydrophobic interaction.*

INTRODUCTION

In the past few years there has been growing interest for the study of electron transfer reaction of transition metal ions in the presence of micelles'(1-5) due to their wide application in the industrial, biological and pharmaceutical processes. Increasing attention has been paid to find out the nature of the association of the reactant with micelles and binding constants, transfer of free energy of the reacting molecule in the presence of surface active agents[6,7].

Recently we have communicated results of kinetics of oxidation of cyclohexanone and 2-hydroxy cyclohexanone by V(V) in presence of SLS (sodium lauryl sulphate)[8]. Thus it was felt necessary to focus the attention on the micellar effect in electron transfer reaction where there is structural variation in the substrate. For this reason the redox reaction of cyclopentanone by V(V) in the presence of SLS at different temperatures which is the main subject matter of this communication.

EXPERIMENTAL

All the chemicals used were of analytical grade. Cyclopentanone (E. Merck), perchloric acid (E. Merck) and meta-ammonium vanadate were used as received. The surfactant sodium lauryl sulphate (NaLS) was used after recrystallisation. All the solutions were prepared in deionised water including stock solution of vanadium (V) and sodium lauryl sulphate. Acidity was maintained by $HClO_4$. The $[H^+]$ concentration in V(V) solution was determined volumetrically by titrating with standard Na_2CO_3 solution to methyl-orange colour change. Reactant solutions of cyclopentanone and vanadium (V) were prepared in 50ml flasks by dilution of an appropriate amount of the stock solution.

Calculated amount of the stock SLS solution was always added to the oxidant flask and then made up. Both the reactants were thermostated for 15 mins to attain equilibrium and the reaction was initiated by mixing 25ml of each in a clean dry bottle maintained at the desired temperature. Progress of the reaction was followed by the estimation of the residual V(V) in 5ml aliquot of the reaction mixture of at different time intervals by iodometry. Rate constants were reproducible within the limits of experimental error. SLS was stable under the experimental condition.

RESULTS & DISCUSSIONS

Although a report on the oxidation of cyclopentanone by V(V) is available[9], the investigation in the aqueous medium was undertaken in order to make a comparative study of the results in presence of SLS. Reduction of V(V) by cyclopentanone followed first order kinetics with respect to V(V) when carried out under the conditions V(V) << cyclopentanone as seen from the constancy of the first order rate constants obtained with respect to [V(V)] in any single run. First order rate constants were constant when performed in the presence of varying sodium perchlorate concentration indicating ionic strength has no influence on the oxidation rate of cyclopentanone by V(V). The data are collected in table-I. This observation is at variance with that reported earlier[9].

Table-1

Pseudo-first order rate constants for the oxidation of cyclopentanone by V(V) in different [$NaClO_4$]. 10^3 [V(V)]= 5.0 mol.dm^3, 10^2 [substrate]=5.0 mol.dm^3 solvent = Aq. medium, Temp=60°C, [$HClO_4$]=1.0 mol.dm^3

10^2 [$NaClO_4$] mol.dm^3	10^3 k_ψ min^{-1}
---	3.20
5.0	3.13
10.0	3.24
15.0	3.33
20.0	3.32

Effect of Substrate Concentration on the Oxidation Rate

Pseudo-first order are constant ($K_\psi$min^{-1}) with respect to vanadium (V) is found to increase with cyclopentanone concentration and the values of k_ψ/[cyclopentanone] are observed to be constant (table-II) indicating unit dependence on the substrate.

Table-2

Pseudo-first order rate constants for the oxidation of different [cyclopentanone] by V(V). 10^3 [V(V)]= 5.0 mol.dm^3, 10^2 solvent = Aq.medium, Temp = 60°C, [$HClO_4$]=1.5 mol.dm^3

10^2 [cyclopentanone]	10^3 k_ψ min^{-1}
5.0	4.09
7.5	7.38
10.0	9.73
12.5	15.0
15.0	16.48

Dependence on [H^+]

Pseudo-first order rate constants obtained at constant substrate and temperature in the presence on varying perchloric acid concentration are presented in the table-III. The k_ψ min^{-1} values increases with [$HClO_4$] and k_ψ/[$HClO_4$] values are fairly constant establishing first order dependence on [$HClO_4$]. The acid dependence suggests that active vanadium species[10] is $[V(OH)_3]^{2+}$ resulting from the hydrolysis of VO_2^+ as follows:

$VO_2 + H_3O^+ \rightleftharpoons [V(OH)_3]^2$ .....(1)

Table-3

Pseudo-first order rate constants for the oxidation of cyclopentanone by V(V) in different $[HClO_4]$.
10^3 [V(V)]= 5.0 mol.dm^3, 10^2 [substrate]=5.0 mol.dm^3 solvent = Aq. medium, Temp=60°C

10 $[HClO_4]$ mol.dm^3	10^3 k_ψ min^{-1}
5.0	2.49
7.5	2.87
8.8	2.04
11.3	3.54
15.0	4.10
20.0	4.67

As V(V) is known as a one electron oxidant, oxidation of organic substrates would involve formation of a radical which can be trapped by acrylamide of acrylonitrile resulting in the precipitation of an insoluble polymer. Polymerisation test is found to be positive and it helps to conclude that V(V) is reduced to V(IV) in the rate limiting step.

Activation parameters for the cyclopentanone oxdidation have been computed from rate data obtained at 50°-65°C at 1.1(M) $HClO_4$ (Table-IV). Energy and entropy of activation values are respectively 48 KJ mole^{-1} and -128 KJ mol^{-1}. Negative entropy of activation is consistent with a transition state with reduced degrees of freedom.

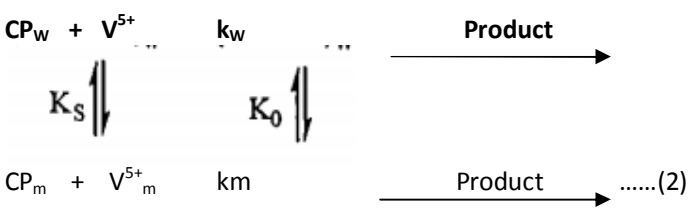
Table-4

Activation parameter in cyclpentanone oxidation with V(V)
10^3 [V(V)]= 5.0 mol.dm^3, 10^2 [substrate]=5.0 mol.dm^3 $[HClO_4]$=1.1 mol.dm^3

10^2[SLS]	Ea(KJ mol^1)	Joule.k^1.mol^{-1}
0.0	48.0	-128.0
1.0	37.96	-158.7

→ Computed using the values at different temperatures derived from eqn.

Consistent with dependence in $[H^+]$, first order dependence in [cyclopentanone] suggests that the oxidant species attacks the ketone to form an unstable complex in which electron transfer occurs forming a free radical and V(IV) in the rate determining step.



[SCHEME - A]

Kinetics in presence of sodium lauryl sulphate [SLS]

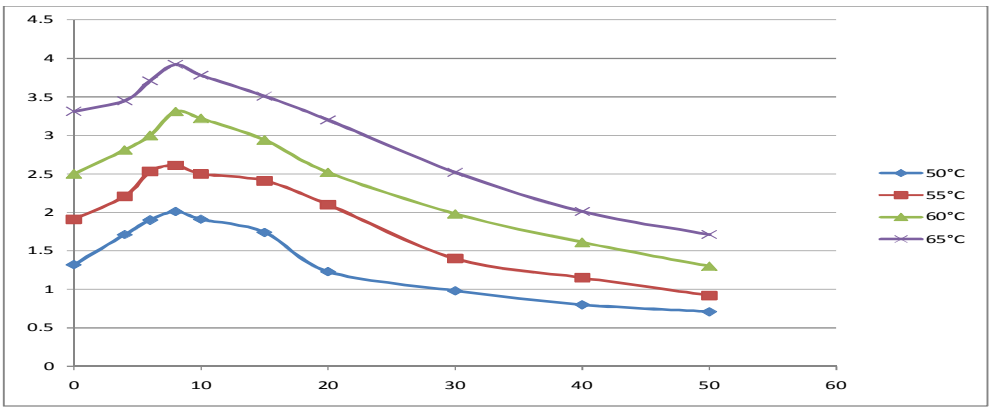
The kinetic data in the presence of SLS are given in table-V. The dependence of rate of oxidation in various components remains virtually unchanged. Only the activation parameters in presence of 0.01 M SLS change in the decreasing direction indicating energy barrier is reduced in the presence of SLS. Therefore validity of rate law for the oxidation of cyclopentanone by V(V) in absence of SLS concentration. However, the oxidation was catalysed in presence of low [SLS] reached a maximum around the cmc or below the cmc

and then decreased with further increase of [SLS]. It appears the cmc is lowered due to presence of added electrolytes or solubilizates[11,12] and hence the maximum of the rate is obtained at lower SLS concentrations.

Table-5

Pseudo-first order rate constants for the oxidation of cyclopentanone by V(V) in presence of SLS. 10^3 V(V)=5.0 mol.dm^3, 10^2 (substrate) = 5.0 mol.dm^3, 10[$HClO_4$] = 11.0, solvent = Aq.medium.

10^3(SLS) [mol.dm^3]	10^3 k_ψ min^{-1}			
	50°C	55°C	60°C	65°C
---	1.32	1.91	2.5	3.31
4.0	1.71	2.21	2.81	3.45
6.0	1.90	2.53	3.0	3.71
8.0	2.01	2.61	3.31	3.92
10.0	1.91	2.50	3.22	3.56
15.0	1.74	2.41	2.94	3.71
20.0	1.23	2.10	2.11	3.30
30.0	0.98	1.40	1.51	2.81
40.0	0.80	1.15	1.61	2.21
50.0	0.71	0.92	1.30	1.71



X- Axis10^3[SLS]and Y-axis 10^3 k_ψ

In the presence of negatively charged aggregates partitioning between the bulk aqueous phase and the micellar pseudo-phase has to be considered for all the species involved in the reaction (2), since both electrostatic and hydrophobic interactions may be operative[13]. Therefore in the present case the reaction scheme applies and the apparent rate constant k_ψ is given by[14] equation 3.

$$k_\psi = \frac{k_w + \bar{k}_m K_s K_o C}{(1+K_s C)(1+K_o C)} \qquad \text{.....(3)}$$

Where $\bar{k}_m = K_m/V$ (V is the volume element of micelle in which reaction takes place) and K_s and K_o are the binding constants of the substrate i.e. cyclopentanone and V(V) respectively. Further k_w term can be neglected compared to the other term in the numerator and the above equation can be re-arranged to:

$$\frac{1}{k_\psi} = \frac{1}{\bar{k}_m K_s K_o C} + \frac{k_s + k_o}{\bar{k}_m K_s K_o} + \frac{C}{\bar{k}_m} \qquad \text{.....(4)}$$

According to the equation the trend of k_{Ψ}^{-1} as a function of C would show a minimum at the value of $C_{mn}=1/(K_sK_o)^{1/2}$ whereas $1/k_{\Psi}$ would be linearly dependant on C' for 'C' values higher than this minimum. In fact plots of $1/k_{\Psi}$ against 'C' (beyond cmc) are found to be fairly linear under different experimental conditions. From the ratio of the intercept and slope values of the linear region $(K_s+K_o)/K_sK_o$ could be evaluated. This combination with $1/(K_sK_o)^{1/2}$ given by C_{min} could lead to computation of K_s,K_o values, Slopes of the plots lead to computation of $\bar{k}_m$ values. The above parameters are presented in table-VI.

Table-6

Binding constants, $\bar{k}_m$ and transfer free energies in the oxidation of values of cylopentanone by V(V) at different temperature in aqueous $HClO_4$ medium 1.1(M) in presence of [SLS].

Temp	K_s	K_o	$10^4 k_m$	$-\Delta\mu^o{}_s$ KJ mol^{-1}	$-\Delta\mu^o{}_{ox}$ KJ mol^{-1}
50°C	2423.26	211.45	119.0	30.7	16.8
55°C	1647.73	110.1	42.5	29.7	22.7
60°C	980.4	13.13	30.6	30.4	17.2
65°C	508.60	8.74	4.0	26.4	16.1

It is conforming to note that $\bar{k}_m$ values increase with increase of temperature. These values have been used to compute the activation parameters in the micellar volume and presented in table. These values are similar to what was calculated from k_{Ψ} values at different temperatures in presence of 0.01M SLS.

Inspection of the binding constants makes it clear that K_s values are larger than K_o i.e. cyclopentanone is strongly bound to the micelles compared to the oxidant. Although examination of K_s and K_o values in different conditions do not show much of a trend among themselves, the values suggest similar order of magnitude among K_s or K_o values demonstrating that binding constants of either the substrate or the oxidant with the micelle are not much affected by either acidity or temperature.

The magnitudes of K_s and K_o values clearly suggest that the substrate and the oxidant are partitioned between the micellar and aqueous phase. Substrate molecules being bound to the core of the micelle through hydrophobic binding and the oxidant is bound to the micellar surface by electrostatic forces. The explanation seems to be quite reasonable as the active oxidant species is positively charged (equn-1) and the micellar surface is negatively charged and most of the reactants being concentrated in the micellar pseudo phase causing higher reactivities.

This is borne out from the transfer free energy[6] values of both the reactants calculated by the expression.

$$-\Delta\mu^o = RTIn(55.5K)$$

and recorded in the table-VI. Relatively higher magnitude of $\Delta\mu^o$ for the substrate over that of the oxidant suggests the presence of the substrate in the core of the micelle orienting its active sites towards the outer surface of the micelle and the oxidant species present in the stem layer. This arrangement of the reactants probably facilitates the reaction in the micellar phase.

At higher [SLS] excluding cmc value the decrease in rate with increase in [SLS] is probably due to dilution of the reactants in the increased micellar concentration.

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