



Kinetics and mechanism of oxidation of cyclohexanol by Pyridinium dichromate – DMSO medium

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ABSTRACT

The kinetics of oxidation of cyclohexanol by PDC has been studied in non-aqueous medium. In this oxidation Cr (VI) is working as two-electron oxidizing agent. The reaction is first order with respect to each [oxidant], [TsOH] and [cyclohexanol]. The reaction is catalyzed by hydrogen ions. Low dielectric constant of the medium favors the reactivity. The observed experimental data have been rationalized as follows: the formation of dichromate ester in a fast pre equilibrium step and then decomposition of the ester in slow step via a compact transition state leading to the product, cyclohexanone.

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Introduction

Among the selectively acting oxo derivatives of variable valence metals, Chromium compounds play a most important role, because the oxidative reactions based on them can be readily carried out. The use of Chromium (VI) reagents in synthetic chemistry is the oxidation of alcohols to carbonyl compounds. Due to this alcohol oxidation with Cr (VI) compounds has been extensively investigated. Selective oxidation of organic compounds under non aqueous conditions is an important transformation in synthetic organic chemistry. For this, a number of different Cr (VI) derivatives have been reported [1-8]. Extensive studies on the mechanism of oxidation of cyclanols viz. cyclohexanol by several oxidants have been reported [9-15]. The literature on the kinetics of oxidation of cyclanols with various oxidant shows that the reactivity varies with the type of oxidant.

As a part of our investigation on the mechanistic aspects of the TsOH catalyzed Cr (VI) oxidations, we report the results of the TsOH catalyzed reaction of cyclohexanol by PDC.

Materials and Methods

PDC was prepared by reported method [16] and its purity is checked by an iodometric method. Para-toluene sulphonic acid (Merck) was used without further purification. The purity of the compound was checked by iodometric assay. Dimethyl sulphoxide was purified by method given in literature [17].

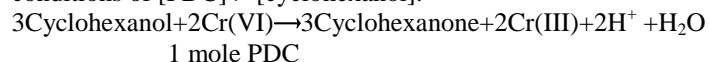
Pseudo-first order conditions were attained by keeping a large excess (10 times or greater) of the cyclohexanol over the oxidant. The reactions were carried out at constant temperature (± 1 K). The solvent was DMSO, unless stated otherwise. The reactions were followed by monitoring the decrease in the concentration of PDC at 350 nm for up to 80 % of the reaction. The Beer's law is valid for PDC within the concentration range used in our experiments. The pseudo-first order rate constant, k_{obs} , was evaluated from the linear plots of $\log [\text{PDC}]$ v/s time.

Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 5\%$. In correlation analyses, we have used Exner's parameter [18].

Results

Stoichiometry and Product Analysis

To determine the stoichiometry of reaction a known slight excess of Pyridinium dichromate was added to a known amount of cyclohexanol, by keeping all other condition of reaction is constant and after 12 hours the residual PDC was determined spectrophotometrically at 350 nm. The Stoichiometry of the reaction was found to correspond to the equation. It was determined by performing the experiment at 303 K, under the conditions of $[\text{PDC}] > [\text{cyclohexanol}]$.



The product analysis was carried out under kinetic conditions. In a typical experiment, cyclohexanol (0.05 mol) and PDC (0.005 mol) were made up to 50 cm³ in DMSO and kept 20 h to ensure completion of the reaction, was then treated with excess (200 cm³) of 2, 4-DNP in 2M HCl and was kept overnight in a refrigerator. The precipitated 2,4 dinitrophenyl hydrazones was filtered off, dried, weighed and recrystallized from ethanol and melting point was then determined. The DNP was found identical (m.pt. and mixed m.pt.) with the DNP of cyclohexanone.

The kinetics of oxidation of cyclohexanol by PDC was investigated at several initial concentrations of the reactants. The reaction proceeds smoothly at 303 K in non aqueous dimethyl sulphoxide medium and the observed results are discussed below.

Test for Free Radicals

The oxidation of cyclohexanol by PDC, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. In blank experiments, with the substrate absent, no noticeable consumption of PDC was observed. The addition of acrylonitrile had no effect on the rate of oxidation (Table 1).

Table 1. Effect of variation of [PDC], [Cyclohexanol] and [TsOH] on the reaction rates in solvent DMSO at 303 K

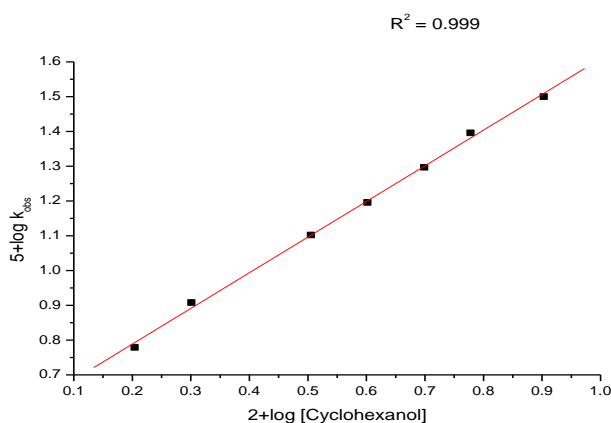
[PDC] 10^3 mole dm^{-3}	[Cyclohexanol] 10^2 mole dm^{-3}	[TsOH] 10^{-2} mole dm^{-3}	$k_{\text{obs}} \times 10^5$ s^{-1}
0.4	2.0	3.0	8.09
1.2	2.0	3.0	8.13
2.0	2.0	3.0	8.25
2.4	2.0	3.0	8.21
3.0	2.0	3.0	8.16
2.0	1.6	3.0	6.01
2.0	2.0	3.0	8.09
2.0	3.2	3.0	12.65
2.0	4.0	3.0	15.72
2.0	5.0	3.0	19.83
2.0	8.0	3.0	31.64
2.0	2.0	0.5	1.46
2.0	2.0	1.0	2.87
2.0	2.0	2.0	6.05
2.0	2.0	3.0	8.37
2.0	2.0	4.0	10.76
2.0	2.0	5.0	15.07
2.0(a)	2.0(a)	3.0(a)	8.01

(a) [acrylonitrile] = $0.001 \text{ mol dm}^{-3}$ **Effect of oxidant concentration**

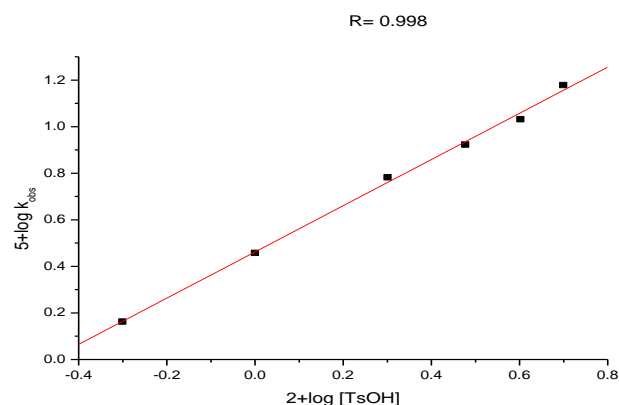
The reaction exhibits first-order dependence on the concentration of PDC. In individual kinetic runs, plots of \log [PDC] *v/s* time were linear. Further, the pseudo-first order rate constants do not depend on the initial concentration of PDC (Table 1). Evaluation of gradients of these lines gave the pseudo-first-order rate coefficients, k_{obs} .

Effect of substrate concentration

The order of the reaction with respect to cyclohexanol was determined by varying its concentrations over a wide range (Table 1). The order of the reaction with respect to the substrate i.e. cyclohexanol is 1.02. A plot of k_{obs} *v/s* [cyclohexanol] is shown in Figure 1. A plot of k_{obs}^{-1} *versus* [cyclohexanol] $^{-1}$ show negligible intercept on the rate axis, indicating the Michaelis-Menten independence on the concentration of the substrate (cyclohexanol).

**Figure 1. Variation of rate with substrate concentration****Effect of TsOH concentration**

The catalytic activity of para-toluene sulphonic acid is shown in Table 1. TsOH enhances the conversion of cyclohexanol. The rate of oxidation increases with an increase in acidity and the dependence is of the form – Rate = $k [\text{H}^+]$. The log-log plot of k_{obs} *v/s* $[\text{H}^+]$, for cyclohexanol, showed the slope = 0.99 and $R = 0.998$.

**Figure 2. Variation of rate with TsOH concentration****Effect of solvent composition**

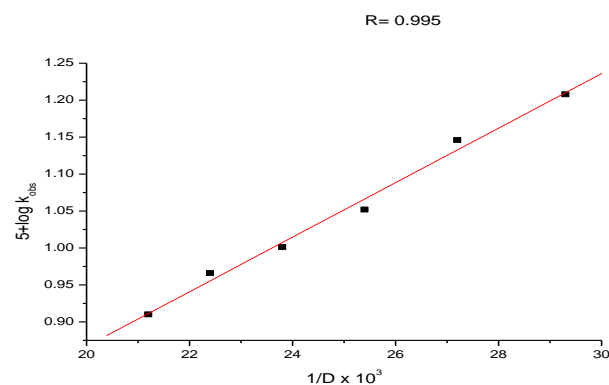
The acid-catalyzed oxidation of cyclohexanol was studied in solutions containing varying proportions of DMSO and Acetone (Table 2). Permittivity (D) values for DMSO : Acetone were estimated from the dielectric constants of the pure solvents [19] and are recorded. Low values of relative permittivity (dielectric constant), ϵ_r of the medium favours the reactivity. At fixed ionic strength and $[\text{H}^+]$ the rate of oxidation of cyclohexanol with PDC increases with decrease in polarity of solvent. In other words an increase in rate with decrease in dielectric constant of solvent is observed. According to Scatchard [20,21] the logarithm of the rate constant of a reaction between ions should vary linearly with the reciprocal of the dielectric constant if reaction involves ion-dipole type of interaction.

A plot of $\log k_{\text{obs}}$ against the inverse of permittivity ($1/D$) is linear ($R=0.995$) with a positive slope (Figure 3). This suggests an ion-dipole interaction in agreement [22] with the observation that in the presence of an acid, the rate-determining step involves a protonated Cr (VI) species. The increase in rate caused by the decrease in solvent polarity was attributed to an equilibrium shift favouring the formation of dichromate ester [23].

Table 2. Dependence of the reaction rate on solvent composition

DMSO : Acetone (v/v)	100:00	90:10	80:20	70:30	60:40	50:50
D	47.20	44.63	42.06	39.44	36.81	34.16
$k_1 \times 10^5$ (s^{-1})	8.13	9.24	10.02	11.26	13.98	16.14

[PDC] = 0.002 M, [Substrate] = 0.02 M, [TsOH] = 0.03 M and $T = 303 \text{ K}$

**Figure 3. Variation of rate with solvent composition**

Effect of temperature

This oxidation reaction was conducted at five different temperatures viz., 303, 308, 313, 318 and 323 K and the measured rate constant values were given in **Table 3**. The activation parameters have been calculated using the Eyring's plot [24]. Eyring's plot of $\log k_{\text{obs}}$ versus $1/T$ were linear ($R = 0.989$) (**Figure 4**) and the activation parameters were obtained from the slope and intercept of the Eyring's plot (**Table 4**).

The data shows that, the rate of reaction increases with increase in temperature and these reactions were characterized by negative value of entropy, suggests that the solvent molecules are strongly oriented around the ions, which results in the loss of entropy [25], the effect being larger in non-polar solvents. This confirms that, the decrease in polarity of medium results increase of the entropy values and the number of unbound molecules in the solution increases [26].

Table 3. Temperature dependence of the oxidation of cyclohexanol by PDC

T (K)	303	308	313	318	323
$k_f \times 10^5$ (s ⁻¹)	8.28	9.77	13.25	15.64	17.46

[PDC] = 0.002 M, [Cyclohexanol] = 0.02 M, [TsOH] = 0.03 M and Solvent = DMSO 100%

Table 4. Thermodynamic Parameters of Cyclohexanol

THERMODYNAMIC PARAMETERS	VALUES
Energy of Activation ΔE_a^\ddagger KJ mol ⁻¹	31.94
Free Energy ΔF^\ddagger KJ mol ⁻¹	80.27
Entropy of Activation ΔS^\ddagger J K ⁻¹ mol ⁻¹	-159.52

R= 0.989

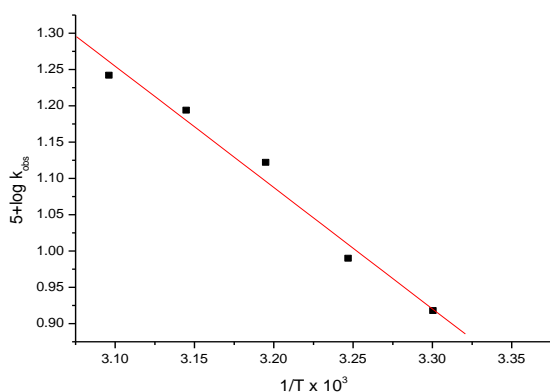


Figure 4. Variation of rate with Temperature

Discussion

Kinetics of oxidation of cyclohexanol by PDC was investigated at several initial concentrations of the reactants. At low concentrations of PDC and when substrates are in large excess, the reaction is found to be first order in PDC. The plot of $\log(a-x)$ i.e. \log absorbance against time is found to be linear, showing first order dependence in PDC. A plot of $\log k_{\text{obs}}$ v/s \log [Cyclohexanol] gave a straight-line with slope ≈ 1 showed first order dependence over substrate.

A study increase in the oxidation rate with an increase in the acidity of the medium suggests the formation of protonated PDC. The plot of $\log k_{\text{obs}}$ against $\log [H^+]$ is linear with a slope of nearly one. The proton may combine with alcohol or oxidant. Since protonation of alcohol is less probable it is more likely that

the proton is used by the oxidant (PDC). para- toluene sulfonic acid acts as a proton donating agent. Solvent dimethyl sulphoxide acts as a weak nucleophile it helps in the dissociation of H^+ ion from TsOH because DMSO is a powerful hydrogen bond acceptor. This is earlier shown by Kingsbury and others [27-29]. There have been earlier reports on the involvement of such Cr (VI) species in chromic acid oxidation [30], QDC, PDC [31-33] etc. Protonated Cr (VI) species have been observed in the presence of p-toluene sulfonic acid in nitrobenzene-dichloromethane mixtures [34,35]. The protonated PDC and alcohol combine to give intermediate, which was also indicated by increase in rate with decrease in dielectric constant of reaction medium.

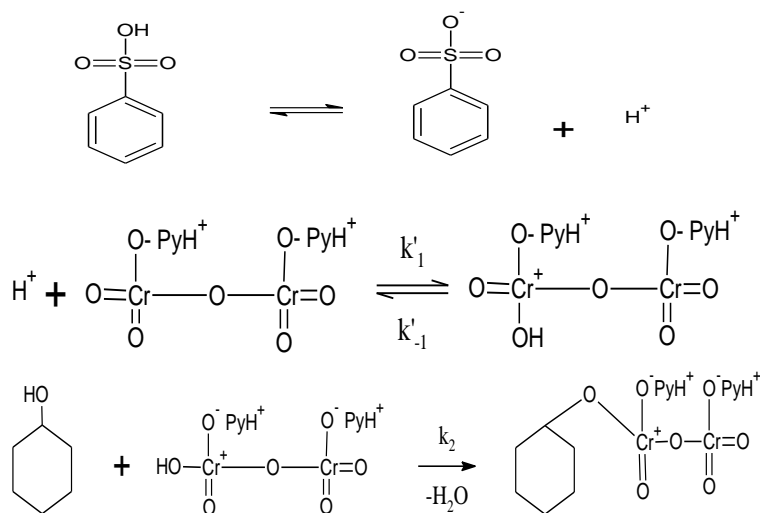
The insignificant rate variations with ionic strength may be attributed to the absence of ion-ion interactions in the rate-determining step. The rate constants increase significantly with increasing the acetone content of the solvent, suggesting a facile reactivity in a medium of low dielectric constant. In general, such rate enhancements in a less polar solvent are ascribed to the facility of formation of Cr (VI) ester [23,36]. Quite likely, the formation of dichromate ester in the present study is favoured in the medium of low permittivity.

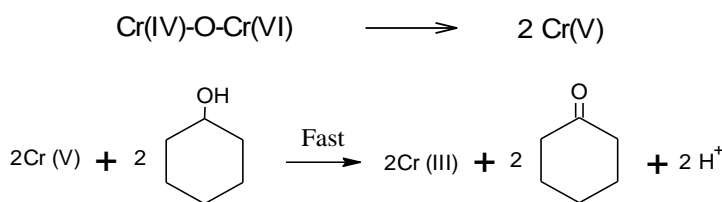
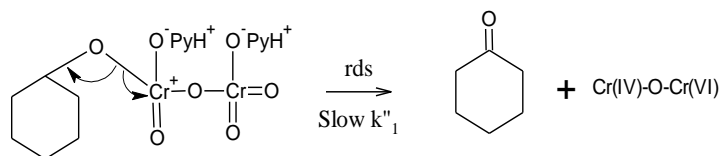
The proposed mechanism is, however, supported by the observed negative entropy of activation. As the charge separation takes place in the transition state, the two ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy. The negative activation entropy additionally accounts for the influence of solvent. Highly negative ΔS^\ddagger value ($159.52 \text{ JK}^{-1}\text{mol}^{-1}$) in the present investigation supports, to a certain extent, the compact structure. Initially Cr (VI) is reduced to Cr (IV). It is likely to rearrange with another Cr (VI) to give Cr (V) which is then reduced in a fast step to the ultimate product Cr (III).

A one-electron oxidation, giving rise to free radicals, is unlikely in view of the failure to induce polymerisation of acrylonitrile.

Hence, the overall mechanism is proposed to involve the formation of a dichromate ester in a fast pre equilibrium step and then a decomposition of the ester in a subsequent slow step via a compact state leading to the product, cyclohexanone.

Mechanism



**Rate Law:**

$$\text{Rate} = -d[\text{PDC}] / dt = k_1'' [\text{C}]$$

$$d[\text{H}^+\text{PDC}] / dt = k'_1 [\text{PDC}] [\text{H}^+] - k''_1 [\text{H}^+\text{PDC}] = 0$$

$$k'_1 [\text{PDC}] [\text{H}^+] = k''_1 [\text{H}^+\text{PDC}]$$

$$R = k_1'' k_2 [\text{Cyclohexanol}] [\text{H}^+\text{PDC}]$$

$$R = k_1'' k_2 [\text{Cyclohexanol}] \cdot (k'_1 / k''_1) [\text{H}^+] [\text{PDC}]$$

$$R = k_{\text{obs}} [\text{PDC}] = k_1 [\text{PDC}]$$

Where,

$$k_{\text{obs}} = k_1'' k_2 [\text{Cyclohexanol}] \cdot k'_1 / k''_1 [\text{H}^+] = k_1$$

$$k_1 = k_s [\text{Cyclohexanol}] [\text{H}^+]$$

where,

$$k_s = k_1'' \cdot k_2 \cdot k'_1 / k''_1 \text{ i.e. Specific rate constant.}$$

$$k_s = k_1'' / [\text{Cyclohexanol}] [\text{H}^+]$$

This rate law and suggested probable mechanism is consistent with all the observed experimental results suggesting that the reaction proceeds via the formation of a dichromate ester.

Conclusion

The reaction between cyclohexanol and PDC in presence of TsOH in DMSO medium gives cyclohexanone as a product. The oxidation of cyclohexanol by PDC is first order with respect to [PDC], [Cyclohexanol] and [TsOH]. The reaction was studied at different temperatures. In the temperature range of 303-323 K, Arrhenius equation is valid. The negative value of entropy indicates that the complex C is more ordered than reactant. The description of the mechanism is consistent with all experimental evidence.

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