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KINETICS AND MECHANISM OF THE OXIDATION OF GERANIOL BY IMIDAZOLIUM DICHROMATE

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Abstract

The kinetics of oxidation of primary allylic alcohol like geraniol by Imidazolium Dichromate (IDC) as an oxidant in acidic non-aqueous medium leads to the formation of aldehyde like geranial. Cr (VI) compound acts as two electron oxidizing agent in this oxidation reaction. The reaction is found to be first order with respect to each [Oxidant], [Alcohol] and [TsOH]. The reaction mixture failed to induce the polymerization of added acrylonitrile. The reaction is catalysed by hydrogen ions. The oxidation reaction of geraniol was studied in ten different organic solvents. The solvent effect was studied by using Kamlet's and Swain's multiparametric equations. Solvent effect shows the importance of the cation-solvating power of the solvent. The reaction has been carried out at four different temperature and the activation parameters were calculated. Negative $\Delta S^{\#}$ values indicate a structured transition state. A suitable reaction mechanism has been suggested.

KEYWORDS: Kinetics, Mechanism, Oxidation, Geraniol, Dichromate.

INTRODUCTION

Selective oxidation of various alcohols to their corresponding aldehydes and ketones is an important conversion in organic chemistry which has received the most attention over many years. Chromium (VI) oxidants are the most efficient and versatile for performing these conversions. So numbers of different chromium (VI) derivatives have been used as an oxidant[1-5]. One of such compounds is Imidazolium Dichromate (IDC) reported by S. Kim et al [6]

The literature survey on the kinetics of oxidation of allylic alcohols with different oxidant reveals that the reactivity of alcohols varies with the type of oxidant used[7-9].

As there is no report available on the oxidation of geraniol by IDC. We report here the kinetics of oxidation of geraniol by IDC in dimethyl sulphoxide (DMSO) as solvent. A suitable mechanism has also been proposed.

EXPERIMENTAL

MATERIALS:

IDC was prepared by the reported method[6] and its purity checked by an iodometric method. Geraniol (Merck) was used as supplied. Due to non-aqueous nature of the solvent, p-toluene sulphonic acid (TsOH) was used as a source of hydrogen ions. Purification of other solvents was carried out by the usual methods of purification[10].

PRODUCT ANALYSIS:

Product analysis was carried out under kinetic conditions. In a typical experiment, Geraniol (0.05 mol) and IDC (0.005 mol) were made up to 50 cm^3 in DMSO and kept for 24 h to ensure completion of the reaction. The oxidation state of chromium in completely reduced reaction mixtures was determined iodometrically and it was found to be +4.

At the end of the reaction, the reaction mixture was taken in ether. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and then concentrated. The product was geranial, whose boiling point agreed with the boiling point reported in the literature. The yield was ~ 80-85%. IR analysis gave carbonyl band at $1685 cm^{-1}$(geranial).

The 2,4-dinitrophenylhydrazone (DNP) derivative of geranial was prepared, and recrystallized from ethanol, dried and weighed (DNP of geranial, m.p. 107°C) The yields of DNP, after recrystallization, were ~ 80-83%.

KINETIC MEASUREMENTS:

The pseudo-first order conditions were attained by maintaining a large excess (×10 or more) of the geraniol over IDC. The solvent used was DMSO. The reactions were followed, at constant temperatures (± 0.1 K), by monitoring the decrease in [IDC] spectrophotometrically at 360 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear (r^2 = 0.990 - 0.999) plots of log [IDC] against time for up to 80% reaction. Duplicate kinetic runs showed that, the rate constants were reproducible to within ± 3%. The second order rate constant, k_2, was evaluated from the relation shown by given formula like $k_2 = k_{obs}/[Geraniol]$. Simple and multivariate linear regression analyses were carried out by the least-squares method on a personal computer by using software RegressIt.

RESULTS AND DISCUSSION

The kinetics of oxidation of geraniol by IDC was studied at different initial concentrations of geraniol in non-aqueous medium and the observed results are discussed below.

STOICHIOMETRY:

The oxidation of geraniol by IDC resulted in the formation of the geranial. The overall reaction may therefore, be represented as equation (1). The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amount of [IDC] over excess [Geraniol]. The estimation of unreacted IDC showed that three moles of alcohol reacts with one mole of IDC.

$$\underset{\text{Geraniol}}{3C_9H_{15}CH_2OH} + \underset{\text{IDC}}{[C_3H_5N_2]_2\,Cr_2O_7} \longrightarrow \underset{\text{Geranial}}{3C_9H_{15}CHO} + 2Cr(III) + 2H_2O + 2H^+ \text{-----(1)}$$

TEST FOR FREE RADICALS:

The oxidation of geraniol by IDC, in an inert atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. In blank experiments, in absence of substrate, there was no noticeable consumption of

IDC. It shows that, the addition of acrylonitrile has no effect on the reaction mixture indicating the absence of free radical mechanism. This indicates a one electron oxidation giving rise to free radicals is unlikely in the present reaction.
Further confirmation for the absence of free radicals during the course of the reaction was checked by adding 0.05 mol dm-3 of 2, 6-di-t-butyl-4-methylphenol (butylated hydroxyl toluene or BHT) in reaction mixture. It was found that, BHT was recovered unchanged, almost quantitatively.

EFFECT OF OXIDANT CONCENTRATION:

At constant [Substrate] and [TsOH], the increase in [IDC] did not affect the rate of reaction. The reactions were found to be first order with respect to IDC. The **Figure-1** and **Table-1** shows a typical kinetic run. In individual kinetic runs, plots of log [IDC] versus time were linear (r^2> 0.990). Further, it was found that the observed rate constant, k_{obs}, does not depend on the initial concentration of IDC.

EFFECT OF SUBSTRATE CONCENTRATION:

At constant [IDC] and [TsOH], the reaction rate increases linearly with increase in the [Geraniol], indicating first order dependence with substrate. **Figure-2** shows the plot of log k_{obs} versus log [Geraniol] gave a straight line with unit slope indicating the first order dependence on substrate. The second order rate constant k_2 is constant suggesting the first order dependence on [Geraniol]. A double reciprocal plot of 1/k_{obs} against 1/[Geraniol] is linear and passing through the origin (r^2> 0.995) as shown in **Figure-3**. It shows first order behavior of this oxidation process and further suggested that no stable complex between IDC (oxidant) and substrate is formed.

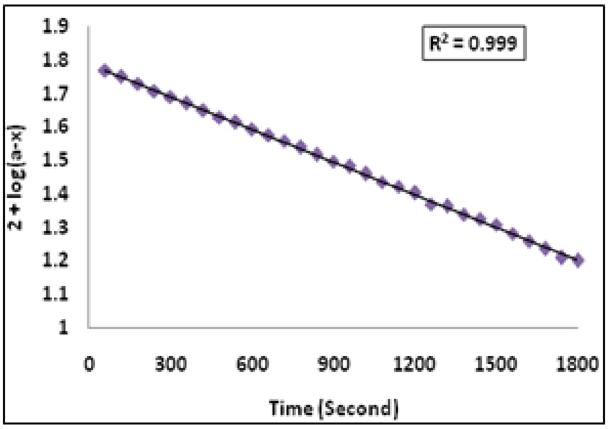


Figure-1: Oxidation of Geraniol by IDC: A typical Kinetic Run

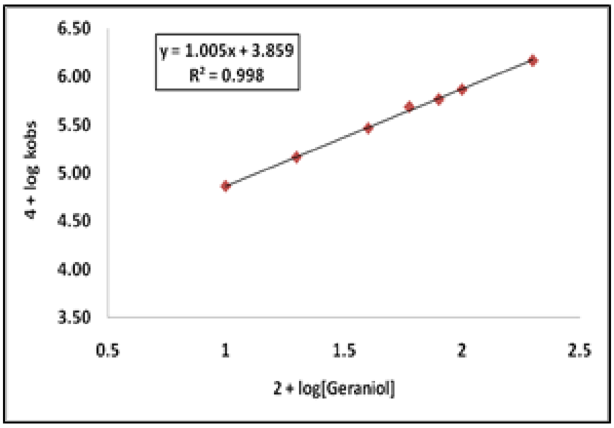


Figure-2: The plot of log k_{obs} versus log [Geraniol]

EFFECT OF TsOH CONCENTRATION:

The reaction is catalyzed by hydrogen ion; the acid catalysis may well be attributed to the protonated ion of IDC to give a stronger oxidant and electrophile. The rate of reaction increases with increase in TsOH concentration as shown in **Table 2**. The plot of log k_{obs} versus log $[H^+]$ are also straight line with nearly unit slope, indicating a first order dependence on $[H^+]$ is shown in **Figure 4.**

EFFECT OF TEMPERATURE:

The rate of oxidation of geraniol by IDC was obtained at different temperatures between 300K and 315K. The values of rate constant (k_2) are recorded in **Table 3**. The activation parameters for the oxidation of geraniol by IDC were calculated from the values of k_2 at different temperatures **(Table 3)**. The log $k_2$values at different temperatures is linearly related to the inverse of the absolute temperatures **(Figure 5).** It proves that, the Arrhenius equation is valid for this reaction.

Table-1: Rate constants for the oxidation of geraniol by IDC at 300K.

10^3[IDC] (mol dm^{-3})	[Geraniol] (mol dm^{-3})	[TsOH] (mol dm^{-3})	$10^4 k_{obs}$ s^{-1}
1.0	0.10	0.10	*7.30*
1.0	0.20	0.10	*14.5*
1.0	0.40	0.10	*29.1*
1.0	0.60	0.10	*48.3*
1.0	0.80	0.10	*58.1*
1.0	1.00	0.10	*73.2*
1.0	2.00	0.10	*147*
2.0	0.10	0.10	*7.32*
4.0	0.10	0.10	*7.31*
6.0	0.10	0.10	*7.34*
8.0	0.10	0.10	*7.33*
1.0	0.10	0.10	*7.32**
**Contained 0.001M Acrylonitrile*			

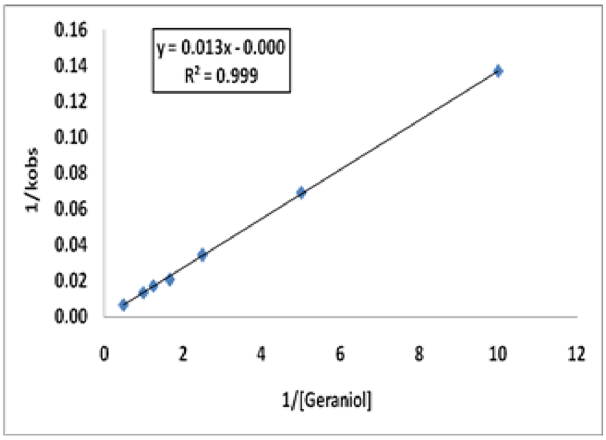


Figure-3: A double reciprocal plot of $1/k_{obs}$ against 1/[Geraniol]

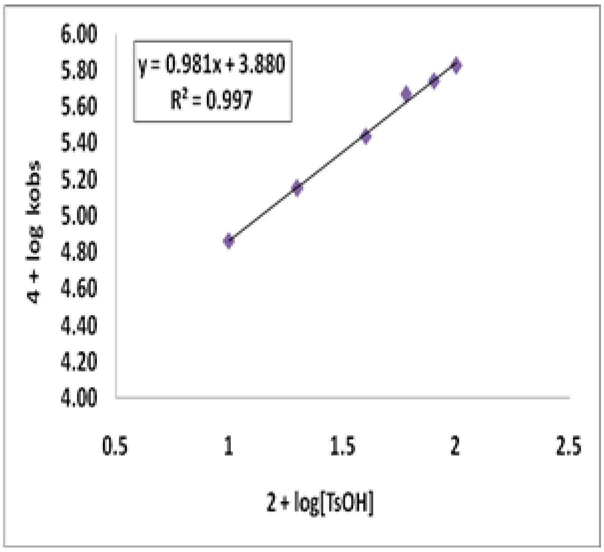


Figure-4: The plot of log kobs versus log [H+]

Rate Laws:

Rate = k' [Oxidant] [Substrate] [H^+]

Rate = k_{obs} [Oxidant]

k_{obs} = k' / [Substrate] [H^+]

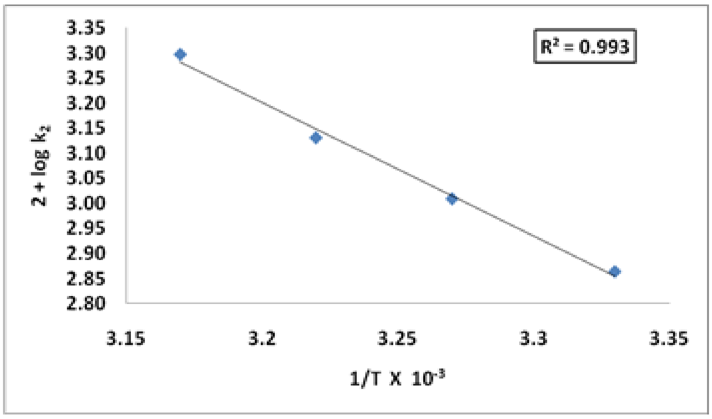


Figure-5: Effect of temperature on rate (Arrhenius plot)

Table-2: Dependence of the reaction rate on hydrogen-ion concentration.

[IDC] = 0.001 mol dm^{-3} ; [Geraniol] = 0.1 mol dm^{-3} ; Temp. = 300K						
[TsOH] /mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{obs}$/s^{-1}	7.30	14.1	27.5	46.2	55.3	66.9

Table-3: Rate constants and activation parameters for the oxidation of Geraniol by IDC.

10^4 k_2 / (dm^3 mol^{-1} s^{-1})				**$\Delta H^{\#}$ (KJ mol^{-1})**	**$\Delta S^{\#}$ (J mol^{-1} K^{-1})**	**$\Delta G^{\#}$ (KJ mol^{-1})**	**Ea (KJ mol^{-1})**
300 K	**305 K**	**310 K**	**315 K**				
7.30	10.2	13.5	19.8	48.85	–142	92.60	51.41

EFFECT OF SOLVENT:

Solvent plays important role during chemical reactions. The effect of solvent on the rate of any reaction can be described in terms of solvation which is a process of stabilization. The rates of oxidation of geraniol were obtained in ten different organic solvents. The selection of solvent was limited due to solubility of IDC and its reaction with the solvent like alcohols. There was no reaction with the solvents selected for study. Similar type of kinetics is observed in all selected solvents. The values of second order rate constants, k_2 are presented in **Table 4**.

Table-4: Effect of solvents on the oxidation of Geraniol by IDC at 300K.

Solvents	**10^5 k_2 / (dm^3 mol^{-1} s^{-1})**	**Solvents**	**10^5 k_2 / (dm^3 mol^{-1} s^{-1})**
Cyclohexane	0.89	Acetic Acid	6.79
Benzene	7.54	Dichloromethane	22.9
Toluene	7.11	Acetophenone	26.3
Chloroform	24.5	Acetone	23.9
Ethyl Acetate	8.73	DMSO	73.0

The rate constants, k_2, in ten different solvents were correlated in terms of the linear solvation energy relationship (Equation 2) presented by Kamlet *et al*[11].

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \qquad \text{.....................(2)}$$

The solvatochromic parameters in above equation (2) like π^*, β and α are characteristic of different solvents. π^* indicates the solvent polarity which is a measure of the ability of solvent to stabilize a dipole or charge due to its dielectric effect. β Indicates the hydrogen bond acceptor basicity which is the ability of solvent to donate an electron pair or to accept a proton in a hydrogen bond between solute to solvent. α shows the hydrogen bond donor acidity which is the ability of a solvent to donate a proton, or accept an electron pair in a hydrogen bond between solute to solvent.

A_0 is the intercept term. It may be state here that, out of the ten solvents shown in **table-4**, six solvents has a value of zero for α . In our correlation analyses, we have used the coefficient of determination (R^2 or r^2), Standard deviation (SD) and Exner's statistical parameter[12], ψ as the measures of the goodness of fit. We analyses the results of correlation in terms of equation (2), a biparametric equation involving a solvatochromic parameters π^* and β, and separately with π^* and β are given below by Equations (3) - (6)

$$\log k_2 = -5.02 + 1.74 (\pm 0.37)\pi^* + 0.092 (\pm 0.41)\beta - 0.076 (\pm 0.26)\alpha \qquad \text{..........(3)}$$
$r^2 = 0.878$; SD = 0.22; $n = 10$; $\psi = 0.35$

$$\log k_2 = -5.02 + 1.69 (\pm 0.31)\pi^* + 0.16 (\pm 0.30)\beta \qquad \text{..................(4)}$$
$r^2 = 0.877$; SD = 0.20; $n = 10$; $\psi = 0.35$

$$\log k_2 = -5.04 + 1.79 (\pm 0.24)\pi^* \qquad \text{.....................(5)}$$
$r^2 = 0.871$; SD = 0.19; $n = 10$; $\psi = 0.36$

$$\log k_2 = -4.18 + 1.11 (\pm 0.52)\beta \qquad \text{......................(6)}$$
$r^2 = 0.357$; SD = 0.44; $n = 10$; $\psi = 0.89$

Here, n represents the number of data points considered in analysis. When kinetic data is correlated with solvatochromic parameters π^*, β and α by using Kamlet's[11] triparametric equation suggests ca. 88% of the effect of solvent on the oxidation. However, according to Exner's criterion[12] the correlation is not even satisfactory (cf. equation 3). Only the solvent polarity parameter gives major contribution. It alone contributed for *ca.* 87% of the data. The solvatochromic parameters like β and α play relatively minor roles and contributed less.

We also used Swain's method for the examination of solvent effect. The data on the solvent effect were analysed by using Swain's equation[13] of cation and anion-solvating concept of the solvents (Equation 7).

$$\log k_2 = aA + bB + C \qquad \text{.............(7)}$$

Here in above equation, A indicates the anion-solvating power of the solvent and B indicates the cation-solvating power. C is the intercept term and (A+B) is used to indicate the solvent polarity. The rates in different solvents were analysed by using equation (7), separately with A and B and with (A+B).

$$\log k_2 = 0.84 (\pm 0.06) A + 1.63 (\pm 0.05) B - 5.16 \quad \ldots\ldots\ldots\ldots\ (8)$$

$r^2 = 0.994$; SD = 0.04; n = 10; $\psi = 0.07$

$$\log k_2 = 0.50 (\pm 0.71) A - 4.06 \quad \ldots\ldots\ldots\ldots (9)$$

$r^2 = 0.057$; SD = 0.53; n = 10; $\psi = 1.23$

$$\log k_2 = 1.52 (\pm 0.23) B - 4.85 \quad \ldots\ldots\ldots\ldots (10)$$

$r^2 = 0.837$; SD = 0.22; n = 10; $\psi = 0.41$

$$\log k_2 = 1.34 \pm 0.15 (A + B) - 5.15 \quad \ldots\ldots\ldots\ldots (11)$$

$r^2 = 0.90$; SD = 0.17; n = 10; $\psi = 0.32$

Swain's equation (Equation-8) shows an excellent correlation for the rates of oxidation of geraniol in different solvents. Only the parameter like cation-solvating power gives major contribution. Cation-solvation alone contributed for *ca.* 84 % of the data (Equation-10).The parameter like anion-solvating power contributed less.

The solvent polarity parameter is represented by (A+B), also contributed for *ca.* 90 % of the data (Equation-11). The rate of reaction was also correlated with the relative permittivity of the solvent. But it was found that, a plot of log k_2 against the inverse of the relative permittivity is not linear ($r^2 = 0.673$; SD = 0.31; $\psi = 0.59$). Indicating that the reaction rate depended on more than one solvent property.

MECHANISM

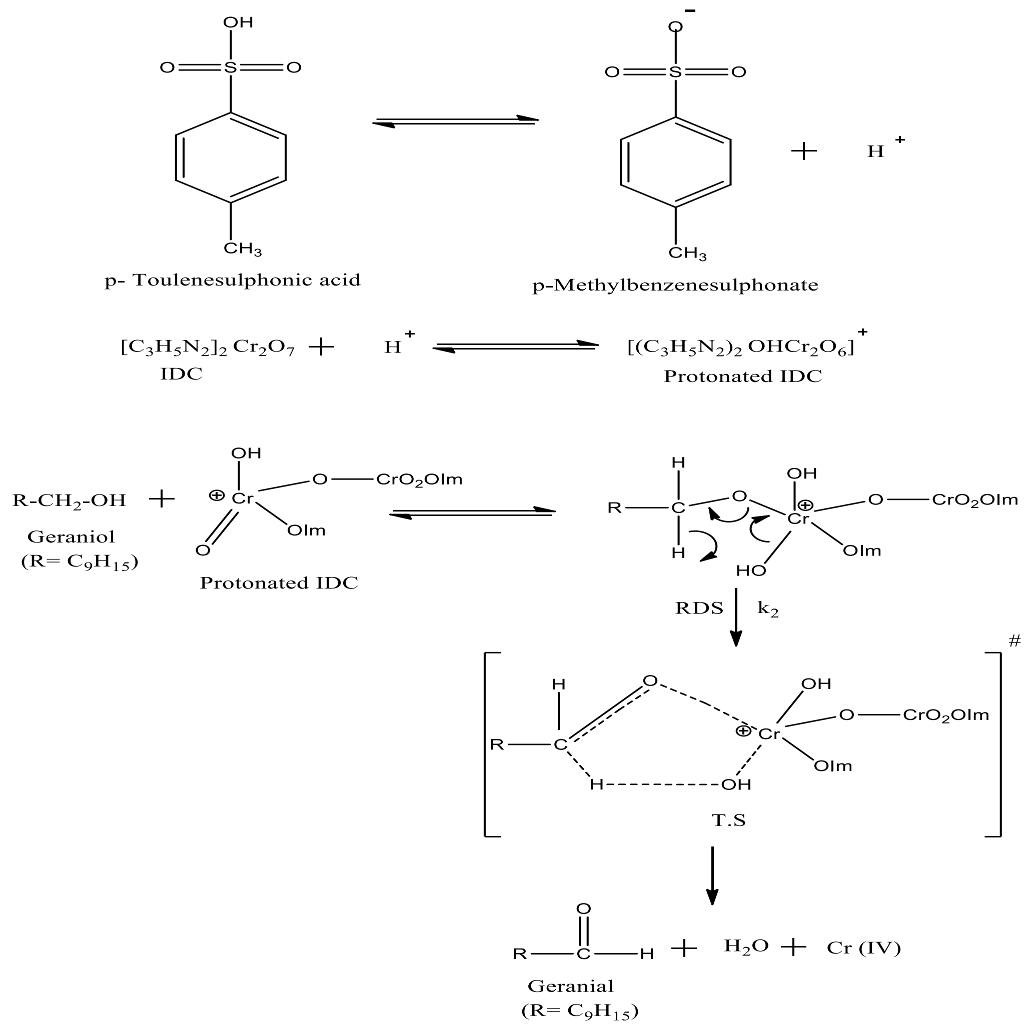
As the reaction is showing first order dependence with respect to oxidant, H^+ ion and substrate. These two species should be involved in the slow step. The large increase in reaction rate with increase in acidity suggests the presence of protonated Cr^{+6} species in the rate determining step.

Since the protonation of alcohol is less probable, there is possibility that the proton is used by the IDC. TsOH acts as a proton donnar. Solvent dimethyl sulphoxide acts as a weak nucleophile which helps in the dissociation of H^+ ion from TsOH because DMSO is a powerful hydrogen bond acceptor, earlier suggested by Kingsbury[14].

The formation of chromate ester as an intermediate in a pre-equilibrium step has been reported earlier in chromic acid oxidation[15], also in the oxidation of alcohols by TriEACC[4], QDC[16], PFC[17], BTEACC[18] etc.

Bordwell[19] has suggested convincing proof against the occurrence of concerted one-step biomolecular processes by hydrogen transfer. It is well introduced that intrinsically concerted sigmatropic reactions, depicted by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer[20]. Littler[21] has also presented that a cyclic hydride transfer takes place in the oxidation of alcohols by Cr (VI) oxidant which involves six electrons and becomes a Huckel-type of system, is an allowed process. Thus, a transition state having a planar, cyclic and symmetrical structure can be predicted for the decomposition of the ester intermediate.

The protonated IDC and alcohol combine to give intermediate. The rate determining step is the decomposition of the chromate ester via cyclic transition state and it involves the ruptures of α C-H bond and forming the product[22, 23]. The overall mechanism suggests the formation of a chromate ester in a fast pre-equilibrium step and then decomposition of the ester intermediate in a subsequent slow step via formation of cyclic concerted symmetrical transition state giving the product. The observed negative value of entropy of activation also supports a polar transition state. The mechanism proposed is shown as **scheme-1**.



Scheme-1: Mechanism of oxidation of geraniol by IDC

CONCLUSION

The reaction was first order with respect to substrate, oxidizing agent and TsOH concentration. The oxidation of geraniol by IDC failed to induce the polymerization of acrylonitrile, confirms a two-electron transfer reaction. Protonated form of IDC is the reactive oxidizing species. The oxidation of geraniol involves the formation of dichromate ester which on decomposition giving the product. A α C-H bond is cleaved in rate-determining step.

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