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1,3-Dichloro-5,5-Dimethylhydantoin mediated oxidation of unsaturated alcohols in aqueous acetic acid medium

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Abstract: In this perspective, the use of redox process are addressed in kinetic study of unsaturated alcohols (α-crotyl and cinnamyl alcohols) by DCDMH. Kinetic evidence for the formation of a DCDMH– unsaturated alcohol 1:1 complex has been assigned. The rate-limiting step involves the breaking of the α-C-H bond to afford corresponding aldehydes in good yields, and oxidizing ability of DCDMH species have been discussed. Mechanism with the associated reaction kinetics is assigned in accordance with the rate law and kinetic parameters.

Key words: 1,3-dichloro-5,5-dimethylhydantoin, α-crotonic acid, cinnamic acid, oxidation, kinetics.

1. INTRODUCTION

The unsaturated alcohols have long been known as natural products widely employed in synthetic polymers, biochemical processes and in the food industry. These alcohols exhibit a variety of reactions owing to presence of double bond and -CH₂OH alcoholic group. The processes of oxidation of unsaturated alcohols have become the subject of numerous studies.[1] The polymer molecules have C-C chain skeleton which can also form the site of depolymerization.[2]

1,3-dichloro-5,5-dimethylhydantoin (DCDMH) emerged as a useful novel and efficient halo oxidant. The chemistries of reactions involving DCDMH has been extensively studied in the oxidation[3-7] and synthesis[8,9] of various organic reagents in the past two decades. Literature survey shows that kinetics of reduction of the unsaturated alcohols to their aldehydes have been rarely available and documented with different oxidants viz. SeO₂,[11] NCS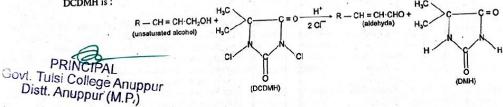A,[12] NaOCl,[13] (NH₄)₂Cr₂O₇ [14] etc. However, the mechanism of crotyl alcohol, and cinnamyl alcohol- DCDMH remains poorly understood. Therefore, it was thought worthwhile to carry out the dynamics of unsaturated alcohols with DCDMH reaction to elucidate their mechanism in this article.

2. EXPERIMENTAL

Reagents: Analytical reagent grade or high purity chemicals were used in research mostly. α-crotyl and cinnamyl alcohols (B.D.H.) was used after its dissolution in demineralized water. The commercial sample of DCDMH (Across) was dissolved in required 80% acetic acid and standardized iodometrically.

Kinetic procedure

A thermostat fitted with thermoregulated thermometer and variable speed magnetic stirrer was used for the kinetic experiments. The temperature of the water bath (308 K) was regulated with a precession of ± 0.1°C. Pseudo first-order conditions were maintained in all runs by using a large excess of [unsaturated alcohol] ≥ ten-fold [DCDMH]. All kinetic measurements were made using freshly prepared solutions. Rate constant (k_{obs}) obtained from multiple determinations were within ± 3% error.

The kinetic study of the reaction was approached by the method of initial velocities adopting to physically control the reaction rate. Reaction was initiated by mixing requisite amount of DCDMH to the other content of the reaction vessel. Progress of the DCDMH-unsaturated alcohol was monitored at regular intervals of time volumetrically by iodometric process. The k_{obs} was evaluated by employing integration method.

3. Stoichiometry and Product analysis

Stoichiometry of the reaction was determined using 1:10 molar ratios of unsaturated alcohol and DCDMH and with excess of [H⁺]. After about 48 h reaction duration, the residual [alcohol] was estimated periodically by iodometric method. The stoichiometric ratio was in the range of 1:1 for unsaturated alcohol : DCDMH. The stoichiometric equation for the unsaturated alcohol oxidation by DCDMH is :

where, R = -CH_3 and C_6H_5 - for corresponding α-crotyl and cinnamyl alcohols and DMH is abbreviation of dimethyl hydantoin respectively.

To identify the nature of the products formed in the reactions were characterized by comparison with the authenticated samples and m.p. of 2:4 DNP derivatives (yield 75 to 80% range) and by TLC method provide supporting evidence for the formation of reaction products. The free radicals test with reaction mixture was found negative with acryloamide thus ignoring its presence and to take into account of dealing mechanism.
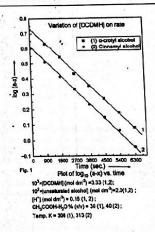
4. Results and Discussion
Effect of [DCDMH] on reaction

Initial rates were directly proportional to [DCDMH] (Table 1) and liner curves obtained from the plots of log [DCDMH] against time (Fig. 1).The unit slope derived from the curves show that order with respect [DCDMH] is one i.e. independent of [DCDMH] oxidant.

Table 1: Variation of [DCDMH] on rate

$10^3 \times$[DCDMH] (mol dm^{-3}) =3.33 (1,2); $10^2 \times$[unsaturated alcohol] (mol dm^{-3})=2.0(1,2) ;
CH$_3$COOH-H$_2$O % (v/v) – 30 (1), 40 (2) ; Temp. K = 308 (1), 313 (2)

1.	α-crotyl alcohol							
Time (sec.)	0	900	1800	2700	3600	4500	5400	6300
log$_{10}$ (a-x)	0.7267	0.6334	0.5440	0.4339	0.3521	0.2671	0.1760	0.0791
10^4 k (sec^{-1})	-	2.38	2.33	2.45	2.39	2.35	2.34	2.36
2.	cinnamyl alcohol							
Time (sec.)	0	1200	2400	3600	4800	6000	7200	8400
log$_{10}$ (a-x)	0.6020	0.5118	0.4149	0.3324	0.2304	0.1461	0.0606	-0.0457
10^4 k (sec^{-1})	-	1.73	1.79	1.72	1.78	1.75	1.73	1.77

* 1. N/800 Sodium thiosulphate solution used, a = 5.33 ml
* 2. N/600 Sodium thiosulphate solution used, a = 4.00 ml

Fig. 1   Plot of log$_{10}$ (a-x) vs. time

$10^3 \times$[DCDMH] (mol dm^{-3}) =3.33 (1,2);
$10^2 \times$[unsaturated alcohol] (mol dm^{-3})=2.0(1,2) ;
[H$^+$] (mol dm^{-3}) = 0.15 (1, 2) ;
CH$_3$COOH-H$_2$O % (v/v) = 30 (1), 40 (2) ;
Temp. K = 308 (1), 313 (2)

Dependence of Reaction Dynamics on Unsaturated Alcohol

The initiated oxidation of individual unsaturated alcohol accelerates the reaction, however, a ratio of k / [unsaturated alcohol] is at very low content of substrate not constant, but in the higher concentration region where its inhibitory effect is observed, the study reveals a complex kinetics between reacting species of oxidant (DCDMH) and substrate at apex point indicating fractional-order kinetics as evidenced by double reciprocal plots of 1/ k$_{obs}$ vs. 1/[substrate] with non-zero intercept on ordinate axis.

Dependence of reaction dynamics on [H$^+$]

The [H$^+$] has significance influence on the rate of dynamics. An increase in acid concentration significantly increased the initial rate and reduced the induction time (Table 2) indicating direct participation of H$^+$ in the rate-determining step. The log initial rate vs. log [H$^+$] plot (Fig. 2) is fairly linear, gave gradient (0.998) confirming first-order dependence with respect to [H$^+$] ion.

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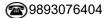Jaithari Road Anuppur, District- Anuppur, Madhya Pradesh, Pin Code:- 484224 www.gtcanuppur.ac.in

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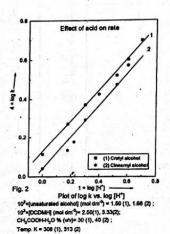Registered Under Section 2 (F) & 12 (B) of UGC Act

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Table 2 : Effect of acidity on rate
$10^2 \times$[unsaturated alcohol] (mol dm^{-3}) = 1.50 (1), 1.66 (2) ;
$10^3 \times$[DCDMH] (mol dm^{-3})= 2.50(1), 3.33(2); CH$_3$COOH-H$_2$O % (v/v)= 30 (1), 40 (2) ;
Temp. K = 308 (1), 313 (2)

[H$^+$] (mol dm^{-3})	10^4 k (s^{-1})	
	α-crotyl alcohol	cinnamyl alcohol
0.100	1.30	-
0.125	-	1.10
0.150	1.87	-
0.166		1.36
0.200	2.35	1.50
0.250	-	1.96
0.333	4.03	2.67
0.400	4.79	2.98
0.500	5.81	3.74

Fig. 2 Plot of log k vs. log [H$^+$]
$10^2 \times$[unsaturated alcohol] (mol dm^{-3}) = 1.50 (1), 1.66 (2) ;
$10^3 \times$[DCDMH] (mol dm^{-3})= 2.50(1), 3.33(2);
CH$_3$COOH-H$_2$O % (v/v)= 30 (1), 40 (2) ;
Temp. K = 308 (1), 313 (2)

Effect of solvent polarity on reaction rate

The reactions were investigated at four different compositions of acetic acid water binary mixtures. The slight enhancement in the oxidation was observed with the increase in the percentage of acetic acid. The Amis plot of log k vs. 1/D is linear with positive slope indicates the decrease in the dielectric constant of the medium shows that reaction is positive ion-dipolar type.

The neutral primary salt, sodium chloride when added to reaction mixture had shown no appreciable affect on oxidation rate. The dimethyl hydantoin (DMH), a reductant product of oxidant DCDMH in different range of concentrations when added to reaction did not show any substantial effect on rate except slow retardation in rate of oxidation. This fact indicates that free radicals based mechanism is completely ruled out in the reactions under investigation.

Reaction mechanism

A possible mechanism which would account for the observed kinetics involves the oxidation of unsaturated alcohols with DCDMH to form complex which then undergoes a redox reaction in a rate determining loss of hydride ion may be proposed. Hypochlorous (HOCl) generated in the system and its protonated form (H$_2$O$^+$Cl) could also attack both the reducing substrate.

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Rate law

The rate law corresponding to this mechanism may be expressed as in equation:

$$Rate = \frac{d}{dt}[complex] = k_1[complex(Y)] + k_2[complex(Z)] \ldots (7)$$

using the mass balance for the DCDMH the rate law (8) was obtained as :

$$k_{obs} = \frac{K_1[S](k_3 k_1 + K_2 k_4 k_2[H^+])}{[DMH] + K_1 + K_1 k_3[S] + K_1 k_2[H^+](1 + K_4[S])} \ldots (8)$$

At higher [S], equation (8) reduces as :

$$k_{obs} = \frac{K_1[S](k_1 K_3 + k_2 K_2 K_4[H^+])}{K_1 k_2[H^+](1 + K_4[S])} \ldots (9)$$

Equation (9) can be rewritten as equation (10)

$$\frac{1}{k_{obs}} = \frac{1}{[S]}\left[\frac{\{DMH\} + K_1}{K_1(k_1 k_3 + k_2 K_2 K_4[H^+])}\right] + \frac{K_3}{(k_1 k_3 + k_2 K_2 K_4[H^+])} \ldots (10)$$

Plots of $1/k_{obs}$ against $1/$[unsaturated alcohol]$_t$ show the expected linear relationship. The Burk- Line-Weaver type double reciprocal plot (i.e. $1/k_{obs}$ vs. $1/$[unsaturated alcohol]) is linear with positive intercept indicating the association of unsaturated alcohol and DCDMH in some pre-equilibrium steps before the electron transfer step.

This indicates that redox reaction in a rate-determining step is in correlation with reactivity.

The unsaturated alcohols studied reveal the order of reactivity as :

α-crotyl alcohol > cinnamyl alcohol.

The existence of ester hypo chlorite formation in pre-equilibrium step directly detachment of hydrogen from, may be departed carbon as H⁺ due to C-H bond cleavage in a slow process. Differin g in their configuration of terminal -CH = CH-, -CH₂OH end, size of ionic radii of additives, besides chain lengths are the main reasons of above reactivity order.

The α-crotyl consists of highest alcoholic percentage showing fastest rate rather than cinnamyl alcohols having lowest alcoholic content form. The cinnamic alcohol has bulky phenyl group (C_6H_5). The cleaved C-H bond is proved by the loss of translational and rotation degree of freedom.

The two ends become highly solvated consequently an immobilization of a large number of solvent molecules cause above loss in in entropy of activation of polar nature of complex at transition state. The oxidation is due to driving force pushing towards a bond sufficient to expel the proton in the reaction. Moreover, water molecule acts as a Lewies base[15] to abstracting agent for proton in slow process.

The examination of Table 3 furnishes ample of evidence that the values of Arrhenius parameters equation was found to be valid i.e. E_a is lowest for fastest reaction and vice-versa as cited in reverse order of reactivity. The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ are in well

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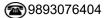### Affiliated to Awadhesh Pratap Singh University Rewa (MP)
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accordance with the reactivity specifically that reactions are enthalpy and entropy controlled. In the same continuation, the values of Gibbs free energy ($\Delta G^{\#}$) lie in a close proximity with one and other leads the existence of prevalence of same mechanistics paths involved in the system.

Table 3 : Thermodynamic parameters for the Michaelis-Menten type of kinetics of the reaction between unsaturated alcohols and DCDMH

Unsaturated alcohol	Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})
α-crotyl alcohol	36.68	34.24	87.06	-170.83
Cinnamyl alcohol	67.37	64.46	89.34	-78.85

CONCLUSION

The prime steps of proposed mechanism proceed through deprotonation of C-H bond. The polar nature of complex at compactness of transition state follows Michaelis-Menten model of kinetics. The order of reactivity of α-crotyl alcohol > cinnamyl alcohol was discussed based on electron withdrawing of C_6H_5 group, ± I effect and differing configuration. The HOCl and H_2O^+Cl species of oxidant participated in reaction mechanism with stoichiometry 1:1 were found in accordance with derived rate law. The corresponding aldehydes were identified as the main products of the unsaturated alcohol- DCDMH reactions.

Conflict of Interest

The authors declare conflict of no interest whatsoever.

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