Kinetic Study of Allyl Alcohol by 1,3-Dichloro-5, 5-Dimethylhydantoin in Aqueous acetic acid medium

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Abstract: A kinetic study of the initiated oxidation of allyl alcohol by 1,3-dichloro-5,5-dimethylhydantoin in aqueous acetic acid medium was reported. Kinetic evidence for the formation of a DCDMH- allyl alcohol 1:1 equilibrium constant for its formation has been determined. The rate-limiting step of the oxidation reaction involves the breaking of the C-H bond in the reaction to yield product acrolein. A multi-step reaction mechanism is proposed with the experimental results.

Key words: Allyl alcohol, 1,3-dichloro-5,5-dimethylhydantoin, kinetics, oxidation, stoichiometry.

1. INTRODUCTION
The process of oxidation of alcohols have become the subject of several studies. In particular, oxidation of allyl alcohol, the main oxidation product of which acrolein is a great importance of synthetic, polymer (textile), biochemical industries owing to its degradation includes the C-C fission and oxidation is an alternative for selective depolymerization.

A considerable number of studied have been devoted to allyl alcohol and was extensively investigated to with different oxidizing agents such as SeO₂, NCSA, ammonium dichromate, ammonium hexanitratocerate(IV). The newly synthesized halo-oxidant 1,3-dichloro-5,5-dimethyl hydantoin (DCDMH) is eco-friendly and source of positive halogens. DCDMH reactions with various organic and inorganic substrates have been successfully used in the oxidation phenol, D-glucose, chalcones, amino acids, and ketones etc.

Therefore, establishing the role of this reaction in the proposed oxidation mechanism, in this communication, we report the kinetics of oxidation allyl alcohol with DCDMH in aqueous acetic acid medium.

2. EXPERIMENTAL
Materials: Allyl alcohol (B.D.H.) : >99%, DCDMH (Across) > 99.7%, acetic acid (B.D.H.), sulphuric acid Anal. Others chemicals used were of reagent grade. The DCDMH solution prepared in acetic acid was used afresh in each set of experiment in standard form.

3. KINETIC MEASUREMENTS
The reaction vessel containing required volumes of reactant was kept in a thermostat maintained at the 35°C, under the pseudo first-order conditions i.e. [allyl alcohol] >> [DCDMH]. The kinetics of the reaction was followed upto 75% to 80% conversion by monitoring the decrease in [DCDMH] iodometrically. The values of kobs from the slopes for more than two kinetic runs were calculated employing integrated differential equation and found within ± 3% of error.

The stoichiometry of reaction was determined at its identical condition and assigned 1:1 mole ratio, DCDMH to allyl alcohol as conformed in equation (1).

\[ \text{CH}_2 = \text{CH} \cdot \text{CHO} + \text{H}^+ \rightarrow \text{HCH} = \text{CH} \cdot \text{CHO} + 2 \text{Cl}^- \]

To identify the acrolein of the main product formed in the reaction, the reaction mixture was subject to obtain 2:4-DNP derivative and characterized by based on modern methods. Moreover, added acrylonitrile did not induce the
polymerization in the reaction mixture hence one electron mechanism is completely unlikely.

4. Results and Discussion

Dependence of reaction dynamics on [DCDMH]
The observed rate constant ($k_{obs}$) were computed at different [DCDMH] but at fixed [substrate], [H$^+$] and temperature. The reaction rate was found to be constant with increasing amounts of [DCDMH]. The independence of $k_{obs}$ at 35°C under the above stated conditions is in agreement with the first-order dependence on [DCDMH] evidenced by the derived slope from the plots of log [DCDMH] vs. time.

Dependence of reaction dynamics on [substrate]
The variation of [allyl alcohol] on reaction rate is shown in Table 1. When inverse rate constant ($k_{obs}$) were plotted against inverse [allyl alcohol], a straight line with positive intercepts on Y-axis and slope less than unity was obtained indicating the order in allyl alcohol to be fractional (Fig.1). The second order rate constant ($k_2$) values does not remain stationary. The reacting species of DCDMH oxidation lead the oxidation of allyl alcohol towards the formation of intermediate complex at transition state.

Table 1: Effect of allyl alcohol on rate

<table>
<thead>
<tr>
<th>$10^2$×[Allyl alcohol] (mol dm$^{-3}$)</th>
<th>$10^4$ k (s$^{-1}$)</th>
<th>$10^2$ [allyl alcohol] mol$^{-1}$dm$^3$</th>
<th>$10^4$ $k$ (s$^{-1}$)</th>
<th>$100$ $k_2 = \frac{k}{[allyl alcohol]}$ l mol$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>1.62</td>
<td>0.6666</td>
<td>0.6172</td>
<td>1.08</td>
</tr>
<tr>
<td>2.00</td>
<td>2.06</td>
<td>0.5000</td>
<td>0.4854</td>
<td>1.03</td>
</tr>
<tr>
<td>2.50</td>
<td>2.39</td>
<td>0.4000</td>
<td>0.4184</td>
<td>0.95</td>
</tr>
<tr>
<td>4.00</td>
<td>3.05</td>
<td>0.2500</td>
<td>0.3278</td>
<td>0.76</td>
</tr>
<tr>
<td>5.00</td>
<td>3.52</td>
<td>0.2000</td>
<td>0.2840</td>
<td>0.70</td>
</tr>
<tr>
<td>6.00</td>
<td>3.70</td>
<td>0.1660</td>
<td>0.2702</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Effect of acidity on reaction Dynamics
The reaction was investigated as a function [H$_2$SO$_4$] at fixed [substrate] and [DCDMH] at 35°C. It is evident that rate constant (k) increases with acidity function of H$_2$SO$_4$ and the values of $k_2 = k_{obs} / [H^+]$ show constancy. The observed results show the reaction is considered to proceed via acid independent pathway i.e. directly participate in the reaction.
mechanism in the protonated form with reacting species of DCDMH. The reaction is acid catalyzed and exhibits unit order with respect to [H⁺] ion.

**Kinetics in presence of CH₃COOH**

The rate of oxidation was found to increase and as a function of composition of acetic acid due to decrease in dielectric constant of the medium at previously set experimental reaction conditions. It is observed that the plot of kobs vs. 1/D is linear with positive intercept suggesting that oxidation involves positive ion dipole rate interaction preferred in rate-determining step.

The alcohol variation experiments with DCDMH were also repeated with added neutral salt (Sodium chloride) to maintain ionic strength (µ), under otherwise identical conditions (Data not included), The observed salt and ionic type strength of the medium have shown insignificant effect on rate. The addition of small quantities of dimethyl hydantoin a reductant product of DCDMH to reaction which under the same conditions is oxidized in slower rate showing inhibition effect significantly reduces the reaction rate that is, it acts as an inhibitor, ruling out its claim as reacting species to initiate reaction mechanism.

**Thermodynamic parameters**

The kinetics of the system was explored at four different temperatures viz. 30°, 35°, 40° and 45°C (Table 2). Various activation parameters such as energy of activation (Ea) and entropy of activation (ΔS°) were determined. The values of Ea was deduced from the Arrhenius plots of log₁₀ k vs. 1/𝑇_ Kı (Fig. 2) graphically.

**Table 2 : Variation of temperature on rate**

<table>
<thead>
<tr>
<th>[Allyl alcohol]× 10² (mol dm⁻³)</th>
<th>10⁴ k (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DCDMH] = 2.50 x 10⁻³ (mol dm⁻³) ; [H⁺] = 0.15 (mol dm⁻³) ; CH₃COOH-H₂O = 30% (v/v)</td>
<td></td>
</tr>
<tr>
<td>Temp. K</td>
<td>303</td>
</tr>
<tr>
<td>2.00</td>
<td>1.50</td>
</tr>
<tr>
<td>2.50</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Fig. 2

**Reaction mechanism**

HOCl generated in the system as hydrolytic product of DCCMH which gets protonated (H₂O⁺Cl⁻) both these prime reacting species could attack the reducing allyl alcohol. The two electron oxidation steps of the mechanism are proposed as :

1. DCDMH + 2 H₂O → HOCl + H⁺ (1,3-dichloro-5,5-dimethyl Hydantoin)  
2. HOCl + H⁺ → H₂O⁺Cl⁻ (protonated)  
3. HCH = CH – C – OH + HOCl → HCH = CH – C – O – Cl (Complex X)
where, S stands for substrate (allyl alcohol)

\[
\text{HCH} = \text{CH} \rightarrow \text{OH} + \text{H}_2\text{O} + \text{Cl}^- \quad \ldots \ldots (4)
\]

On the basis of above scheme and assumptions, the following kinetic relationship may be deduced as rate law:

\[
k_{\text{obs}} = \frac{K_1[S](k_1k_3 + k_2K_4[\text{H}^+])}{[\text{DMH}] + K_1 + K_2K_3[S] + K_1k_2[\text{H}^+](1 + K_4[S])} \ldots \ldots (7)
\]

The credibility of equation (7) might be examined for Michaelis-Menten model of kinetics by rewritten as equation (8)

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{[S]} \left[ \frac{K_1(k_1k_3 + k_2K_4[\text{H}^+]) + K_3}{K_1(k_1k_2 + k_2K_4[\text{H}^+])} \right] \ldots \ldots (8)
\]

CONCLUSION

A kinetic scheme of the process of oxidation of allyl alcohol by two reacting species viz. HOCl and \( H_2OCl \) of oxidant DCDMH and rate law equation describing the oxidation are proposed. The rupture of C-H bond occur in alcohol with the expulsion of proton yielding aldehyde as the oxidation product. The thermodynamic characteristics of elementary steps of oxidation were calculated. The complex nature of complex with stoichiometric ratio DCDMH to allyl alcohol 1:1 was discussed. The corroboration of double reciprocal plots \( \frac{1}{k_{\text{obs}} \text{ vs.}} \frac{1}{[\text{allyl alcohol}]} \) gave rise non-zero slope on ordinate axis. The order was derived unity each for [DCDMH] and [H\(^+\)].

Acknowledgement

The authors are indebted to Prof. R.N. Patel, Head Department of Chemistry, A.P.S. University, Rewa (M.P.) for laboratory facilities and some eminent scientists for useful discussion on the chemistry of the mechanism.

Conflict of Interest

The authors declare conflict of no interest whatsoever.

REFERENCES: