Hydrogenation of some allylic alcohols catalysed by anchored montmorillonitebipyridinepalladium(II) acetate - A kinetic study

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Hydrogenation of some allylic alcohols like 2-methyl-2-propen-1-ol, 4-penten-3-ol, trans-2-buten-1-ol, trans-3-penten-2-ol and 4-methyl-3-penten-2-ol has been carried out by anchored montmorillonitebipyridinepalladium(II) acetate in THF medium. Under the reaction conditions 100 % saturation of carbon-carbon double bond is observed and there is neither polymerisation nor isomerisation. The observed rate has been found to be first order each with respect to partial pressure of hydrogen and [substrate] and fractional order with respect to [catalyst]. The rate of hydrogenation follows the order: 2-methyl-2-propen-1-ol > 4-penten-3-ol > trans-2-buten-1-ol > trans-3-penten-2-ol > 4-methyl-3-penten-2-ol. Thermodynamic parameters have been evaluated, rate law and a plausible mechanism have been proposed.

One of the most intensively investigated research areas in recent years in the field of catalysis is immobilization of transition metal complexes on solid supports like organic polymers and inorganic oxides. Serious interest in these catalysts originated with efforts to develop industrially competitive homogeneous catalysts to supplant heterogeneous catalysts, which met with limited success due to the separation problem associated with homogeneous systems. In addition to providing a solution to this problem, the new anchored catalysts have attractive features of being reproducible, allowing control and knowledge of the nature of the incipient species immobilized on the support. Inorganic supports that have been used are silica, alumina, glasses, zeolites and clay. Of all these, clays are shown to be good catalyst supports. The clay used in our study is montmorillonite, a smectite clay. This clay possesses large amounts of highly reactive species which can be readily exchanged by inorganic complexes. Apart from this, the intra-crystal space can be swelled by various polar solvents. The degree of swelling depends on the interlayer cations, the substrate and negative charge density on silicate sheet. Keeping these advantages in mind, Choudary et al synthesized a series of montmorillonite functionalised palladium(II) complexes. Number of attempts were made to hydrogenate the olefinic compounds, using anchored catalysts, however only in few instances detailed kinetic study has been undertaken. We report a detailed kinetic study of hydrogenation of some allylic alcohols catalysed by anchored montmorillonitebipyridine-palladium(II) acetate.

The influence of structure on reactivity is a topic of current interest in the study of the mechanism of alkene hydrogenation on supported metal catalysts. Therefore in this study, to determine as how olefin structure influences rate of hydrogenation, the catalyst was tested with a series of olefins of varying double bond substitution like 2-methyl-2-propen-1-ol (I), 4-penten-3-ol (II), trans-2-buten-1-ol (III), trans-3-penten-2-ol (IV) and 4-methyl-3-penten-2-ol (V)(Scheme.1)

Scheme-1

In all cases, the reaction is a function of substituents on the olefinic bond. The catalyst was very effective towards 100% selectivity in the hydrogenation of carbon-carbon double bond without any polymerisation and isomerisation. This is in contrast to the hydrogenation of allyl alcohols catalysed by other catalysts like polymer bound palladium catalysts where isomerisation is a side reaction.
Table 1 — Effect of [substrate] on reaction rates

<table>
<thead>
<tr>
<th>[S]x10^2</th>
<th>2-methyl-2-propen-1-ol</th>
<th>4-penten-3-ol</th>
<th>t-2-buten-1-ol</th>
<th>t-3-penten-2-ol</th>
<th>4-methyl-3-penten-2-ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>300</td>
<td>306</td>
<td>288</td>
<td>300</td>
<td>306</td>
</tr>
<tr>
<td>0.50</td>
<td>0.36</td>
<td>0.41</td>
<td>0.44</td>
<td>0.29</td>
<td>0.36</td>
</tr>
<tr>
<td>0.75</td>
<td>0.54</td>
<td>0.62</td>
<td>0.66</td>
<td>0.44</td>
<td>0.53</td>
</tr>
<tr>
<td>1.00</td>
<td>0.73</td>
<td>0.80</td>
<td>0.85</td>
<td>0.56</td>
<td>0.73</td>
</tr>
<tr>
<td>2.00</td>
<td>1.43</td>
<td>1.63</td>
<td>1.73</td>
<td>1.15</td>
<td>1.41</td>
</tr>
<tr>
<td>2.50</td>
<td>1.79</td>
<td>2.04</td>
<td>2.16</td>
<td>1.44</td>
<td>1.76</td>
</tr>
<tr>
<td>4.00</td>
<td>2.83</td>
<td>3.24</td>
<td>3.44</td>
<td>2.28</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Reaction conditions : [catalyst] : 0.20 X 10⁻³ m.mol, [H₂] : 1.063 X 10² kNm², Solvent : THF.

Materials and Methods

Montmorillonite(1.2m eq g⁻¹) employed in the system was obtained from Fluka chemicals, Switzerland. Bipyridine and silicone rubber septa (14 joint) white were obtained from Aldrich, USA. Palladium acetate was obtained from Alchem laboratories, India. n-Butyl lithium was obtained from E Merk, Germany. All other chemicals were obtained from S D Fine chemicals, India. Air and moisture sensitive reactions were carried out in an intert atmosphere. All the reagents have been either recrystallised or distilled where ever necessary by adopting standard methods reported in literature²¹.

The catalyst was prepared according to the procedure cited in the literature⁹ ESCA data of the catalyst montmorillonitebipyridine palladium(II) acetate indicated that the palladium is present in the divalent state before and after hydrogenation, with well resolved spin doublets with Pd 3d₂5/₂ binding energy (E_b) of 338.8 (corrected to Si 2s E_b = 153.4 ± 0.2 eV). Band at 1560 cm⁻¹ in IR spectrum indicated the presence of acetate ligands. X-Ray powder diffraction (thin film) showed a basal region expansion(Δd₀₀₁) of 15.0 Å for the catalyst. The hydrogenation kinetics was carried out on a specially fabricated system²². The hydrogen was purified by passing over a deoxo catalyst, through molecular sieves and drying tubes before admission into the vacuum system. Hydrogenation reactions were carried out in a 100ml two necked round bottomed flask. The side arm was packed with a silicone rubber septa and the other arm to a glass vacuum manifold equipment with a manometer, a gas burette, and a gas-inlet. A weighed amount of the catalyst was placed in the reaction vessel and was attached to the reaction system. To this 10 ml of dry THF was added and the whole system was evacuated and flushed three times with pure hydrogen. The mixture was shaken for 30 minutes in the presence of hydrogen. The weighed amount of substrate(olefin) in a measured quantity of solvent was injected into the pre-equilibrated reaction system. The shaking was carried out at such a speed to ensure that the reaction rate does not depend on shaking. Hydrogen uptake commenced without any induction period. The rate of hydrogen uptake was monitored at regular time intervals. At the end of each run, the catalyst was separated by filtration and thoroughly washed with dry THF. The filtrate was spectroscopically analysed by IR and NMR for qualitative identification of reaction products. To carry out the reactions at different temperatures, water was circulated through the outer jacket of the reaction system by using thermostat or cryostat.

Results and Discussion

Stoichiometry and product analysis

The stoichiometry of the reaction was determined by keeping an excess of hydrogen with an olefin(substrate) for several hours and hydrogen consumed was measured. It was found that the total hydrogen consumption corresponds to complete hydrogenation of the carbon-carbon double bond that was present in the substrate. The sto-
Table 2 — Effect of [catalyst] on reaction rates

<table>
<thead>
<tr>
<th>[C]X10²</th>
<th>2-methyl-2-propen-1-ol</th>
<th>4-penten-3-ol</th>
<th>t-2-buten-1-ol</th>
<th>t-3-penten-2-ol</th>
<th>4-methyl-3-penten-2-ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>300</td>
<td>306</td>
<td>288</td>
<td>300</td>
<td>306</td>
</tr>
<tr>
<td>0.15</td>
<td>0.59</td>
<td>0.66</td>
<td>0.70</td>
<td>0.48</td>
<td>0.57</td>
</tr>
<tr>
<td>0.20</td>
<td>0.72</td>
<td>0.81</td>
<td>0.88</td>
<td>0.57</td>
<td>0.70</td>
</tr>
<tr>
<td>0.25</td>
<td>0.83</td>
<td>0.96</td>
<td>1.02</td>
<td>0.66</td>
<td>0.82</td>
</tr>
<tr>
<td>0.30</td>
<td>0.93</td>
<td>1.08</td>
<td>1.16</td>
<td>0.73</td>
<td>0.92</td>
</tr>
<tr>
<td>0.40</td>
<td>1.08</td>
<td>1.28</td>
<td>1.39</td>
<td>0.84</td>
<td>1.08</td>
</tr>
<tr>
<td>0.50</td>
<td>1.20</td>
<td>1.44</td>
<td>1.57</td>
<td>0.93</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Reaction conditions: [substrate] : 1.00 X 10⁻² m.mol., PH₂ : 1.063 X 10² kN.m⁻², Solvent : THF.

Kinetic studies
The hydrogenation of allylic alcohols were carried out under different reaction conditions to study the mechanism of hydrogenation. The respective rates (accuracy ±4%) at three different temperatures in the temperature range 288K - 300K (accuracy ±0.5K) are presented in Table 1. The plot of log V versus log [substrate] was linear with a unit positive slope indicating first order dependence with respect to [substrate]. The same trend is observed for all substrates. This is in contrast to the order obtained for hydrogenation of crotonaldehyde and crotonic acid, which are structurally similar to allylic alcohols except for the functional groups, where the order is fractional²⁻³. The presence of non bonded electrons of OH group in allyl alcohols seem to be affecting the nature of the intermediate complexes resulting in the change in complex formation leading to change in order from fractional to unity. The variation in catalyst concentration also affected the rates of hydrogenation, as with increase in catalyst concentration rates were found to increase (Table 2). The plots of log V versus log [catalyst] revealed fractional order dependence on the catalyst concentration. However, the plot of log V versus log[H₂] indicated a unit order dependence on the partial pressure of hydrogen (Fig.1). Plots of reciprocal rates versus reciprocal hydrogen partial pressure were linear with intercepts on the rate axis (Fig.2), indicating the probable formation of intermediate hydride species in reversible equilibrium step.

Based on the above data the following mechanism is proposed which is in accordance with the one proposed by Turkervich²⁴ for hydrogenation of ethylene in heterogeneous catalysis involving palladium, represented...
by equations 1-3 and Scheme 2. This is also parallel with the mechanism proposed by Terasawa et al.\textsuperscript{14} and Nayak et al.\textsuperscript{15} for the hydrogenation of various olefins catalysed by polymer bound palladium(II) complexes.

\[ C + H_2 \overset{K_1}{\rightleftharpoons} C_1 \]  
\( \text{...}(1) \)

\[ C_1 + S \overset{K_2}{\rightleftharpoons} C_2 \]  
\( \text{...}(2) \)

Thus the mechanism involves the initial complex(C\textsubscript{1}) formation between catalyst(C) and hydrogen involving hydride ion transfer to the palladium replacing acetate ion. In the second equilibrium step initially olefin(S) forms a \( \pi \)-complex(C\textsubscript{2}) with the palladium and simultaneously hydride ion transfer takes place from palladium to olefin. The last step is rate determining, which involves the transfer of proton to substrate leading to the separation of the hydrogenated product from the catalyst. Thus the catalyst is regenerated.

\[ \text{The rate law derived is as follows:} \]
\[ \frac{d[S]}{dt} = -\frac{d[H_2]}{dt} = \frac{kK_1K_2[C][H_2][S]}{1 + K_2[C]} \]  
\( \text{...}(4) \)
Table 3- Thermodynamic parameters at 300K involving equilibrium constant $K$

<table>
<thead>
<tr>
<th>Parameters</th>
<th>2-methyl-2-pren-1-ol</th>
<th>4-penten-3-ol</th>
<th>t-2-buten-1-ol</th>
<th>t-3-penten-2-ol</th>
<th>4-methyl-3-pren-2-ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\Delta G$ (kJ mol$^{-1}$)</td>
<td>13.2</td>
<td>13.6</td>
<td>13.6</td>
<td>13.8</td>
<td>13.0</td>
</tr>
<tr>
<td>$-\Delta H$ (kJ mol$^{-1}$)</td>
<td>18.6</td>
<td>19.9</td>
<td>20.3</td>
<td>19.5</td>
<td>21.1</td>
</tr>
<tr>
<td>$-\Delta S$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>17.9</td>
<td>21.0</td>
<td>22.4</td>
<td>19.0</td>
<td>27.1</td>
</tr>
</tbody>
</table>

Table 4- Activation parameters at 300K

<table>
<thead>
<tr>
<th>Parameters</th>
<th>2-methyl-2-pren-1-ol</th>
<th>4-penten-3-ol</th>
<th>t-2-buten-1-ol</th>
<th>t-3-penten-2-ol</th>
<th>4-methyl-3-pren-2-ol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a^#$ (kJ mol$^{-1}$)</td>
<td>8.0</td>
<td>9.2</td>
<td>15.9</td>
<td>18.6</td>
<td>21.2</td>
</tr>
<tr>
<td>$\Delta G^#$ (kJ mol$^{-1}$)</td>
<td>62.6</td>
<td>63.0</td>
<td>63.3</td>
<td>63.4</td>
<td>64.0</td>
</tr>
<tr>
<td>$\Delta H^#$ (kJ mol$^{-1}$ K$^{-1}$)</td>
<td>5.5</td>
<td>6.7</td>
<td>13.4</td>
<td>16.2</td>
<td>18.8</td>
</tr>
<tr>
<td>$-\Delta S^#$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>190.5</td>
<td>187.8</td>
<td>166.2</td>
<td>157.5</td>
<td>151.0</td>
</tr>
</tbody>
</table>

Equation (4) accounts for the first order dependence on $[H_2]$ and [substrate] and fractional order dependence on [catalyst].

Taking reciprocals of Eq. (4)

$$\frac{1}{V} = \frac{1}{kK_1K_2[C][H_2][S]} + \frac{1}{kK_2[H_2][S]} ...(5)$$

Keeping $[H_2]$ and $[S]$ constant and varying $[C]$, the plot of $1/V$ versus $1/[C]$ was linear with a positive slope and an intercept. The ratio of intercept and slope gave the value of $K_j$. Corresponding thermodynamic parameters have been presented in Table 3. Owing to the complexity of the rate equation, equilibrium constant $K_j$ and rate constant $k$ could not be evaluated. The formation of initial complex $C_j$ seems to be spontaneous as indicated by the negative values of both $\Delta G$ and $\Delta H$, but less compact as indicated by positive $\Delta S$ values.

As $k$ could not be evaluated from the data, the pseudo first order rate constant, $k'$ was evaluated by dividing $V$ by hydrogen partial pressure in Eq. (4). $k'$ was evaluated at three different temperatures and the corresponding activation parameters were reported in Table 4. Since these values are composite, much inference could not be drawn about the nature of the activation complex.

In the catalytic hydrogenation of the olefins the activity and their relative rate strongly depends on the substrate used in the reaction and electrostatic interaction between the substrate and the clay support. The olefin which forms a $\pi$-complex more easily will have more rate of hydrogenation, in other words the higher nucleophilicity of olefin plays a vital role in the preferential complexation and subsequent faster rate of hydrogenation. The relative rates are in the order: $I > II > III > IV > V$. It appears that the rates of terminal olefins are greater than the internal olefins which may be due to the preferential complexation of the olefins with the catalyst in the interlayers of montmorillonite. Both the steric and electronic effects seem to be playing a role. The increase in rate from $I$ to $II$ can be attributed to the electronic effects both of which are terminal olefins. But the presence of additional methyl group on the double bond seems to be activating by means of inductive and meso-
meric effects leading to faster rate, the remaining alcohols are internal olefins. The decrease in rate can be attributed to steric factors. The least rate of V clearly supports this view. Even though the methyl substituents on carbon-carbon double bond are activating the olefin, the steric effect may be hindering in entering the interlayers of the catalyst resulting in the lower rates. In general, the order of reactivity of olefins is as follows.

\[ \text{Scheme 3} \]

This order is based on the results obtained for the hydrogenation of allyl alcohol and its analogues. The order of rates parallels the relative stabilities of \( \pi \)-bonded Pd-olefin intermediates toward olefin dissociation and also the predicted relative stabilities of the alkyl-palladium intermediates formed from the corresponding olefins toward Pd-H elimination. The stabilities of the alkyl-palladium intermediates would be predicted to decrease in the order: \( \pi \)-allyl complexes (formed from conjugated dienes) > \( \pi \)-chelated complexes (from nonconjugated dienes) > \( n \)-alkyl complexes (from terminal alkenes) > \( n \)-alkyl complexes (from internal alkenes)\(^{25} \). Therefore the higher rate of terminal olefins is justified. Hence, it may be concluded that electronic factors are influencing the rate in the case of terminal olefins while for internal olefins steric factors are dominating.

Acknowledgement

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References