Hydrogenation kinetics and mechanism of stilbene, cinnamaldehyde and cinnamic acid by anchored montmorillonite-bipyridine-palladium(II) acetate

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Hydrogenation of olefinic compounds catalysed by anchored catalysts is of current interest. A detailed kinetic study of the hydrogenation of some olefinic compounds over anchored montmorillonite-bipyridine-palladium(II) acetate catalyst which belongs to a new generation catalytic system is presented. The effects of substrate concentration, partial pressure of hydrogen, catalyst concentration, solvent and temperature have been studied. Based on the results a mechanism is proposed, rate law derived and the corresponding thermodynamic parameters have been evaluated. Product analysis is confirmed by H-NMR, IR and GLC.

The recent trend is to devise catalysts which have both the homogeneous and heterogeneous catalytic properties. The ideal catalyst would have the specificity and controllability of the homogeneous type and separability of the heterogeneous system. Enhanced reaction rates are obtained when metal complex homogeneous catalysts are attached to suitable support. Experience has shown that the presence of both support and catalyst can have synergically beneficial effects. Inorganic supports that have been used include silica, alumina, glasses, zeolites and clay. Among these, clays have greater potential as catalyst supports. Smectite clay which includes hectorite and montmorillonite possesses mica like structure in which the crystallites are made up of alternating layers of cations and negatively charged silicate sheets. However, unlike mica, the cations can be readily exchanged by complexes. The intra-crystal space can be swelled by water, alcohol and organic solvents. The degree of swelling depends on the interlayer cations, the substrate and negative charge density on silicate sheet. Pinnavaia and Welta demonstrated the intercalated cationic medium hectorite complexes hydrogenated by terminal alkynes, while the internal alkynes are unaffected. Choudary and co-workers demonstrated that montmorillonite support hosting the palladium chloride complexed to diphenyl phosphine is covalently bonded in the interlayers of clays. The first example of chelation in smectite clays is montmorillonite-bipyridine-palladium(II) catalyst. Palladium salts anchored via a bipyridine group in the interlamellar region of montmorillonite have been synthesised and characterised. Since the early work on the catalytic hydrogenation of olefinic compounds considerable progress has been made in understanding the mechanism of these reactions. However, little attention has been paid to kinetic study for understanding the mechanism. The hydrogenation mechanism of stilbene, cinnamic acid and cinnamaldehyde over montmorillonite-bipyridine-palladium(II) acetate catalyst is still to be clarified. We report here in a detailed kinetic study of hydrogenation of these olefinic compounds.

Experimental
The catalyst was prepared according to the procedure cited in the literature and the hydrogenation kinetics was carried out on a specially fabricated system.

Results and discussion
Hydrogen consumption for the reaction showed that the total hydrogen consumed corresponds to complete saturation of the C=C which was present in the substrate. Peaks corresponding to olefinic protons of substrate were absent in the hydrogenated products. This was also confirmed by NMR and IR spectroscopic results. The stoichiometry for the hydrogenation of substrates over montmorillonite-bipyridine-palladium(II) acetate catalyst at different concentrations of three substrates were found to be 1:1.

Kinetic studies
In order to know the catalytic reaction mechanism for the hydrogenation of stilbene, cinnamaldehyde and cinnamic acid in the presence of anchored montmorillonite-bipyridine-palladium(II) acetate, detailed kinetic studies were carried out under different reaction conditions. The results summarized in Table 1 show the effect of substrate (stilbene, cinnamaldehyde and cinnamic acid) concentration on reaction rates. The order in [substrate] is found to be fractional.
Table 1—Hydrogenation of stilbene(I), cinnamaldehyde(II) and cinnamic acid(III), in the presence of montmorillonitebipyridinepalladium(II) acetate: Effect of substrate concentration

<table>
<thead>
<tr>
<th>Substrate m mol</th>
<th>Rate Vx 10^1 m mol . s^-1</th>
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<tbody>
<tr>
<td></td>
<td>300 K</td>
</tr>
<tr>
<td>0.25</td>
<td>II 0.71 II 0.50 II 1.00</td>
</tr>
<tr>
<td>0.50</td>
<td>II 1.10 II 1.45 II 1.50</td>
</tr>
<tr>
<td>1.00</td>
<td>II 1.45 II 2.00 II 2.50</td>
</tr>
<tr>
<td>1.25</td>
<td>II 1.58 II 2.00 II 2.50</td>
</tr>
<tr>
<td>2.00</td>
<td>II 2.00 II 2.50 II 3.00</td>
</tr>
<tr>
<td>2.50</td>
<td>II 2.00 II 2.50 II 3.00</td>
</tr>
</tbody>
</table>

Figure 1 (A, B, C) shows that the plots of log V versus log P H_2 were linear with positive slope equal to unity, which indicates that the order with respect to hydrogen partial pressure is one. Fractional order is found in catalyst concentration. In Fig. 1 D, E, F plots of log Y versus log |cat| were linear with slope values of 0.56, 0.77, 0.41 for stilbene, cinnamaldehyde and cinnamic acid respectively.

As observed from the data the fractional dependence on |substrate| and fractional order with respect to |catalyst| probably indicate the formation of intermediate complexes between hydrogen and catalyst and further with substrate. This is similar to the mechanism proposed by Turkervich for hydrogenation of ethylene, in heterogeneous catalysis involving palladium.

The catalysed reaction could be represented by Eqs 1-3 and Scheme 1.

\[ \text{C} + \text{H}_2 \xrightarrow{K_1} \text{C}_1 \]  

\[ \text{C}_1 + \text{S} \xrightarrow{K_2} \text{C}_2 \]  

\[ \text{C}_2 \xrightarrow{k_{\text{slow}}} \text{P} + \text{C} \]  

Where C is the catalyst, C_1 is the intermediate species (Complex-1) between catalyst and hydrogen, C_2 is complex formed in second equilibrium step between C_1 and substrate (S), C_2 gives the end product (P) and catalyst (C) back. Equation (3) is the rate determining step.

From the above mechanism the rate law derived is

\[ \frac{d[P]}{dt} = V = \frac{k K_1 K_2 [C][H_2][S]}{1 + K_1[C] + K_2[S] + K_1 K_2 [C][S]} \]  

Equation (4) accounts for the order with respect to catalyst to be fractional and order in hydrogen partial pressure to be unity. The experimental kinetic results for stilbene, cinnamaldehyde and cinnamic acid are in agreement with the equation (4).

In order to evaluate the individual constants K_1, K_2, and k, Eq. (4) is modified in terms of k', the pseudo-first order rate constant at constant hydrogen partial pressure (Eq. 5).

\[ k' = \frac{V}{[H_2]} = \frac{k K_1 K_2 [C][S]}{1 + K_1[C] + K_2[S] + K_1 K_2 [C][S]} \]  

Taking the reciprocals of Eq. (5), the least squares plot of 1/k' versus 1/[S] was linear with the positive slope and an intercept which enabled us to evaluate K_2.

\[ \frac{1}{k'} = \frac{1}{k K_1 K_2 [C][S]} + \frac{1}{k K_2 [S]} + \frac{1}{k K_1 [C]} + \frac{1}{k} \]  

Thermodynamic parameters involving K_2 at 300 K have been calculated and summarized in Table 2.
Table 2—Hydrogenation of stilbene, cinnamaldehyde and cinnamic acid in the presence of montmorillonitebipyridinepalladium(II) acetate: Thermodynamic parameters involving $K_2$ (the values of parentheses calculated using $K_1$)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Stilbene</th>
<th>Cinnamaldehyde</th>
<th>Cinnamic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\Delta H^0$ (kJ mol$^{-1}$)</td>
<td>23.03</td>
<td>16.02</td>
<td>36.48</td>
</tr>
<tr>
<td>(27.11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\Delta G^0$ (kJ mol$^{-1}$)</td>
<td>17.71</td>
<td>12.04</td>
<td>13.03</td>
</tr>
<tr>
<td>(12.32)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-\Delta S^0$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>17.74</td>
<td>13.26</td>
<td>28.18</td>
</tr>
<tr>
<td>(49.08)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On similar lines from Eq. 6, the least squares plot of $1/k'$ versus $1/[C]$ was drawn at constant [substrate]. $K_1$ was evaluated at different temperatures from the ratio of intercept and slope, the corresponding thermodynamic parameters have been calculated at 300 K and summarised in Table 2.

Knowing the values of $K_1$ and $K_2$ the rate constant of the slow step, $k$ (Eq. 3) was evaluated at different temperatures from intercept of $1/k'$ versus $1/[S]$ plot. The corresponding activation parameters were presented in Table 3.

The fact that $\Delta G^0$ and $\Delta H^0$ values are negative for all the substrates indicate that the formation of complex $C_2$ is highly favourable. $\Delta S^0$ is also found to be negative in all these cases indicating the compactness of the structure of the $C_2$ complex compared to the reactants.

The $\Delta S^0$ value involving $K_1$ is negative in all the cases due to the complex formation, which has relatively more rigid structure. It is interesting to note that the magnitude of $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ for cinnamaldehyde complexes $C_1$ and $C_2$ (equilibrium constants $K_1$ and $K_2$) are almost of similar magnitude. This indicates close similarity in the orientation of complexes $C_1$ and $C_2$ formed in be-
tween the layers of the anchored montmorillonite clay catalyst.

However, in the case of stilbene there is vast difference in the $\Delta S^0$ values of complexes, $C_1$ and $C_2$ probably due to presence of bulkier phenyl groups.

The activation parameters indicate another interesting difference in the reactivity of substrates. Cinnamaldehyde and cinnamic acid have similar magnitudes owing to the structural similarities, however $E_a, \Delta S^+$ values are markedly different for stilbene when compared to the two substrates.

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References