Hydrogenation of phenylacetylene by Pd/Al₂O₃ and PdCl₂: Intermediates and selectivity

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In the hydrogenation of phenylacetylene by PdCl₂ and 5% Pd/Al₂O₃, two Pd(II) intermediate complexes have been identified. The intermediate of PdCl₂/PhC=CH reaction mixtures is [PdCl₂(PhC=CH)₂], (I), and the intermediate of Pd/Al₂O₃/PhC=CH reaction mixtures is [Pd(PhC=CH)₂(PhC=CH)₂] (II). A mixture of intermediates (I) and (II) is formed when a few drops of conc. HCl are added to the hydrogenation mixture of Pd/Al₂O₃ and PhC=CH. These two intermediates, which are also formed when hydrogen is not present, have been identified by IR and UV/vis spectroscopy. Also, with PdCl₂ catalyst, a black colloidal Pd-metal is precipitated and HCl gas is evolved. The selectivity of PdCl₂ and Pd/Al₂O₃ towards the production of styrene are 74% and 97%, respectively. The selectivity of Pd/Al₂O₃ in the presence of a few drops of conc. HCl is 73%. The rate of hydrogenation of phenylacetylene by Pd/Al₂O₃ is ~4 times higher than that when PdCl₂ is used as a catalyst.

Although a considerable amount of work was done on the hydrogenation of olefins by Pd supported on different surfaces, less work was done on the hydrogenation of alkynes catalysed by Pd metal and its compounds. Some researchers have studied this reaction over other transition metals and their alloys. Palladium metal has the highest activity and semi-hydrogenation selectivity among the platinum group metals.

In this paper we report the selectivities of Pd/Al₂O₃ and PdCl₂ in the hydrogenation of PhC=CH and the complex intermediates of phenylacetylene with palladium formed during this hydrogenation.

Materials and Methods

PdCl₂ was a pure sample obtained from Ferak GMBH (Berlin). Phenylacetylene was a reagent grade sample of Ferak GMBH (Berlin) which was checked for purity (98% pure). Cyclohexane was a spectranal sample from Reidel-dehaen of 99.7% purity.

Catalyst preparation

Pd/Al₂O₃ is 5% Pd-metal supported on Al₂O₃ which was prepared by impregnating 9.50 g Al₂O₃ (Merck) with 10.0 ml of an aqueous solution (15.4% w/v) of pure K₂PdCl₄ (Fluka AG). The samples were dried overnight in air at 70°C, then calcinated for two hrs in flowing air at 400°C. Helium, then hydrogen were passed through the samples for four hrs at 550°C to ensure complete reduction of the metal oxides. PdCl₂ was used as it was without any further treatment.

Hydrogenator

A simple hydrogenator similar to the Parr-hydrogenator was built for the purpose of hydrogenating small volume samples (10.0-50.0 ml). This hydrogenator consisted of a hydrogen reservoir (~500 ml) with a pressure gauge (0-100 psi) connected to a thick wall glass reaction bottle (100 ml) by a tygon pressure rubber tubing which was in turn connected to a stainless-steel tubing passing through a rubber stopper into the reaction bottle. The reaction bottle was hooked to a mechanical shaker. The total volume of this hydrogenator was measured by the reduction of cyclohexane over Adam's catalyst at 25°C and found to be ~600 ml.

Method for hydrogenation

A 35.0 ml portion of a solution of PhC=CH in cyclohexane (1:10 v/v) was transferred with 0.50 g of the catalyst into a 100 ml reaction vessel. The hydrogenator was then evacuated and hydrogen was introduced into it at 40 psi (gauge pressure). The reaction was carried out at room temperature and constant hydrogen pressure.
Table 1 – G.C. analysis data of the hydrogenation of phenylacetylene by PdCl$_2$, Pd/Al$_2$O$_3$, and Pd/Al$_2$O$_3$ with a few drops of conc. HCl.

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<th>Catalyst</th>
<th>% Consumed</th>
<th>% Phenyl</th>
<th>% Styrene</th>
<th>% Ethyl</th>
<th>Selectivity$^a$</th>
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<td>74.0</td>
<td>26.0</td>
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<td>(63.5)</td>
<td>0</td>
<td>73.0</td>
<td>27.0</td>
<td>73$^b$</td>
</tr>
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</table>

$^a$ Selectivity = \(\frac{\% ~\text{Styrene}}{\% ~\text{Styrene} + \% ~\text{Ethylbenzene}}\) \times 100

$^b$ These values are obtained from graphs representing the hydrogenation data for all catalysts, at the point where PhC$\equiv$CH concentration first reaches zero.

Samples for G.C analysis were taken from the reaction mixture every few minutes by a gas-tight sampling valve connected to a 1.6 mm O.D stainless-steel tubing pierced through the rubber stopper of the reaction bottle into the reaction mixture.

Spectral studies

Phenylacetylene (0.10 g) dissolved in cyclohexane was mixed with an equivalent amount of PdCl$_2$ (0.18 g) or 2.2 g of Pd/Al$_2$O$_3$. The mixture was shaken well and left for two hrs. Two drops of the reaction mixture were squeezed between dry NaCl discs and the spectra were run on a Pye-Unicam SP3-300 spectrophotometer. A Varian-Cary 2390 spectrophotometer was used for the purpose of recording UV/vis spectra of the samples of the reaction mixture in a 10 mm quartz cell.

G.C. analysis

A Pye-Unicam G.C. instrument with a FID detector and a 1.5 m \times 6.3 mm stainless steel column packed with 10% PEGA on CAW was used for component analysis. An electronic integrator (Varian 4290) was connected to the gas chromatograph.

Results and Discussion

The reaction mixture of Pd(II) and PhC$\equiv$CH shows, instantly, a deep red brownish colour, which is different from that of the faint yellow PheC$\equiv$CH whether we use equivalent amounts of the reactants or excess of Pd(II) indicating the formation of a new compound. Also, the reaction of Pd/Al$_2$O$_3$ with an excess amount of PhC$\equiv$CH shows a change of the faint yellow colour of PhC$\equiv$CH to the red brownish colour after ~20 min of mixing. When equivalent amounts of Pd/Al$_2$O$_3$ and PhC$\equiv$CH are used the colour of the reaction mixture changes to slightly brownish. This colour change indicates the formation of phenylacetylene palladium(II) complexes in the reaction of PhC$\equiv$CH with each of Pd/Al$_2$O$_3$ and PdCl$_2$, but the complex formation is slower in the case of the reaction with Pd/Al$_2$O$_3$.

The brownish colour of the reaction mixture disappears when the hydrogenation of PhC$\equiv$CH is completed, i.e., the complete conversion of phenylacetylene to ethylbenzene, indicating the formation of Pd(II) complex intermediates with both catalysts. Isolation of these complexes was not achieved, so the work was also done on equivalents of PhC$\equiv$CH with each of the catalysts before hydrogenation in order to identify the complexes by IR and UV/vis spectroscopy.

Phenylacetylene shows a strong stretching absorption band, $\nu(\equiv C-H)$, at 3260 cm$^{-1}$, and bending absorption bands at 1235 cm$^{-1}$, 610-685 cm$^{-1}$, 515 cm$^{-1}$, and 530 cm$^{-1}$ in KBr discs. Palladium(II) chloride shows an absorption band, $\nu(Pd-Cl)$, at 335 cm$^{-1}$ in KBr pellets. In the reaction mixture of PhC$\equiv$CH and PdCl$_2$, $\nu(\equiv C-H)$ at 3260 cm$^{-1}$, 1235 cm$^{-1}$, and 1235 cm$^{-1}$, 515 cm$^{-1}$ and 610-685 cm$^{-1}$ disappear while the bands at 750 cm$^{-1}$, 910 cm$^{-1}$, 1020 cm$^{-1}$ due to bending $\nu(C-C)$ of phenylacetylene, and the bands at 1060 cm$^{-1}$, 1430 cm$^{-1}$ and 1470 cm$^{-1}$ due to stretching $\nu(C-C)$ do not change. Also, the reaction mixture of PhC$\equiv$CH with Pd/Al$_2$O$_3$ shows...
the same IR spectral changes as those of PhC=CH with PdCl₂. This indicates the presence of some changes in the C≡C bond and consequently, in the C≡H bond, presumably due to the formation of a phenylacetylene/palladium(II) complex.

In the hydrogenation of PhC=CH catalysed by PdCl₂ using H₂ gas under pressure, there was a distinct evolution of HCl gas and a precipitation of the black colloidal palladium in the reaction bottle. Also, there was a complete disappearance of the stretching \(\nu(\equiv C-H)\) at 3260 cm\(^{-1}\) and the bending \(\nu(\equiv C-H)\) at 610-685 cm\(^{-1}\) and 1235 cm\(^{-1}\), and the emerging of \(\nu(\equiv C-H)\) at 985 cm\(^{-1}\).

The reaction mixtures containing equivalent amounts of PdCl₂ and PhC=CH in an excess of cyclohexane, as a solvent, exhibit the absorption maxima at 427 and 342 nm. In contrast, the aqueous solution of PdCl₂ has \(\lambda_{\text{max}}\) at 410 nm and 313 nm, and the phenylacetylene has \(\lambda_{\text{max}}\) at 370 and 330 nm. The appearance of the new \(\lambda_{\text{max}}\) at 342 nm after reaction, which is absent in PhC=CH and PdCl₂ spectra, indicates the formation of a new compound during reaction.

The reaction mixtures containing equivalent amounts of Pd/Al₂O₃ and PhC=CH show maxima at 380, 342 and 327 nm. A comparison with PhC=CH spectra shows that \(\lambda\) 370 in PhC=CH spectra has shifted to \(\lambda\) 380. The appearance of \(\lambda\) 342 indicates the formation of a new compound with some similarity to that of PdCl₂ with PhC=CH mixture. When comparing the spectra of the reaction mixtures of PhC=CH and PdCl₂, and PhC=CH and Pd/Al₂O₃, a \(\lambda_{\text{max}}\) at 342 nm is seen with both mixtures, but other maxima are different. This gives the indication that the intermediates of the two reactions are different.

The addition of a few drops of conc. HCl to the reaction mixture of PhC=CH with Pd/Al₂O₃ caused some changes in the UV/vis absorption spectrum of this reaction mixture. The HCl addition showed a spectrum of \(\lambda_{\text{max}}\): 425 nm, 390 nm, 342 nm and 327 nm. The comparison of this spectrum with those of the reaction mixtures of PhC=CH with each of Pd/Al₂O₃ and PdCl₂ led us to suggest the possibility of the formation of a mixture of the intermediates which were formed by the other two reactions, i.e., intermediates (I) and (II). PdCl₂ coordinates with PhC=CH according to the equation:\(^{17}\)

\[
2 \text{PhC} = \text{CH} + 2 \text{PdCl}_2 \rightarrow [\text{Pd}(\text{PhC} = \text{CH})\text{Cl}_2]_2 \\
\text{(I)}
\]

The complexation of Pd/Al₂O₃ with PhC=CH can be explained by the occurrence of oxidation of Pd metal to Pd\(^{2+}\) by PhC=CH\(^{18}\), as follows:

\[
\text{Pd} + 2 \text{PhC} = \text{CH} \rightarrow \text{Pd}(\text{PhC} = \text{C})_2 + \text{H}_2
\]

Then Pd\(^{2+}\) possibly coordinates with PhC=CH in the following way:

\[
\text{Pd}(\text{PhC} = \text{C})_2 + 2 \text{PhC} = \text{CH} \rightarrow \text{Pd}(\text{PhC} = \text{CH})_2(\text{PhC} = \text{C})_2 \\
\text{(II)}
\]
Hydrogenation

Table 1 lists the data of the phenylacetylene hydrogenation by Pd/Al₂O₃, PdCl₂, and Pd/Al₂O₃ with a few drops of conc. HCl. The semi-hydrogenation selectivity as a percentage of styrene to all products and the percentage composition of the hydrogenation mixtures at different percentages of the consumed hydrogen are given in Table 1. The selectivity of PdCl₂ in this hydrogenation is lower than that of Pd/Al₂O₃ (Table 1 and Figs 1 and 2). For instance, at the point where PhC=CH concentration first reaches zero, the selectivities of PdCl₂ and Pd/Al₂O₃ are 74% and 97%, respectively. This difference in the selectivity between the two catalysts may be due to the following reasons:

(i) The kind in the kind and relative population of the active sites on the surfaces of the two catalysts, i.e., Pd/Al₂O₃ and colloidal Pd of PdCl₂. Concerning the hydrogenation with PdCl₂, the liberated HCl gas may have poisoned some of the sites responsible for producing styrene and thus lowering its selectivity.

(ii) The kind of intermediates formed by the catalysts in their reaction mixtures; PdCl₂ forms intermediate (I) and catalyzes the hydrogenation according to the following equations:

\[
2\text{PdCl}_2 + 2\text{PhC} = \text{CH} \rightleftharpoons [\text{Pd}(\text{PhC} = \text{CH})\text{Cl}_2] \quad \ldots (1)
\]

\[
[\text{Pd}(\text{PhC} = \text{CH})\text{Cl}_2]_2 + 5\text{H}_2 \rightleftharpoons \text{PhCH} = \text{CH}_2 + \text{PhCH}_2\text{CH}_3 + 2\text{Pd} + 4\text{HCl} \quad \ldots (2)
\]

Pd/Al₂O₃ possibly forms intermediate (II) and catalyzes the reaction through the following pathway:

\[
\text{Pd} + 2\text{PhC} = \text{CH} \rightleftharpoons \text{Pd}^2+ + 2\text{PhC} = \text{C}^- + \text{H}_2 \quad \ldots (3)
\]

\[
\text{Pd}^2+ + 2\text{PhC} = \text{C}^- + 2\text{PhC} = \text{CH} \rightleftharpoons \text{Pd}([\text{PhC} = \text{C}]_2[\text{PhC} = \text{CH}])_2 \quad \ldots (4)
\]

\[
\text{Pd}([\text{PhC} = \text{C}]_2[\text{PhC} = \text{CH}])_2 + 3\text{H}_2 \rightleftharpoons \text{PhCH} = \text{CH}_2 + \text{PhCH}_2\text{CH}_3 + \text{Pd} \quad \ldots (5)
\]

When Pd/Al₂O₃ is used with a few drops of conc. HCl, the selectivity is 73% (Table 1). This reduction in selectivity compared to Pd/Al₂O₃ is possibly due to a partial poisoning of the surface of Pd/Al₂O₃ by HCl, and the formation of the intermediates (I) and (II).

Finally, the rate of hydrogenation of phenylacetylene by Pd/Al₂O₃ was ~4 times faster than that of PdCl₂.

Acknowledgement

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References