

Hydrogenating ability of wilkinson's catalyst



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Wilkinson's catalyst was prepared from rhodium (III) chloride and refluxed in ethanol with triphenylphosphine, with a measured yield of 72.7%. The efficacy and regioselectivity of Wilkinson's catalyst was then assessed by reaction with carvone in an atmosphere of hydrogen gas at 1 atm, and the product was analysed by $^1\text{H-NMR}$ spectroscopy.

Introduction

Tris-(Triphenylphosphine)chloro rhodium(I) was discovered and first profiled by Wilkinson et al in 1965, and noted for its ability to selectively hydrogenate terminal alkenes to alkanes[1]. It was only with the further publishing in 1968 that Wilkinson's catalyst was thoroughly characterised.[2] It was the first homogenous catalyst with the ability to perform this function at a rate similar to that of heterogenous catalysts, without having to resort to high pressures or temperatures in the process. Wilkinson's catalyst is unusual in its ability to easily form a dihydride, despite it being a diphosphine, since these compounds are often either short-lived or difficult to detect.[3]

In the above diagram, Wilkinson's catalyst (1) undergoes ligand substitution with a solvent molecule to create the active form of Wilkinson's catalyst (2) [4]. Hydrogen is then attached via oxidative addition (3)4, oxidising Rhodium from +1 to +3 oxidation state and resulting in a change of colour from red to yellow[5]. The prepared catalyst is then injected into the mixture, at which point it complexes with the rhodium centre via the pi bond (4)[6]. The solvent then leaves the complex (5). H' migrates to the alkene first due to proximity, with H'' migrating second[7]. A solvent molecule takes the place of the leaving alkane, converting the catalyst back to its active form (7).

The pi bond formed between the alkene and the Rhodium is characterised by back-donation from a d-orbital overlap with the π^* anti-bonding orbital. This back donation, coupled with donation from the π bond on the alkene results in the π bond being much weaker and more susceptible to being broken than uncoordinated ethene.

^{13}C -NMR has shown that bonds formed between the a rhodium centre and other alkene complexes bond show significant s-character, typified by downfield shift, or in other words, lack of electron density surrounding them compared to typical alkene spectrum[9]. This lack of electron density makes the carbon atoms very attractive targets for the hydride ligands attached to the Rhodium to migrate to. It is this ability to remove electron density from the alkene π orbital, while simultaneously back-donating density to the π^* that makes Wilkinson's catalyst so effective.

Wilkinson's catalyst cannot hydrogenate areas of conjugation, so theoretically only bond (3) should be hydrogenated in the presence of hydrogen and Wilkinson's catalyst[10]. This experiment will assess the selectivity of the hydrogenating abilities of Wilkinson's catalyst, and its regioselectivity and chemoselectivity in regards to a molecule with several areas' capable of hydrogenation. The products in this experiment will be analysed using ^1H -NMR data.

Experimental

Preparation of catalyst

Triphenylphosphine (0.52g, 1.98mmol) was dissolved in ethanol (20ml).

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.08g, 0.3mmol) was dissolved in ethanol (4ml). Both

solutions were degassed with nitrogen. The rhodium solution was then added

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to the PPh₃ solution and this was refluxed in a nitrogen atmosphere for 90 minutes. After cooling, the remaining solution and precipitate were removed and filtered via sinter funnel filtration. The yield for the Wilkinson catalyst was determined (0.180g, 0.218mmol, 72.7%).

Hydrogenation of carvone

Under a pressure of one atmosphere of hydrogen, a flask was injected with the previously prepared catalyst. Carvone (0.5g, 3.33mmol), in a solution of toluene (2ml) was then added to this flask. Consumption of hydrogen, measured using syringes, was recorded at 46cm³, (2.05mmol) representing a 61.6% yield of the hydrogenated carvone product.

Results

Colour changes

Rhodium (III) chloride powder is a black powder. As reflux progressed and the Wilkinson's catalyst was produced, the solution went slowly from black to a brown-red suspension. This is illustrated in figure 4.

Hudson et al have also reported an unknown brown precipitate, which appeared to exhibit similar catalytic properties[11]. Wilkinson et al also reported orange precipitate with identical chemical properties[12].

Yields and Errors

A total of 0.180g of Wilkinson's catalyst was produced in the experiment, a 72.7% yield, which compares favourably with other studies indicating yields of between 60[13]-88[14]%.

46cm³ of hydrogen gas was absorbed in the process of the experiment, representing a total absorbance of 2.05mmol of hydrogen gas. In passing

gas through the solution, it turned yellow, which is consistent with other experimental observations[15] [16]. Considerable agitation of the solution was required so as to allow adequate complexation of the hydrogen gas. Assuming the entirety of this gas hydrogenated the terminal olefin group in carvone; this represents a 61.6% yield of hydrogenation. However, it is entirely likely that a higher yield would have been obtained had the experiment continued for a longer period of time. The yield of hydrogen gas may also be misleading since it is difficult to completely hermetically seal all the apparatus, and it is also difficult to estimate the extent to which gas may have escaped from the reaction vessel.

Products obtained from hydrogenation

Carvone has several sites available for hydrogenation/reduction. However, $\text{RhCl}(\text{PPh}_3)_3$ will only selectively hydrogenate terminal alkenes, as described by Wilkinson et al. This hypothesis is supported by $^1\text{H-NMR}$ data[17] of carvone and the product of hydrogenation.

There is no change at peaks 6.69ppm, indicating that this protons' environment was not affected by the hydrogenation. The slight downfield shift of the protons of signal between 2.2-2.7ppm to an area between 1.9-2.5ppm indicates that there is less electron density surrounding these protons. These signals were assigned to groups near to the hydrogenated bond, and so this is fairly conclusive evidence that the terminal bond was hydrogenated. The minor signal at 4.72 and 4.75ppm indicate a slight contamination of the sample with carvone.

Conclusion

The yield obtained by the method followed to synthesize Wilkinson's catalyst afforded values similar to that given in literature. The experiment clearly demonstrated by ¹H-NMR data that Wilkinson's catalyst efficiently hydrogenates terminal alkene bonds selectively. A more quantitative study could be performed, wherein systems containing non-conjugated alkene systems were tested for hydrogenation. This would allow more stringent analysis and more precise definition of the hydrogenation abilities of Wilkinson's catalyst.

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