

Experiment IV.¹

Organometallic Compounds and Catalysis: Synthesis and Use of Wilkinson's Catalyst.

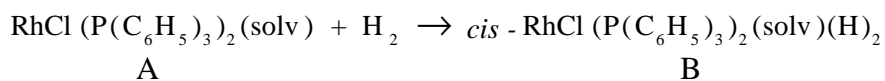
Organometallic chemistry is the chemistry of compounds which contain a metal carbon bond. Research interest in this area is largely fueled by potential applications of organometallic compounds as catalysts in industrial chemistry. A catalyst is defined as a substance that accelerates the rate of achieving chemical equilibrium, and which can be recovered unchanged at the end of a reaction. Catalytic processes can be broadly defined into two categories: 1) homogeneous catalysis, a process where the catalysts and reactants remain in the same phase; and 2) heterogeneous catalysis, where the reactants and catalysts are in different phases. In most heterogeneous catalytic systems the catalyst is in the solid phase and the reactants are liquids or gases.

In this experiment you will prepare the most successful homogeneous organometallic catalyst to date, $\text{RhCl}(\text{PPh}_3)_3$, which catalyzes the hydrogenation of olefins. Interestingly, the catalytic discovery was made independently and nearly simultaneously by Wilkinson and Coffey in 1964.² Wilkinson fully explored the scope, selectivity, and mechanism by which the complex catalyzes the hydrogenation of olefins and the compound is now commonly referred to as "Wilkinson's catalyst." The major mechanistic features of the reaction sequence can be shown by using what is known as a catalytic cycle or a Tolman loop, Figure 1. While a detailed discussion of the underlying mechanism is beyond the scope of this lab, a few general comments are worthwhile.

Note how $\text{RhCl}(\text{PPh}_3)_3$ does not appear in the catalytic cycle of Figure 1. Wilkinson's catalyst is not a catalyst but, rather a catalyst precursor! The actual catalyst is believed to be the solvento complex, $(\text{solvent})\text{RhCl}(\text{PPh}_3)_2$. The problem of identifying the true active catalyst in catalytic systems is exceedingly difficult. Only through detailed mechanistic studies can an experimentalist gain any certainty of the active catalyst. There exist many reports in the scientific literature of 'catalysts' which in reality are not catalysts at all. Often impurities or decomposition products catalyze the reactions of interest.

Figure 1.

The catalytic cycle in Figure 1 contains several important steps central to many organometallic reaction mechanisms. A key example is the reaction of dihydrogen with the solvento complex to form a *cis*-dihydride species:



This reaction is known as an oxidative-addition reaction. Note that in this chemical transformation, A is bound to only four ligands while B is bound to six. We call species A a four-coordinate “coordinately unsaturated” compound and B is “coordinately saturated”. Note also that species A is a Rh(I) complex with 16 total valence electrons and species B is a Rh(III) complex with 18 valence electrons. Thus in an oxidative-addition reaction the coordination number of the metal changes from four to six and the oxidation state of the metal increases by two. The reverse of an oxidative-addition reaction is also common and is termed a reductive-elimination reaction. In today’s experiment, you will observe the above reaction by a color change and will actually characterize a fluxional five-coordinate species which forms in a subsequent step.

Hazards.

Rhodium (III) chloride hydrate (CAS No. 20765-98-4) is harmful if swallowed, inhaled, or absorbed through the skin. ORL-RAT LD50: 1302 mg/kg.

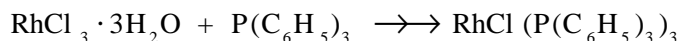
Triphenylphosphine (CAS No. 603-35-0) is a mild lachrymator and can cause skin irritation. ORL-RAT LD50: 700 mg/kg.

Hydrogen (CAS No. 1333-74-0) is an explosive gas. There must be no open flames when hydrogen is in use. It is a non breathable gas, so care should be exercised.

Cyclohexane (CAS No. 110-83-8) may be harmful if inhaled, ingested or absorbed through the skin. OSHA Standard-AIR: TWA 300 ppm.

Experimental Procedure.

A. Synthesis and Characterization of Wilkinson's Catalyst.

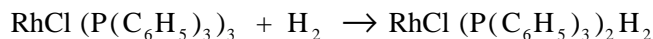


Place 10 mL of absolute ethanol (graduated cylinder) in a round bottom flask equipped with a magnetic stirring bar. Attach a water condenser and place the apparatus in a sand bath upon a magnetic stirring hot plate. Heat the ethanol to just below its boiling point. Remove the condenser momentarily, and add 300 mg of triphenylphosphine to the hot ethanol and stir until the solid is dissolved. A small amount of solid may remain at this point. This is OK.

Remove the condenser once again and add 50 mg of hydrated Rh(III) chloride to the solution and continue to stir. Heat the solution to a gentle reflux for ~ 30 minutes. Bright shiny burgundy-red crystals should form at this time.

Collect the product crystals by suction filtration on a Hirsch funnel while the solution is hot. Wash the crystals with three 1-mL portions of ether. Dry the crystals on the filter by continuous suction. Calculate the percentage yield and determine the melting point of the product. Obtain the IR spectrum and the ^1H NMR spectrum of the compound. Save the product in a labeled vial.

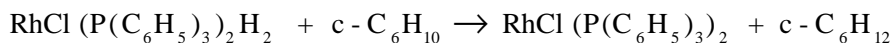
B. Absorption of Hydrogen by Wilkinson's Catalyst.



Place 25 mg of $\text{RhCl}(\text{PPh}_3)_3$ and a stir bar in a side arm flask with an addition funnel. Evacuate and purge the apparatus three times. Add 3 mL of chloroform to the addition funnel and deoxygenate by bubbling with H_2 for 10 minutes. Add the chloroform to the $\text{RhCl}(\text{PPh}_3)_3$ with stirring. Allow the reaction to proceed for 5 minutes. Then remove the addition funnel and concentrate the solution under the flow of H_2 gas. When the solution is sufficiently concentrated (~0.2 mL) add deoxygenated ether dropwise until precipitation occurs. Cool the flask in an ice water bath and collect the light yellow crystals by suction filtration using a Hirsch funnel.

Calculate the percentage yield. Obtain the IR and ^1H NMR spectra. Compare them with the spectra you obtained for Wilkinson's catalyst.

C. Catalytic Hydrogenation of Olefins.



Place 25 mg of $\text{RhCl}(\text{PPh}_3)_3$ and a stir bar in a side arm flask with an addition funnel. Evacuate and purge the apparatus three times. Add 10 mL of deoxygenated toluene with stirring under a hydrogen ambient. Stir the resulting pale yellow solution for 5 minutes.

Discontinue the stirring and add 1 mL of cyclohexene with a pipetman. Cap the side arm flask with a 14/20 stopper and continue to stir for 5 minutes until the solution lightens to a pale yellow. Discontinue the hydrogen flow and the stirring.

Remove a small sample of the solution for GC analysis. The presence of cyclohexane formed should be evident in the chromatogram. Calculate the percentage conversion of cyclohexene to cyclohexane from the relative areas of the peaks.

Current Research Efforts

Organometallic chemistry is central to a significant fraction of academic inorganic research.³ Some important specific examples of organometallic catalysts include: 1) Hydroformylation, the reaction of an olefin with CO and H_2 in the presence of a metal carbonyl to form aldehydes; 2) Wacker Process, an olefin is oxidized to an aldehyde or ketone in the presence of a soluble palladium salt; 3) Ziegler Natta Process, olefins are polymerized using an organoaluminum-titanium catalyst to form stereoregular polymers; and 4) Fischer-Tropsch Reactions, the reductive polymerization of CO to form straight-chain hydrocarbons, olefins and alcohols. The role inorganic chemists often play in this field is to prepare new homogeneous catalysts and develop mechanistic models for their formation and reactivity. Homogeneous catalysts offer the possibility of understanding more complex heterogeneous catalytic systems on a molecular level.

A growing area of research is the study of main group and lanthanide organometallic chemistry as opposed to the transition metal chemistry explored in this experiment. An advanced course in Organometallic Chemistry is offered annually in the Chemistry Department at JHU.

References

1. This experiment is adapted from: Szafran, Z.; Pike, R.M.; Singh, M.M. "Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience", **1991**, John Wiley & Sons, New York, NY, pg 271.
2. a) Young, J.F.; Osborn, J.A.; Jardine, F.H.; Wilkinson, G. *Chem. Commun.* **1965**, 131. b) Osborn, J.A.; Jardine, F.H.; Young, J.F.; Wilkinson, G. *J. Chem. Soc. (A)* **1966**, 1711.
3. Collman, J.P.; Hegedus, L.S. "Principles and Applications of Organotransition Metal Chemistry", **1987**, Oxford University Press. Mill Valley, CA.