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# Hydrogenation of alkenes and aromatic hydrocarbons using water-soluble $RuCl_2(TPPTS)_3$ in aqueous medium

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**Abstract**

Water-soluble ruthenium complex $RuCl_2(TPPTS)_3$ have been used for the catalytic hydrogenation of unsaturated hydrocarbons, namely, 1-hexene, 1-heptene, styrene, cyclooctadiene, cyclooctene and benzene. Hydrogenation reactions were carried out under mild conditions. Optimum conditions for hydrogenation was evaluated and all substrate were studied at optimum conditions. The catalytic hydrogenation performances have been compared for aliphatic and aromatic hydrocarbons analogues. Results shows aliphatic hydrogenation occurs more easily compared to aromatic hydrogenation. Effect of addition of zinc chloride to aqueous solution on the hydrogenation of benzene showed that at some critical concentration of zinc chloride, partial hydrogenation of benzene to cyclohexene occurs.


*Keywords:* Hydrogenation; Water-soluble ruthenium complex; Biphasic catalytic system and benzene

## 1. Introduction

One of the main drawbacks of homogeneous metal/metal complex catalyzed reactions is the difficulty in recovering the metal/metal complexes after their use. Due to stringent regulation regarding the discharge of chemicals into effluent and high cost of metal, it is necessary to recover these from the reaction products. Commercially several methods like distillation, heterogenization and recovery by reverse osmosis have been tried to overcome this problem. However, distillation of reaction products is energy intensive, the use of polymer bound catalysts [1,2] is beset with leaching of metal/complex and reverse osmosis processes [3] have not been developed industrially because of their poor productivity. An elegant solution for this lies in using a liquid–liquid biphasic system [1,4,5]. The choice of water, which is non-miscible with a wide range of classical organic solvents, has recently allowed the industrial development of such a technology. In this case, catalyst system is water-soluble while reactants and products remain in the organic phase. Several catalytic reactions have been reported in such biphasic systems like hydroformylation of alkenes [5,6], hydrocyanation of dienes [7], telomerisation of olefins and dienes [8], addition of active methylene compounds to dienes [9], hydrogenation of pyruvic and crotonic acid [10], hydrogenation of αβ-unsaturated aldehyde [11](a),

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and reduction by hydrogen transfer of aromatic or aliphatic aldehydes [11](b). However, carrying out homogeneous catalytic reaction in water requires the development and understanding of a relatively unexplored field of organometallic chemistry in aqueous medium. Since early work by Barbier [12], Grignard [13] and Ziegler [14], water has often been considered as a poison for organometallic reactions, though in 1960s, hydrogenation of alkenes was reported [15] in water in the presence of cobalt(II) salts. Apparently, water did not interfere in the catalytic cycle. More recently, studies on the transformation of nitriles into amide with palladium(II) complex have shown that water can intervene in the catalytic cycle and behaves not only as a solvent but also as a reactant [16].

A catalytic reaction will occur in water if the catalyst is water-soluble which is achieved by modifying the ligands to make them water-soluble; like water-soluble phosphanes [17], hydroxylphosphanes, carboxylphosphanes, aminophosphane and sulfonated phosphanes. The TPPTS ligand (TPPTS = $p(C_6H_4\text{-}SO_3Na)_3{\cdot}3H_2O$) trisodium salt of tri(*m*-sulfophenyl)-phosphine is probably one of the ligands, which is highly soluble in water (solubility > 1200 $g l^{-1}$).

In this paper, we are reporting the preparation of water-soluble $RuCl_2(TPPTS)_3$ complex, along with the synthesis of TPPTS ligand (TPPTS = $p(C_6H_4\text{-}SO_3Na)_3{\cdot}3H_2O$) and catalytic hydrogenation of various unsaturated and aromatic compounds using this complex under mild conditions.

## 2. Experimental

### 2.1. Materials

The trisodium salt of tri(*m*-sulfophenyl)-phosphine (TPPTS) was prepared in accordance with method described in the literature [18]. The hydrogen (99.8%) used was from Hydro Gas India Pvt. Ltd., India. All the alkenes and hydrocarbons used were from Aldrich Chemicals, USA. The sodium salt of tri(*m*-sulfophenyl)-phosphine oxide as an impurity was less then 5% and water content was less then 10%. Ethanol (99.5% pure) used was from Baroda Chemicals Industries Ltd., India and was further purified by journal literature method. $RuCl_3{\cdot}3H_2O$ used in reaction was purchased from Johnson Matthey, UK.

### 2.2. Instrumentation

All the reactions were performed in 300 ml PARR reactor model No. 4561(PARR Instrument, USA). NMR measurements were done by Bruker avance DPX 200 MHz FT-NMR and IR spectra has been recorded on by Perkin-Elmer spectrum GX FT-IR system and CHN analysis has been done on Perkin-Elmer C, H, N, S and O analyzer. Products were analyzed using SHIMADZU GC-17A gas chromatograph using flame ionization detector (FID) having 5% diphenyl and 95% dimethylsiloxane capillary column (60 m length, 0.25 mm diameter). Column temperature was kept initially at 40 °C for 5 min and then raised to 150 °C at 10 °C $min^{-1}$. Nitrogen was used as a carrier gas (1.2 ml $min^{-1}$).

### 2.3. Synthesis

Water-soluble ruthenium complex, $RuCl_2(TPPTS)_3$, was prepared by taking 100 mg of $RuCl_3{\cdot}3H_2O$ in 7 ml of ethanol to which 500 mg of TPPTS dissolved in water was added and solution was stirred under reflux for 3 h. The volume of the reaction mixture was reduced to minimum and cold acetone was added to precipitate the complex. The complex was filtered and washed with cold acetone and finally re-crystallized from water:acetone mixture.

### 2.4. Catalytic reaction

One millimole of catalyst, $RuCl_2(TPPTS)_3$, dissolved in 100 ml water and 2 gm of substrate was taken in stainless steel autoclave 300 ml reactor (model 4561, Parr Reactor, USA). The reactor was flushed with nitrogen three times followed by flushing hydrogen twice at room temperature after which reactor was pressurized to 10 bar pressure with hydrogen and brought to desired reaction temperature. The reaction was initiated by stirring and after desired reaction time, the stirring was stopped and reactor was cooled over night. Separating funnel was used to separate cooled reaction mixture and organic layer was analyzed on GC.

## 3. Results and discussion

### 3.1. Synthesis and characterization

TPPTS ligand is prepared by sulfonation of triphenylphosphine ($PPh_3$). Typically, 2 mmol (524 mg) of triphenylphosphine was taken in 50 ml round bottom flask along with magnetic bar and was flushed with nitrogen twice and then 2 ml of sulfuric acid was added to dissolve $PPh_3$ at room temperature. The $PPh_3$ solution was then cooled to 0–5 °C. and finally 10 ml oleum ($H_2SO_4$ containing 30% $SO_2$, Merck) was added drop wise to the reaction mixture. The reaction temperature was maintained below 5 °C. The complete sulfonation of the $PPh_3$ was confirmed by $^{31}P$ NMR spectra of the reaction mixture (Fig. 1) taken at different time intervals, i.e. 3–6 days. The tri-sulfonated sodium salt of triphenylphosphine gives singlet at −5.36 ppm [19] in $^{31}P$ NMR spectra. $^{31}P$ spectra of reaction mixture taken at the interval of 3–6 days (Fig. 1) indicate the complete sulfonation of triphenylphosphine after 144 h. IR spectrum shows peaks at 1202, 1041 $cm^{-1}$. It also gave peaks at 791 and 691 $cm^{-1}$ (Fig. 2) indicated the mono substitution on phenyl ring. From these data, it is evident that initially mono-sulfonated, followed by di-sulfonated and finally after 144 h triphenylphosphine is completely sulfonated to tri-sulfonated product, TPPTS. However some triphenylphosphine is oxidized to give its analogues oxide. Once the sulfonation is complete as confirmed by $^{31}P$ NMR, the reaction mixture is poured into crushed ice (≈100 g) and is neutralized

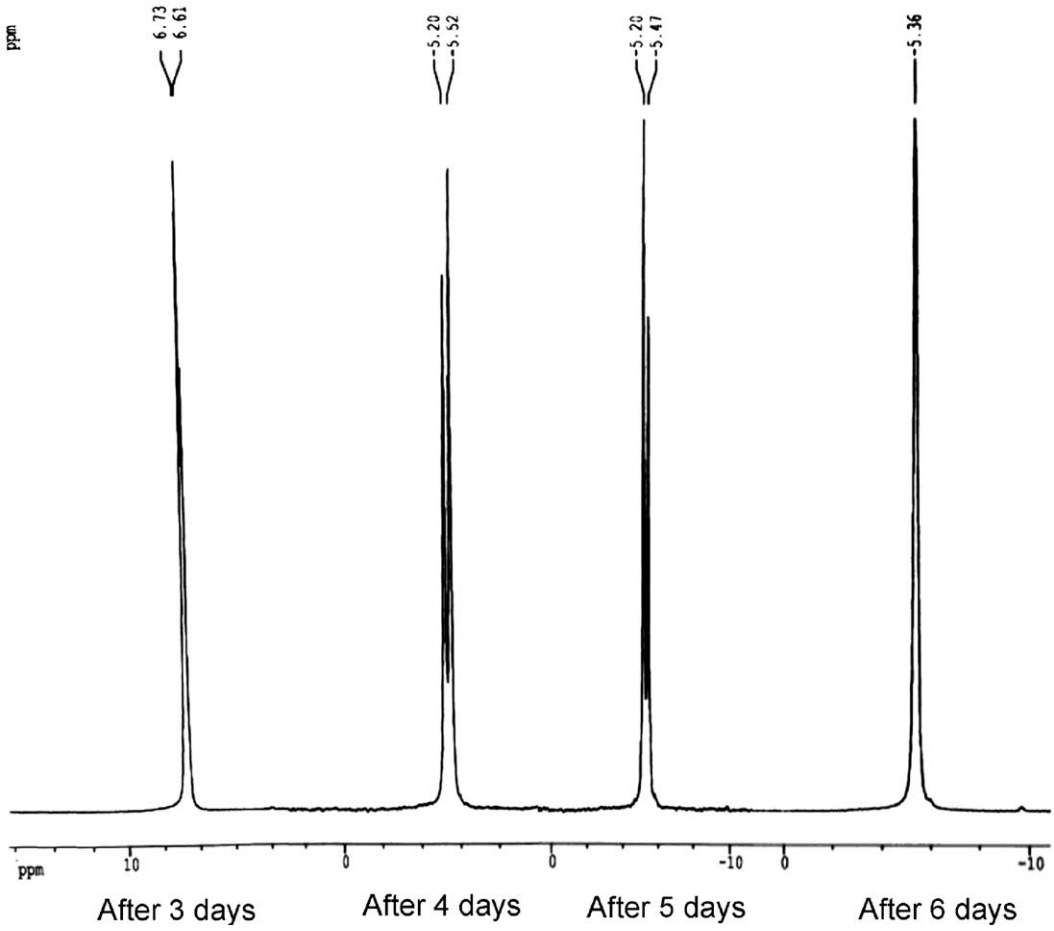



Fig. 1. $^{31}P$ NMR spectra of TPPTS during its synthesis by the reaction of $PPh_3$ with oleum ($H_2SO_4$ containing 30% $SO_2$, Merck).

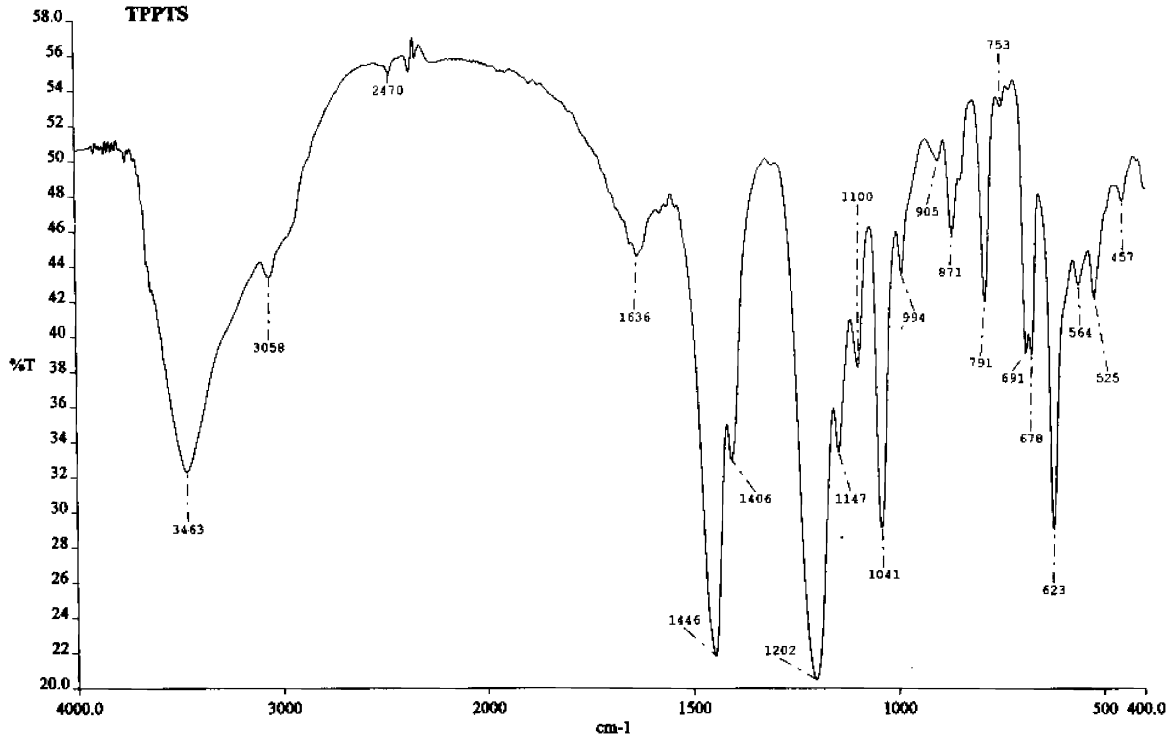



Fig. 2. IR spectrum of the TPPTS ligand.

with 50% NaOH solution while maintaining the solution temperature below 5 °C. After neutralizing the reaction mixture with NaOH, cold methanol was added to the neutralized mixture and solid separated out was filtered (mainly $Na_2SO_4$) and the filtrate was concentrated and further addition of cold methanol gave desired product, TPPTS, which was collected by filtration. More products were collected from the filtrate by evaporating it to dryness after which slight yellow solid comes out (yield = 65%).

Water-soluble complex was prepared by the reaction of $RuCl_3{\cdot}3H_2O$ with trisodium salt of tri(*m*-sulfophenyl)-phosphine; TPPTS was characterized by physicochemical technique. The C, H, N analytical data obtained for ruthenium(II) complex $RuCl_2(TPPTS)_3$ is as: calc. (found) C: 63.3 (62.4); H: 4.3 (3.9). $^{31}P$ NMR spectra of the isolated complex gave a singlet at 57.78 ppm indicating all the three phosphorous of TPPTS are equivalent. IR spectra of the isolated complex gave band at 1202 and 1041 $cm^{-1}$ due the sulfonation of phenyl ring of $PPh_3$.

The catalytic hydrogenation of various α-unsaturated aliphatic and aromatic hydrocarbons was carried out at 150 °C and 10 atm pressure of hydrogen. The results are given in Table 1. The hydrogenation of α-unsaturated aliphatic hydrocarbons is almost complete under the studied reaction conditions. Cyclooctadiene is selectively converted to cyclooctane with

Table 1
Hydrogenation of selected aliphatic and aromatic unsaturated hydrocarbons using $RuCl_2(TPPTS)_3$ as catalyst

| Reactant | Conversion (%) |
|---|---|
| 1-Hexene | 95.31 |
| 1-Hepetene | 95.27 |
| Styrene | 94 |
| Cyclooctadiene | 55 |
| Cyclooctene | 95.5 |
| Benzene | 18.81 |
| Cyclooctene + 1-hexene | 68 + 99 |

Reaction conditions: $[RuCl_2(TPPTS)_3]$, 1 mmol; substrate, 23.04 mmol; decane, 0.5 ml; solvent (water), 100 ml; temperature, 150 °C; $P_{H_2}$, 1 MPa; and reaction time, 420 min.

55% conversion and cyclooctene to cyclooctane with more then 95% conversion. From the catalytic results, it is evident that $RuCl_2(TPPTS)_3$ is selective for converting di-alkenes to saturated hydrocarbons in a consecutive reaction as we could not observe the formation of mono-alkene, cyclooctene during cyclooctadiene hydrogenation. The hydrogenation of benzene was also investigated using $RuCl_2(TPPTS)_3$ catalyst in presence and absence of $ZnCl_2$. Under these reaction conditions, it was observed that in absence of zinc chloride the catalyst gave only cyclohexane as a hydrogenation product (18.81%) but in the presence of 0.025 mmol of $ZnCl_2$, cyclohexane formation increases to 49% and further increase in the salt concentration from 0.025 to 0.075, decreases the conversion of benzene to cyclohexane. However after a critical concentration of $ZnCl_2$ (0.250 mmol) gives equivalent amount of cyclohexane and cyclohexene (Table 2). With further increase in the $ZnCl_2$ concentration to 1 mol, there is a decrease in the yield of cyclohexane and increase in the yield of cyclohexene (Fig. 3).

There are reports [20,21] for the partial hydrogenation of benzene to cyclohexene using heterogeneous ruthenium based catalysts wherein the effect of various salt have been investigated. The primary function of the added salt generally is to make the ruthenium catalysts hydrophilic. The hydrophilicity causes the catalyst to be surrounded by a strong water layer with which the rate of hydrogenation of cyclohexene is strongly suppressed due to the very low solubility of cyclohexene in water. In our system, as we are carrying out the reaction in biphasic media, water being one of the solvents and catalyst being water-soluble, addition of inorganic salt will definitely depress the hydrogenation of cyclohexene due to its very low solubility in water. We are studying the effect of other cations and anions in order to have an insight on the possible mechanistic details in water-soluble catalyst system for the selective hydrogenation of benzene to cyclohexene.

Table 2
Effect of $ZnCl_2$ on the hydrogenation of benzene using $RuCl_2(TPPTS)_3$ as catalyst

| $[ZnCl_2]$ | Conversion (%) | Selectivity (%) | |
|---|---|---|---|
| | | Cyclohexane | Cyclohexene |
| 0.025 | 49.44 | 100 | – |
| 0.050 | 37.81 | 100 | – |
| 0.075 | 24.17 | 100 | – |
| 0.10 | 18.08 | >95 | <5 |
| 0.25 | 15.08 | 50 | 50 |
| 0.50 | 19.19 | 22.04 | 77.95 |
| 1.00 | 20.62 | 8.77 | 91.22 |

Reaction conditions: $[RuCl_2(TPPTS)_3]$, 1 mmol; [benzene], 23.04 mmol; decane, 0.5 ml; solvent (water), 100 ml; temperature, 150 °C; $P_{H_2}$, 1 MPa; and reaction time, 420 min.

A competitive hydrogenation reaction was also carried out by selecting a mixture of α-unsaturated alkene (1-hexene) and cyclic alkene (cyclooctene). It was

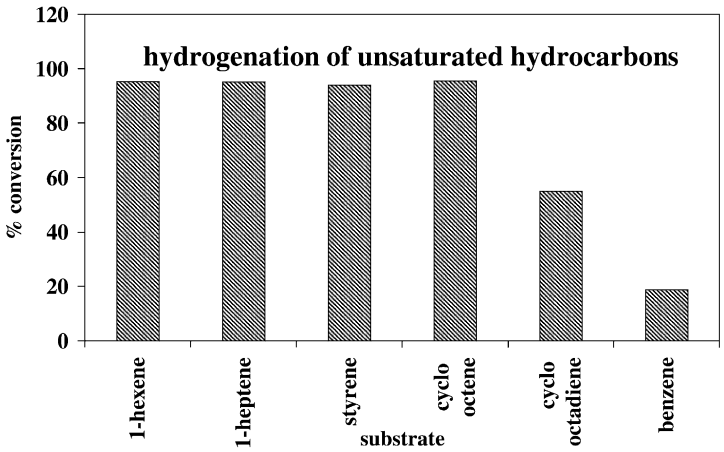
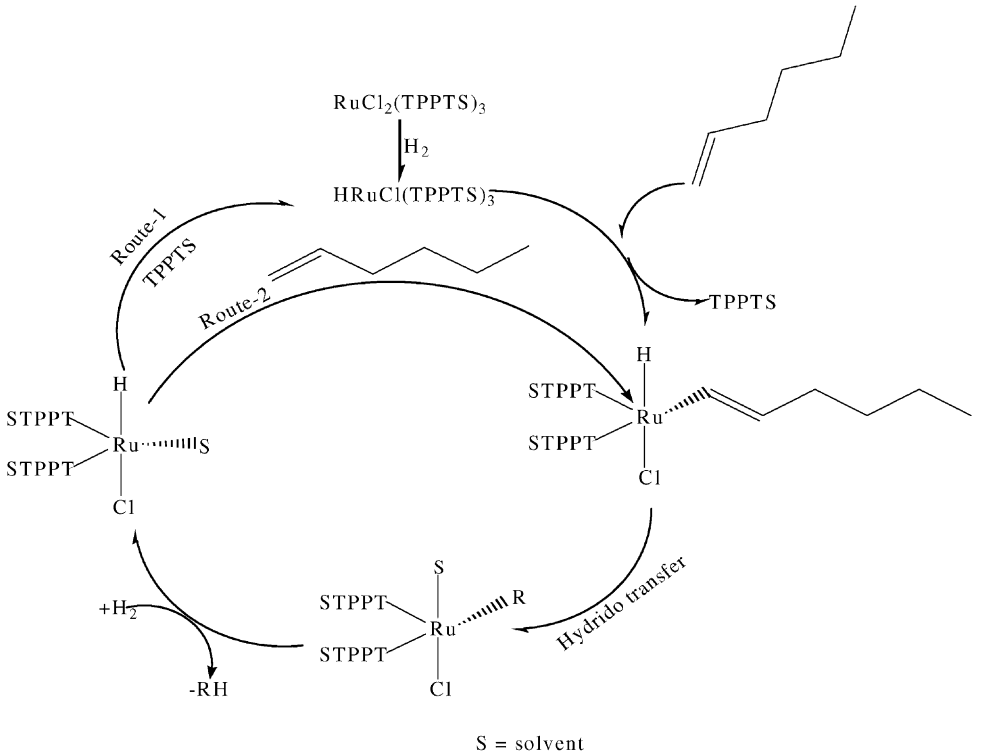



Fig. 3. Hydrogenation of selected aliphatic and aromatic unsaturated hydrocarbons. Reaction conditions: $[RuCl_2(TPPTS)_3]$, 1 mmol; [benzene], 23.04 mmol; decane, 0.5 ml; solvent (water), 100 ml; temperature, 150 °C; $P_{H_2}$, 1 MPa; and reaction time, 420 min.




Scheme 1.

observed that in competitive reaction, α-unsaturated alkene is completely hydrogenated whereas cyclic alkene is hydrogenated only 50% which indicates that in mixture of 1-hexene and cyclooctene, catalyst is more selective towards the hydrogenation of linear alkene then cyclic alkenes and while comparing the hydrogenation reactions of aliphatic alkenes and aromatic hydrocarbon, it is more active toward as former.

A general mechanism as given in Scheme 1 is proposed for the hydrogenation reaction using $RuCl_2(TPPTS)_3$. In case of hydrogenation of 1-hexene, 1-heptene and functionalized aromatic hydrocarbons, i.e. styrene, the catalyst intermediate, $HRuCl(S)(TPPTS)_2$, is found more active catalyst for hydrogenation of α-alkenes.

## 4. Conclusion

Under the optimized conditions for the hydrogenation of various unsaturated hydrocarbons such as 1-hexene, 1-heptene, styrene, cyclooctene, cyclooctadiene, benzene, we can conclude that water-soluble catalyst, $RuCl_2(TPPTS)_3$, can hydrogenate aliphatic unsaturated hydrocarbons more efficiently than aromatic hydrocarbons. Use of biphasic system reported in this study for hydrogenation is more effective for separation of product and also for the recovery of catalyst. Addition of zinc chloride in specific amounts leads to partial hydrogenation of benzene to cyclohexene.

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