Homogeneous Hydrogenation of Cyclohexene Catalyzed by Ruthenium(II) Complexes

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Ruthenium(II) complexes, viz RuCl₃(AsPh₃), RuCl₃(SbPh₃), RuCl₃(DMSO)₄, RuCl₃(DMSO) (SbPh₃), RuCl₃(DPPE)₃, RuCl₃(DPAE)₃ [DPPE = 1,2-bis(diphenylphosphino)ethane, DPAE = 1,2-bis(diphenylarsino)-ethane], RuCl₃(SnCl₃)(PPh₃)₃, RuCl(SnCl₃)(AsPh₃) have been used as catalysts in the homogeneous hydrogenation of cyclohexene at 30°C and 1 atmosphere of hydrogen pressure. A mechanism is proposed whereby the six-coordinate complexes dissociate a phosphine or an arsine group in a pre-equilibrium step and a five-coordinate species results in solution. The dependence of the rate of hydrogenation on factors such as catalyst concentration, substrate concentration and the nature of the ligand is reported.

The catalytic activity of ruthenium complexes has been demonstrated in a variety of catalytic reactions. Very few ruthenium complexes, however, have been used as catalysts for the homogeneous hydrogenation of olefins. These include the hydridocarboxylato complexes Ru(H(OCOR))(PPh₃)₃ (ref. 5), hydridochloro complex RuHCl(PPh₃)₃ (ref. 6) and tertiary phosphine cationic complexes [Ru₃Cl₅L₆]⁺ Cl⁻ (L = PPh₃ or PEtPh₃) (ref. 7). In this paper we report the homogeneous hydrogenation of cyclohexene catalysed by a variety of ruthenium(II) complexes, viz. RuCl₃(AsPh₃), RuCl₃(SbPh₃), RuCl₃(DMSO)₄, RuCl₃(DMSO) (SbPh₃), RuCl₃(DPPE)₃, RuCl₃(DPAE)₃ [DPPE = 1,2-bis(diphenylphosphino)ethane, DPAE = 1,2-bis(diphenylarsino)-ethane], RuCl₃(SnCl₃)(PPh₃)₃, RuCl(SnCl₃)(AsPh₃).

The presence of a halogenic group like SnCl₃ in the coordination sphere of the metal ion markedly increases the catalytic activity of the complex.

Materials and Methods

The complexes RuCl₃(AsPh₃)₃ (ref. 9), RuCl₃(SbPh₃)₃ (ref. 9), RuCl₃(DMSO)₄ (ref. 10), and RuCl₃(DMSO) (SbPh₃)₃ (ref. 9) were synthesized by published procedures. Cyclohexene was obtained by the dehydrogenation of cyclohexanol. Benzene (BDH, AR) was used in all the hydrogenation studies. Indicator solution (a 5% sodium chloride solution containing a drop of methyl orange) was employed to fill manometers for measuring volume changes during hydrogenation reactions. An all glass apparatus with leak-proof Sprinham stopcocks was used for the measurement of the rate of absorption of hydrogen. To keep the system air tight high vacuum silicone grease was applied to the stopcocks. The temperature of the reaction was maintained constant by circulating water at a particular temperature (30°C) through a water jacketed glass cell. All the experiments were conducted at one atmosphere of hydrogen pressure.

Hydrogen gas from the cylinder was purified by passing first through a saturated potassium permanganate solution to free it from olefins and finally through concentrated sulphuric acid. The concentration range of cyclohexene was 0.0025–0.015 M and that of catalyst was 0.3–2.0 × 10⁻³ M. The solvent mixture employed for the hydrogenation consisted of ethanol-benzene (1:3, v/v).

A known weight of the catalyst was taken in the reaction cell, which was previously evacuated and flushed with hydrogen several times to ensure that complete hydrogen atmosphere prevailed in the reaction cell. A known quantity of the alkene, dissolved in the solvent, was rapidly added to the catalyst and a total volume of 10 ml was maintained in the reaction cell. The solution was rapidly stirred to keep it saturated with hydrogen. Sufficient time was given for the solution to attain equilibrium. The absorption of hydrogen was then noted at suitable intervals of time by the change in the level of indicator solution in the burette. Since the solvents used were volatile a blank was run simultaneously to nullify the effect of solvent vapour pressure and to ensure the change in volume as a result of absorption of hydrogen.

Since the rate of reaction was much slower than the rate of dissolution of hydrogen, the solution was considered to be saturated with respect to hydrogen at all times. The solubility of hydrogen was assumed to obey Henry’s law. The standard hydrogen pressure used was 760 m and conversion to the rate of consumption of substrate in M min⁻¹ was made by the stoichiometric relationship \(-\frac{d[H_2]}{dt} = -\frac{d[S]}{dt}\).

Results

The rates of hydrogenation of cyclohexene by various ruthenium(II) catalysts measured at constant [catalyst] and [substrate] decrease in the order: RuCl₃
In the catalytic homogeneous hydrogenation of alkenes by RuHCl (PPh$_3$)$_4$, Hallmann et al. have suggested the four-coordinate RuHCl (PPh$_3$)$_2$ to be the active species. Similarly for the complex RuCl$_4$ (PPh$_3$)$_2$ dissociation of one of the phosphine group takes place to form a four-coordinate complex, RuCl$_4$ (PPh$_3$)$_2$ which is the active catalyst involved in the catalytic reactions. A prototype of this complex is the species RuCl$_3$ (AsPh$_3$)$_2$ which is studied as a hydrogenation catalyst in the present work. Except this catalyst in all the other cases a pre-equilibrium as shown in Eq. (1) exists in solution. In subsequent discussion catalysis by the five-coordinate catalytic species has been taken into consideration.

The dependence of reciprocal of the initial rate of hydrogenation $1/\text{d}[\text{H}_2]/\text{dt}$ on [substrate] is of the form

$$1/R = 1/([\text{olefin}. C + C'])$$

A mechanism which is in accord with the above mentioned relationship may be formulated as

$$\text{HRuXLL'} + \text{olefin} \rightleftharpoons \text{RuXLL'}' (\text{Alkyl}) \quad \ldots(2)$$

$$\text{RuXLL'} (\text{Alkyl}) + \text{H}_2 \quad \overset{k}{\longrightarrow} \quad \text{HRuXLL'} + \text{Alkane} \quad \ldots(3)$$

In Eqs (2) and (3) L = AsPh$_3$, L' = 0; X = Cl; L = 2 DMSO, DPPE, DPAE, L' = 0, X = Cl; L = L' = PPh$_3$, AsPh$_3$, X = SnCl$_2$; and L = SbPh$_3$, L' = DMSO, X = Cl.

A rate law for the above mechanism may be formulated as

$$R = -\frac{d[\text{olefin}]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{kK_1[\text{olefin}][\text{H}_2]T_M}{1 + K_1[\text{olefin}]+L/K} \ldots(4)$$

where $T_M = \text{HRuXLL'} + \text{Ru X L L'}$ (alkyl)

or $1/R = \frac{1}{kK_1[\text{olefin}][\text{H}_2]T_M} \ldots(5)$

if $L/K \ll 1$.

$$1/R = \frac{1}{kK_1[\text{H}_2]T_M[\text{olefin}]} + \frac{1}{k[H_2]T_M} \ldots(6)$$

Equation (6) is in accord with the experimentally observed relationship where $C = \frac{1}{kK_1[\text{H}_2]T_M}$ and $C' = 1/k[H_2]T_M$. A plot of $1/R$ vs $1/[\text{olefin}]$ should, therefore, be linear with the intercept equal to $1/k[H_2]T_M$ and slope equal to $1/kK_1[\text{H}_2]T_M$. Relationship (6) has been verified for the hydrogenation of cyclohexene catalysed by RuClX L. The values of $K_1$ and $k$ are given in Table 1. For those complexes that appreciably dissociate in solution, the assumption that $L/K \ll 1$ is valid and the values of $K_1$ given in Table 1 refer to the stability of the mixed ligand olefin complex. In the case of chelating ligands like DPPE
and DPAE a chelate has to be broken in order to give a vacant coordination position on the metal ion. In such cases the dissociation of a ligand in pre-equilibrium step (1) may be very small and $L/K^+ \gg 1$. The value of $K^+$ in such cases is an apparent constant and may not necessarily indicate the stability of metal-olefin complex.

The catalytic activity of ruthenium-II complexes depends as a first approximation on the $\pi$-acceptor capacity of the neutral ligand and decreases in the order $\text{PPh}_3 > \text{AsPh}_3 > \text{DMSO} \sim \text{SPh}_3$. In the last two cases the presence of another strong $\pi$-acceptor like $\text{SnCl}_4$ in the coordination sphere of the metal ion considerably enhances the catalytic activity of the complex as compared to the chloro-complex. Since $\text{SnCl}_4$ has a higher trans-effect than chloride it helps in labilizing the hydride in the hydride transfer step to the olefin.

### References