

Homogeneous Hydrogen Transfer from Alcohols to Cyclohexanone Catalyzed by Transition Metal Complexes

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The catalytic activity of some ruthenium and iridium complexes for the hydrogen transfer from propan-2-ol to cyclohexanone decreases in the following order: $\text{RuCl}_2(\text{PPh}_3)_3 > \text{RuCl}_2(\text{DPPTP})_3 > \text{RuI}_2(\text{DPPTP})_3 > \text{RuBr}_2(\text{DPPTP})_3 > \text{RuH}(\text{CH}_3\text{COO})(\text{PPh}_3)_3 > \text{Ir}(\text{SbPh}_3)_3\text{Cl}$. Ni(II), Fe(II), Co(II) and Pd(II) complexes have no catalytic activity. Polar solvents other than acetonitrile inhibit the reduction of the ketone. Among the various bases *n*-butylamine is the best promoter. Compared to other alcohols 1-phenylethanol and its substituted derivatives are excellent hydrogen donors. Hammett plot of $\log k/k_0$ versus σ^+ is linear with a slope, $\rho = -1.8$ at 143°C, suggesting the generation of a positive charge in the transition state.

IN the catalytic transfer hydrogenation of aldehydes and ketones to the corresponding alcohols trihydridotris(triphenylphosphine)cobalt(III)¹, chlorotris(triphenylphosphine)rhodium(I)², dichlorotris(triphenylphosphine)ruthenium(II)³, trichlorotris(trimethyl phosphite) iridium(III)⁴ and dihydridotetrakis(triphenylphosphine)ruthenium(II)⁵ have been used as homogeneous catalysts along with a variety of organic compounds as hydrogen donors. Transition metal ions having the *d*⁶-configuration and an electron affinity of about 24 eV when coupled with π -acceptor ligands like alkyl or aryl substituted phosphines and CO have been found to be good catalysts⁶⁻⁸. In this paper several transition metal complexes and hydrogen donors have been examined for the reduction of cyclohexanone with the aim of understanding the mechanism of the hydrogen transfer process.

Materials and Methods

The following transition metal complexes were used: dichlorobis(triphenylphosphine)palladium(II)⁹, dichlorotris(triphenylphosphine)ruthenium(II)¹⁰, dichlorotris(diphenyl-*p*-tolylphosphine or DPPTP)ruthenium(II)¹⁰, chlorotris(triphenylstibine)iridium(I)¹⁰, dichlorobis(triphenylphosphine)nickel(II)¹¹, dichlorobis(diphenyl-*p*-tolylphosphine)cobalt(II)¹², hydridoacetatotris(triphenylphosphine)ruthenium(II)¹³, dichlorobis(triphenylphosphine)cobalt(II)¹³, tris(acetylacetonato)iron(III)¹⁴, bis(acetylacetonato)cobalt(II)¹⁰, bis(acetylacetonato)nickel(II)¹⁴, tris(acetylacetonato)cobalt(III)¹⁴, dibromotris(diphenyl-*p*-tolylphosphine)ruthenium(II)¹⁵, diiodotris(diphenyl-*p*-tolylphosphine)ruthenium(II)¹⁰, bis(dimethylglyoximato)cobalt(II)¹⁶ and bis(dimethylglyoximato)nickel(II)¹⁶.

Propan-2-ol (BDH, analar) dried over anhydrous sodium sulphate was distilled and the fraction boiling at 81.5°C was collected. Benzyl alcohol (LR, Pfizer) was purified as suggested by Martin and George¹⁷.

p-Xylene (Riedel) was dried over anhydrous sodium

sulphate and fractionally distilled (138°). Diphenyl ether after passing through a basic alumina column, was distilled under reduced pressure (118°-20°/16mm) and stored in the dark. 1-Phenylethanol (Fluka) was dried over anhydrous calcium sulphate, shaken with animal charcoal, kept overnight, distilled under reduced pressure (84°-86°/3 mm) and stored in the dark.

Cyclohexanone and other solvents were purified by standard methods¹⁸. All the substituted benzylalcohols and 1-phenylethanols were prepared from the corresponding aldehydes and ketones by reduction with sodium borohydride.

Kinetic runs were carried out under nitrogen atmosphere in a double walled vessel with provisions for degassing by bubbling nitrogen gas, mechanical stirring, mercury well for measuring the reaction temperature, and withdrawal of aliquots. The reaction mixture in the vessel could be maintained at the appropriate temperature by circulating in the annular space the vapour of a liquid of the required boiling point. All the solvents and substrates were thoroughly degassed by passing nitrogen gas. A weighed amount of the catalyst was transferred into the vessel followed by the solvent, diphenyl ether and then the donor. The mixture was heated to the reaction temperature and then the acceptor (ketone) was added. This time was noted as the zero time for the kinetic run. Aliquots were withdrawn at regular time intervals, quenched in an icebath and then analysed by GLC at 110° using 1 m × 3 mm stainless steel tube columns packed with 20% Carbowax (PEG) 1540 M on Chromosorb W.

For measuring the initial rate the percentage conversion of cyclohexanone to cyclohexanol was plotted against time. At the initial stage of the reaction the conversion was almost linear with time. However the linearity did not hold when conversion was more than 15% and a limiting conversion was reached in the region of 24.5% to 26%.

For the reaction 1-phenylethanol + cyclohexanone \rightleftharpoons cyclohexanol + acetophenone, the equilibrium constant computed with the experimental limiting conversion (0.1234) was in reasonably good agreement with the value calculated from literature¹⁹ data (0.1453). The initial rate of the reaction was determined from the linear portion of the concentration-time curve.

Results and Discussion

Catalytic activity of d^6 - d^8 complexes — The results for the catalytic activity of some d^6 - d^8 transition metal complexes for hydrogen transfer from propan-2-ol to cyclohexanone with added KOH are summarized in Table 1. Pd(PPh₃)₂Cl₂, Ni(PPh₃)₂Cl₂, Co(DPPTP)₂Cl₂, Co(PPh₃)₂Cl₂, Fe(acac)₃, Co(acac)₂, Ni(acac)₂, Co(acac)₃, Co(DMG)₂ and Ni(DMG)₂ are found to be devoid of any catalytic activity. RuCl₂(PPh₃)₃ is found to have the highest activity among the complexes used. The dissociation step has been postulated as a prerequisite in the mechanism of hydrogen transfer by ruthenium complexes^{20,21}. In agreement with this a decrease in the activity is observed when PPh₃ is replaced by diphenyl-*p*-tolylphosphine (DPPTP) in RuCl₂(PPh₃)₃. In hydridoacetatotriss (triphenylphosphine) ruthenium(II) the acetate ligand is strongly coordinated through two co-ordination sites of the metal ions. In this case, the formation of the hydrido complex with both donor and acceptor molecule involves a seven coordinate complex which is difficult. Hence the yield of cyclohexanol is very small compared to other ruthenium complexes.

Besides an optimum electron affinity of metal ion (≈ 24 eV) and the presence of strong π -acceptor ligands, other requirements for a transition metal complex to be a catalyst are co-ordinative unsaturation in the complex and lability of the intermediate hydrido complex²². The available data for the complexes used in this investigation are given in Table 2.

The presence of low lying orbitals in the metal ions capable of accepting electrons from the ligands should be reflected by the electron affinity²³. The lability of the hydrido complex (actual catalytic species for the hydrogen transfer reaction) depends on the total ligand field stabilization energies of both the original catalyst and the hydrido complex²⁴. According to Chatt and Shaw^{25,26} the energy separation (Δ) between the highest occupied orbital (bonding or non-bonding) and the lowest antibonding level must be greater than some critical value in order to confer stability on the hydrido complex. When a π -acceptor ligand like tertiary phosphine is used in the case of metal ions, Pd²⁺, Co²⁺, and Ni²⁺ back bonding interaction between the metal ion and the ligands leads to lowering of bonding orbital levels and hence Δ increases. So the electrons from the metal-hydrogen σ bond are not easily promoted to the lowest vacant antibonding orbital resulting in lesser dissociation of the metal-hydrogen bond. In the

TABLE 1 — CATALYTIC ACTIVITY OF SOME TRANSITION METAL COMPLEXES

[Catalyst] = 1.3×10^{-3} M; temp. = 100°C; [Propan-2-ol] = 10.3M; time = 13.5 hr [Cyclohexanone] = 1.16M; N₂ atm. [KOH] = 3.44×10^{-2} M; solvent = acetonitrile

Complex	Yield of cyclohexanol (%)
Ir(SbPh ₃) ₂ Cl	0.8
RuCl ₂ (DPPTP) ₃	86.0
RuBr ₂ (DPPTP) ₃ *	76.9
RuBr ₂ (DPPTP) ₃	21.0
RuI ₂ (DPPTP) ₃	44.8
RuH(CH ₃ COO)(PPh ₃) ₃ *	6.6
RuH(CH ₃ COO)(PPh ₃) ₃	5.0
RuCl ₂ (PPh ₃) ₃	98.0

*In hydrogen atmosphere

TABLE 2 — ELECTRON AFFINITY AND STRUCTURAL DATA OF TRANSITION METAL COMPLEXES INVESTIGATED

Complex	Electron affinity of metal ion ⁶ (eV)	Electronic configuration of metal ion	Ligands	Formal coordination number
RuCl ₂ (PPh ₃) ₃	24	Kr, 4d ⁶	PPh ₃ and Cl ⁻	5
RuCl ₂ (DPPTP) ₃	24	Kr, 4d ⁶	DPPTP and Cl ⁻	5
RuI ₂ (DPPTP) ₃	24	Kr, 4d ⁶	DPPTP and I ⁻	5
RuBr ₂ (DPPTP) ₃	24	Kr, 4d ⁶	DPPTP and Br ⁻	5
RuH(CH ₃ COO)(PPh ₃) ₃	24	Kr, 4d ⁶	H ⁻ , CH ₃ COO ⁻ and PPh ₃	6
Ni(acac) ₂	25.8	Ar, 3d ⁸	Acac	4
Co(acac) ₃	—	Ar, 3d ⁶	Acac	6
Co(acac) ₂	25.2	Ar, 3d ⁷	Acac	4
Ni(PPh ₃) ₂ Cl ₂	25.8	Ar, 3d ⁸	PPh ₃ and Cl ⁻	4
Co(DPPTP) ₂ Cl ₂	25.2	Ar, 3d ⁷	DPPTP and Cl ⁻	4
Fe(acac) ₃	—	Ar, 3d ⁶	Acac	6
Co(DMG) ₂	25.2	Ar, 3d ⁷	DMGH	4
Pd(PPh ₃) ₂ Cl ₂	27.9	Kr, 4p ⁶ , 4d ⁸	PPh ₃ and Cl ⁻	4
Ir(SbPh ₃) ₂ Cl	—	Xe, 4f ¹⁴ , 5d ⁷ , 6s ¹	SbPh ₃ and Cl ⁻	4
Co(PPh ₃) ₂ Cl ₂	25.2	Ar, 3d ⁷	PPh ₃ and Cl ⁻	4

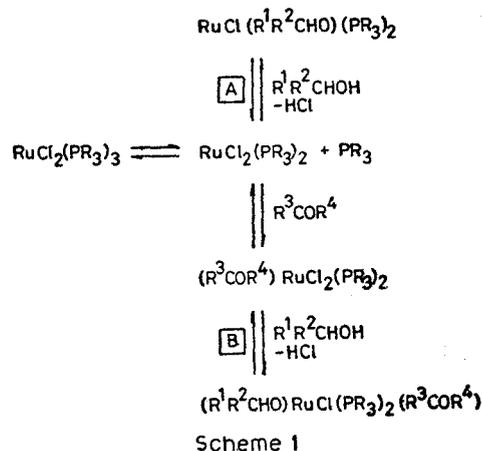
case of ruthenium complexes in spite of this lowering of bonding orbital one may have a Δ which is less than the critical value. DMGH₂ and AcacH are poor π -acceptors when compared to the tertiary phosphines. Moreover they are sterically crowded around the metal ion. To accommodate both donor and acceptor the complex may expand its coordination shell. But then the formation of hydrido complex involves a seven co-ordinate species which is very difficult. Elimination of acetylacetonate ligand or DMGH⁻ from one co-ordination site to accommodate a hydride ligand is not easy under the reaction conditions. In the case of iridium complex the ligand (SbPh₃) is a poor π -acceptor.

Hydrogen acceptor — Among the hydrogen acceptors benzophenone, cyclohexanone and ethyl methyl ketone, cyclohexanone is found to be reduced most easily.

The effect of solvent as well as the added bases has been investigated using benzyl alcohol as the hydrogen donor since the dehydrogenated product, benzaldehyde is relatively resistant to reduction. Analyses of the products show that cyclohexanol and benzaldehyde are formed in equimolecular proportions.

The percentage yields of cyclohexanols for the hydrogen transfer reaction in various solvents are given in Table 3. The catalysts dissolved easily in these solvents at the reaction temperature. Excepting acetonitrile, in other polar solvents, e.g. DMSO, the extent of reduction of ketone was very low. The most probable coordination of DMSO to Ru²⁺ will be through sulphur. As Ru²⁺ is a soft acid and sulphur in DMSO is a soft base strong Ru-S bond is formed and hence the complex is very stable. This prevents the coordination of the reactants. In the case of MeCN the nitrogen is a hard base and therefore a less stable complex is formed. Moreover, the coordinating powers of alcohol and ketone are not so weak and acetonitrile promotes the displacement of the dehydrogenation product by reactants. Therefore the yield of cyclohexanol is good in this solvent. The reaction proceeds easily in most aromatic hydrocarbon solvents.

Effect of added bases — In the general mechanism of the hydrogen transfer⁸ reaction catalysed by ruthenium complexes (Scheme 1),



both the steps A and B involve a loss of one molecule of HCl. This should be favoured by bases like amines and alkalis. The effect of adding an alkali, an aliphatic primary amine, a tertiary amine and a cyclic polyamine on the reduction of cyclohexanone have been investigated and the data are summarised in Table 3. It is observed that *n*-butylamine facilitates the reaction much more than the other amines and KOH. *n*-Butylamine probably helps in abstracting the proton with the least amount of steric hindrance. In the presence of the primary amine the ease of reduction of ketone in different solvents follows the order: acetonitrile > benzene \approx toluene > chlorobenzene \approx xylene > DMSO. In the case of KOH as reported by Freidlin *et al.*,²⁷ both the basic reaction, hydrogen transfer, and self-condensation of ketone might take place.

Hydrogen donating ability of some organic compounds—As quite a long period of heating is required at 100°C to get significant amounts of cyclohexanol with propan-2-ol and benzyl alcohol as donors, various other alcohols have also been tried as hydrogen donors at 136°C. Since RuCl₂(DPPTP)₃ undergoes decomposition to give ruthenium metal at this temperature, RuCl₂(PPh₃)₃ has been employed as the catalyst. The results are given in Table 4. 1-Phenylethanol and its substituted derivatives show excellent hydrogen donating ability as compared to other alcohols. This is because the resulting dehydrogenated ketones have a lower oxidation potential than cyclohexanone²⁸. Hence the hydride could attack the co-ordinated ketone with the higher oxidation potential to give the alkoxide which would be converted into alcohol by reaction with HCl⁸.

Dependence on catalyst concentration—A plot of initial rate against the concentration of the catalyst (Fig. 1) shows that the reaction is zero order in the catalyst. This is probably due to solubility limits which make it difficult to investigate a wide range of concentrations, and dimerization²⁹ of the dissociated ruthenium catalyst, RuCl₂(PPh₃)₂.

Dependence on donor and acceptor concentrations—A plot of initial rates against total concentrations of donor and acceptor taken in equimolar concentrations (Fig. 1) shows that the total order with respect to donor and acceptor is unity.

TABLE 3 — INFLUENCE OF SOLVENTS AND BASES ON TRANSFER OF HYDROGEN FROM BENZYL ALCOHOL TO CYCLOHEXANONE

[RuCl₂(DPPTP)₃] = 2 × 10⁻³ M; [Benzyl alcohol] = 4.79 M;
[Cyclohexanone] = 1.85 M; [Additive] = 8.29 × 10⁻³ M;
temp. = 100°C; time = 13.5 hr; N₂ atm.

Solvent	Yield of cyclohexanol (%)				
	—	KOH	Et ₃ N	<i>n</i> -Butyl amine	Hexamine
Acetonitrile	19	14	26	31	24
Benzene	18	22	18	24	20
Chlorobenzene	9	3	7	19	15
DMSO	0	7	5	4	0
Toluene	14	13	16	23	15
<i>p</i> -Xylene	15	8	17	18	7

TABLE 4—TRANSFER HYDROGENATION OF CYCLOHEXANONE BY ALCOHOLS

$[\text{RuCl}_2(\text{PPh}_3)_2] = 1.392 \times 10^{-3}M$; $[\text{Cyclohexanone}] = 1M$;
 $[\text{Donor}] = 1M$; temp. = 136°C ; time = 4 hr; N_2 atm;
 solvent = *p*-xylene

Donor	Yield (%) of cyclohexanol
<i>p</i> -Chlorobenzyl alcohol	6.3
<i>m</i> -Nitrobenzyl alcohol	3.7
1-(<i>p</i> -Methoxyphenyl)ethanol	22.8
1-Phenylethanol	26.1
1-(<i>p</i> -tolyl)ethanol	29.3
1-(<i>p</i> -chlorophenyl)ethanol	7.7
<i>p</i> -Methoxybenzyl alcohol	3.9
2-Methoxyethanol	1.5
<i>n</i> -Octanol	2.9
Tetrahydrofurfuryl alcohol	3.2
Benzyl alcohol	4.8
1-Phenylpropanol	6.3
Amyl alcohol	6.6
Benzhydrol	7.5
<i>p</i> -Hydroxybenzyl alcohol	0*

*Black precipitate was formed during the reaction

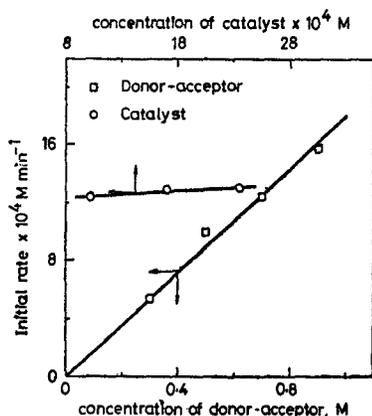


Fig. 1—Dependence of rate of reduction of cyclohexanone on concentration

Substituent effect—To check the electronic effect, various substituted 1-phenylethanols have been used as donors for the reduction of cyclohexanone (Table 5). The logarithm of ratio of first order rate constant of substituted alcohol (k) to unsubstituted 1-phenylethanol (k_0) is plotted against σ^+ and from this linear plot the reaction constant (ρ) is found to be equal to -1.8 (Fig. 2). The rate constant obtained with the *p*-methoxy derivative is not reliable because of side reaction. Balfe *et al.*²¹ reported that when 1-(*p*-methoxyphenyl) ethanol alone was heated on a steam-bath for 1 hr, the carbinol decomposed with the formation of *p*-methoxystyrene (10%) and bis[1-(*p*-methoxyphenyl)ethyl] ether (20%). From the reaction product in the present case the side products have been separated using preparative TLC plates coated (1 mm thick) with alumina G adsorbent.

TABLE 5—EFFECT OF SUBSTITUENTS ON RATE CONSTANTS OF HYDROGEN TRANSFER REACTION

$[\text{RuCl}_2(\text{PPh}_3)_2] = 1.04 \times 10^{-3}M$; $[\text{Donor}] = 0.5M$;
 $[\text{Cyclohexanone}] = 0.5M$; temp. = 143°C ; N_2 atm;
 solvent = diphenyl ether

Donor	Rate $\times 10^4$ mol. litre $^{-1}$ min $^{-1}$	Rate constant $\times 10^4$ min $^{-1}$	log k/k_0	σ^{+20}
1-Phenylethanol	10	20	0	0
1-(4-Chlorophenyl)-ethanol	5.8	11.6	-0.2366	0.114
1-(4-Methylphenyl)-ethanol	33	66	0.5224	-0.31
1-(4-Methoxyphenyl)-ethanol	20	40	0.3010	-0.78

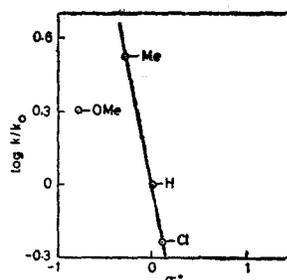
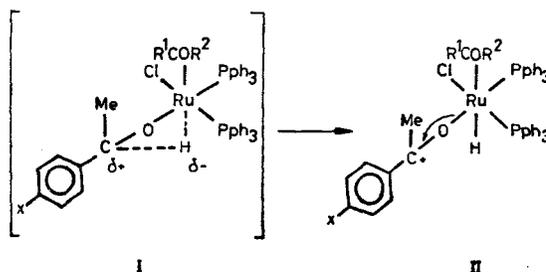


Fig. 2—Plot of log k/k_0 vs σ^+

CCl_4 has been used as the eluent and iodine vapour as the detecting agent. The alumina corresponding to the side product is scraped off, extracted with acetone, filtered and the filtrate evaporated to dryness *in vacuo*. Finally a viscous yellow liquid along with some white crystals is obtained. This is identified as a mixture of *p*-methoxy-styrene and bis[1-(*p*-methoxyphenyl)ethyl] ether by PMR and mass spectral analysis.

The negative value of ρ suggests the generation of a positive charge at the secondary carbon atom of the donor in the transition state (I) leading to a carbonium ion (II). The role of solvent, diphenyl ether, as in the case of acetonitrile may be to facilitate the displacement of the dehydrogenated product, acetophenone, from the coordination sphere of the complex.



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