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Review

Homogeneous catalytic hydrogenation of aldehydes and aldoses in organic solvents and water

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Abstract

Homogeneous catalysts used in hydrogenation of aldehydes and aldoses, mechanistic aspects of their activity, and modes of their deactivation are reviewed. Particular attention is paid to water soluble homogenous catalysts used for hydrogenation of sugars.

Keywords: Hydrogenation by dihydrogen; Transfer hydrogenation; Nitrogen ligands; Water soluble phosphine ligands

1. Introduction

Homogeneous catalytic hydrogenation of aldehydes in organic solvents by organometallic complexes was intensively studied. These studies comprise complexes between various transition metals and ligands with phosphor and nitrogen as donor atoms [1–3]. Even more attention has been paid to homogeneous hydrogenation of ketones, however, since their reduction usually leads to compounds with a new stereogenic (chiral) centre. Stereoselectivity (enantioselectivity) in reduction of ketones is therefore one of the main issues in the application of chiral homogeneous catalysts [4,5]. The difference between these two substrates resides not only in the fact that hydrogenation of aldehydes does not create new chiral centre (unless the isotope ^{1}H is used), but also in the tendency of aldehydes to undergo catalytic decarbonylation, whereas ketones are stable in the presence of the same homogeneous catalysts.

Hydrogenation of aldoses, or sugars generally, is traditionally performed under elevated hydrogen pressure in the presence of heterogeneous catalysts [6–8]. Because of their complete insolubility in organic solvents, where most homogeneous catalysts are operative, homogeneous catalytic hydrogenation of aldoses in aqueous solution is only recently reported [9]. This review covers therefore in the first part the application of homogeneous catalysts in hydro-

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genation of aldehydes in aqueous solvents, and in the final part it reports on the use of analogous water-soluble catalytic species.

2. Hydrogenation of aldehydes by molecular hydrogen in organic solvents

Complexes of transition metals with triphenylphosphine, such as $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$, and $IrH_3(PPh_3)_3$, have been proven as effective catalysts in hydrogenation of multiple C–C bond and carbonyl group [2]. Tsuji and Suzuki have performed hydrogenation of aldehydes with $RuCl_2(PPh_3)_3$ (**1**) in benzene at 50–80°C and hydrogen pressure 10–20 bar [10]. Under these conditions both aromatic and aliphatic aldehydes are reduced quantitatively to primary alcohols. These authors have also demonstrated that completely selective hydrogenation of benzaldehyde in the presence of benzophenone or nitrobenzene can be achieved under specific conditions, although it was known that complex **1** is an effective catalyst for hydrogenation of nitrobenzene to aniline [11–13].

$[RuH_2(PPh_3)_4]$ (2)

$[RuH_2(CO)(PPh_3)_3]$ (3)

$[RuCl_2(PPh_3)_3]$ (4)

$[RhH(PPh_3)_4]$ (5)

$[RhCl(CO)(PPh_3)_2]$ (6)

$[CoH[P(OPh)_3]_3]$ (7)

$[FeCl_2(PPh_3)_2]$ (8)

$[NiCl_2(PPh_3)_2]$ (9)

$[CoCl_2(PPh_3)_2]$ (10)

$[PdCl_2(PPh_3)_2]$ (11)

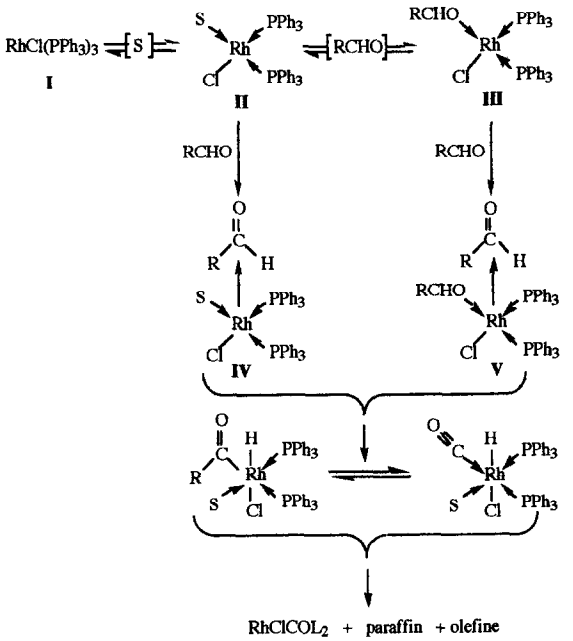
$[PtCl_2(PPh_3)_2]$ (12)

$i-[RhCl(PPh_3)_3]$ (13)

Dicarbonyl congener of **1**, $RuCl_2(CO)_2(PPh_3)_2$, is an effective catalyst for hydrogenation of linear and branched aliphatic aldehydes at relatively low hydrogen pressure (15 bar) and elevated temperatures, 160–200°C. Such harsh conditions led to the formation of the side products, in particular with linear aliphatic aldehydes [14].

$RhCl(PPh_3)_3$ is a highly efficient catalyst for hydrogenation of alkenes, conjugated and non-conjugated dienes, and alkynes [15], but during hydrogenation of aldehydes it also acts as decarbonylating agent. Carbonylic complex that is formed, $RhCl(CO)(PPh_3)_2$, is completely catalytically inactive [15]. Primary aldehydes are decarbonylated by $RhCl(PPh_3)_3$ already at ambient temperature; after 24 h in dichloromethane 90% of n-heptanal is decarbonylated [16]. Decarbonylation of secondary aldehydes can be achieved at reflux of toluene, sterically more impeded aldehydes proved unreactive [16].

Decarbonylation of aldehydes by Rh complexes have been studied by Ohno and Tsuji [17], and Baird et al. [16], who proposed the mechanism outlined in Scheme 1.



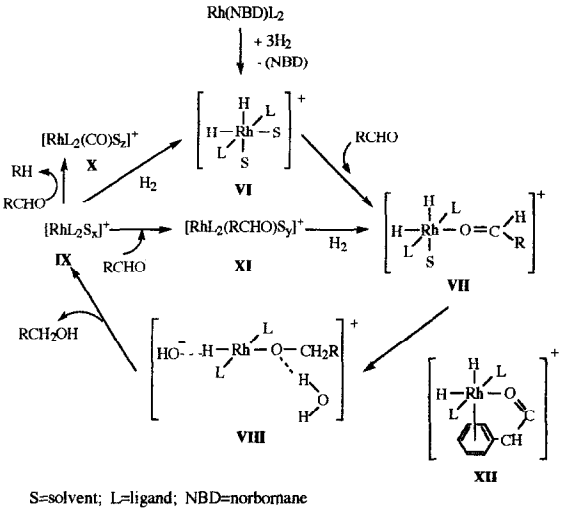
S=solvent; L=ligand

Scheme 1.

Osborn et al. have demonstrated solvation of **I** to diphosphine **II** [15]. This species posses strong affinity for CO and forms stable complex $RhCl(CO)(PPh_3)_3$. Baird et al. pointed out the coordination of aldehyde in **III** as an alternative or subsequent step to the formation of **II** [16]. Both **II** and **III** are 16-electron species, however, and can oxidatively add a second mol of aldehyde forming complexes **IV** or **V**. The last part of the cycle initiates the transfer of hydrogen to metal, and results from decarbonylation of aldehyde and formation of alkane. The overall rate of decarbonylation represents a process of autoinhibition of the catalyst, and is determined by the oxidative addition step. Once formed, acyl complex undergoes fast decarbonylation by migration of the alkyl group. Carbonylation can be monitored by the colour change of the solution from deep–red to yellow [16].

Complexes of the type $[Rh(NBD)(PR_3)_2]^+ClO^{4-}$ (NBD-norbornadiene, *R*-alkyl group) also catalyst hydrogenation of aldehydes [18]. Their catalytic activity is strongly dependent on the type of trialkyl phosphine. The complex with PEt_3 ligand proved notably more active than with PMe_3, PPh_3-complex was active only with phenylacetaldehyde whereas $Ph_2P–CH_2CH_2–PPh_2$ (diphos) complex was catalytically completely inactive in hydrogenation. The overall rates are generally rather low at low hydrogen pressures; $[Rh(NBD)(PEt_3)_2]^+ClO_4^-$ has converted ca. 40% of n-butanal to n-butanol after 24 h at 30°C and 1 bar hydrogen pressure. Propane and propene have been identified in the reaction mixture, revealing contemporaneous decarbonylation. Deactivation of the catalyst by the substrate diminishes in the order: n-butyraldehyde ≥ phenylacetaldehyde ≥ benzaldehyde. Hydrogenation of aldehydes by cationic Rh complexes is proposed to follow the pathway depicted in Scheme 2 [18].

Stereoelectronic bases of the outlined mechanism, in particular for the step **IX** → **X**, resides in high polarization of the sterically relatively



Scheme 2.

unhindered C=O group, which became more reactive than hydrogen molecule in the oxidative addition step. The complex **X** cannot be regenerated to catalytically active species **VI** at low hydrogen pressure; at higher pressures process **IX** → **VI** becomes reversible and suppresses self-deactivation of the catalyst.

Stereoelectronic arguments are offered only for selective activity of PPh_3-complex with phenylacetaldehyde; coordination of phenyl group within cationic Rh complex leads to formation of particularly reactive **XII** in Scheme 2 [18].

The only reported Ir complex active in hydrogenation of aldehydes, $IrH_3(PPh_3)_3$ involves formation of $[Ir(H_2)(CH_3COO)(PPh_3)_3]$ as the actual catalytic species in acetic acid [19]. Butyraldehyde is quantitatively hydrogenated at 50°C and 1 bar hydrogen pressure. Hydrogenation completely ceased in toluene or in neat butyraldehyde, addition of acetic acid initiates the reaction, however. All these data converge to $[Ir(H_2)(CH_3COO)(PPh_3)_3]$ as the actual catalytic complex whose formation in the presence of acetic acid is documented [20]. According to Coffey [19] hydrogenation of aldehydes catalyzed by this Ir complex can be accommodated by the pseudo first-order kinetics, calculated on the concentrations of aldehyde and catalyst.

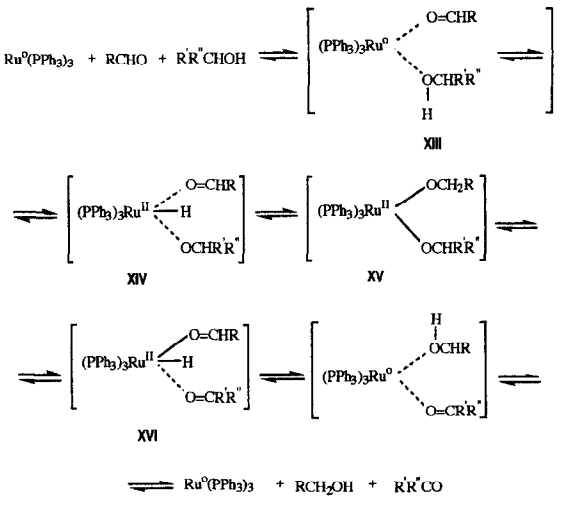
3. Hydrogenation of aldehydes by transfer hydrogenation in organic solvents

Many complexes of Rh, Ir and Ru promote hydrogen transfer from an hydrogen donor to aldehydes [2]. As the usual sources of hydrogen are used primary and secondary alcohols, formic acid and its salts. Imai et al. [21] have performed first systematic study of catalytic activity of phosphine complexes of various metals (**2–13**) in transfer hydrogenation of n-hexanal with benzylalkohol as hydrogen donor. With complex **2** 90% conversion, and with **3** 78% conversion after 150 min at 120°C was achieved. Complex **4** was far less catalytically active, while complexes **5–12** were completely inactive under cited conditions. For **13** was confirmed that deactivation is result of decarbonylation of aldehyde [17,18,22,23]. With complex **2** other sources of hydrogen, as 2-propanol, cyclohexanol or 2,5-dihydrofurane, proved also convenient; on the bases of kinetic measurements Imai et al. proposed the mechanism outlined in Scheme 3 [21].

Starting from $Ru(PPh_3)_3$, aldehyde and alcohol, addition complex **XIII** is formed. Oxidative addition of the OH group to Rh atom. accompanied by the hydride transfer, affords hydride–alkoxyde–complex **XIV**, which affects hydride transfer to the carbonyl group forming dialkoxyde complex **XV**. Finally, this complex rearranges to **XVI**, which reduces aldehyde and oxidizes alcohol.

Various formiates are well known sources of hydrogen in homogeneous catalytic transfer hydrogenation of unsaturated substrates such as dienes [24], alkynes [25], nitro-compounds [26], ethylethers and esters [25], alkenes [27], and arylchlorides [28]. The examples are given in the Table 1. Low solubility of formiates in most organic solvents limits their application to highly polar ones like DMSO or DMF [29], or to the phase transfer catalytic systems [30], where formiate anion is extracted from the aqueous to organic phase by lipophilic quaternary ammonium or phosphonium salts. Bar and Sasson [31] have studied hydrogenation of aldehydes and ketones by the phase-transfer catalysis, using sodium formiate and $RuCl_2(PPh_3)_3$ in the presence of Aliquat 336. Hydrogenation of aromatic aldehydes was performed under argon in the two-phase system xylene–water at 90°C; after 30 min 50–70% conversion was achieved.

On recycling the catalyst, the authors regis-



Scheme 3.

Table 1
Catalytic reductions with formates

Compound reduced	Catalytic system	Product	Yield (%)	Ref.
$1,3\text{-}(NO_2)C_6H_4$	$Et_3NH_2^+COO^-/Pd$	$3\text{-}NO_2C_6H_4NH_2$	77	[28]
$2,4\text{-}(NO_2)C_6H_3CH_3$		$2\text{-}NO_2\text{-}4\text{-}NH_2C_6H_3CH_3$	92	[28]
$C_6H_5C \equiv C(CH_2)_3CH_3$		$Z\text{-}C_6H_3CH{=}CH(CH_2)_3CH_3$	48	[25]
$4\text{-}OCHC_6H_4C \equiv CC_6H_5$		$Z\text{-}OCHC_6H_4CH{=}CHC_6H_5$	58	[25]
$E\text{-}C_6H_5C \equiv CCH{=}C(CH_3)COOCH_3$		$E,Z\text{-}C_6H_5CH{=}CHCH{=}C(CH_3)COOCH_3$	84	[25]
$4\text{-}BrC_6H_4CH_3$	$HCOONa/Pd(Ph_3)_4$	$C_6H_5CH_3$	62	[29]
$4,4'\text{-}Br(C_6H_4)_2$		$C_6H_5\text{–}C_6H_5$	81	[29]
$3\text{-}BrC_6H_4COOCH_3$		$C_6H_5COOCH_3$	48	[29]

tered loss of activity in the second cycle already, as a consequence of the formation of inactive species $RuCl_2(CO)_2(PPh_3)_3$ [32] and $RuCl_2(CO)(PPh_3)_2$ [33]. Pillai et al. [34] demonstrated that $RuCl_2(PPh_3)_3$ catalyses dehydrogenation of some alcohols from natural sources, like menthol, cholesterol and β-cytronelol, but carbonylation of the catalyst by the formed aldehydes was also observed.

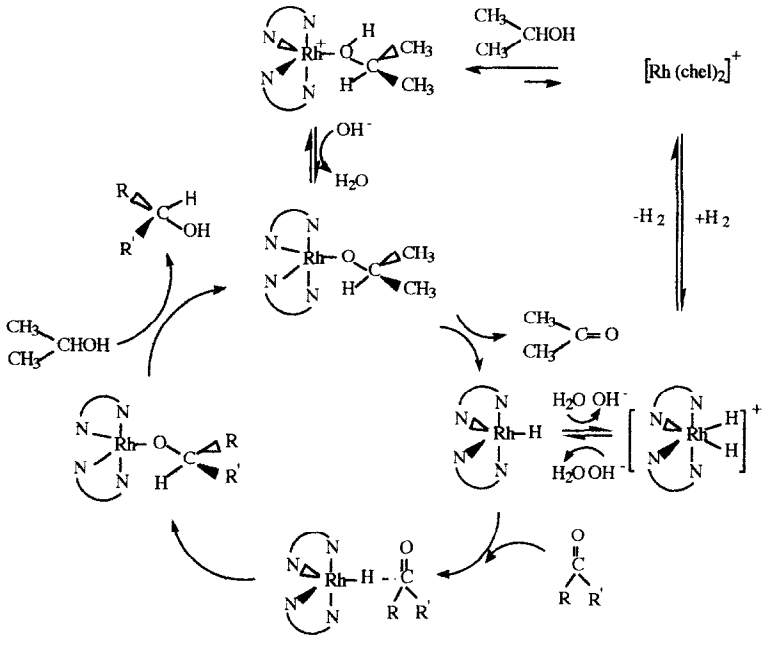
Crowdhury and Bäckvall [35] performed detailed studies of the transfer hydrogenation of cyclohexanone by primary and secondary alcohols in the presence of $RuCl(PPh_3)_3$ and $RuH_4(PPh_3)_3$. Whereas 2-propanol proved very effective with both catalytic species, reaction in ethanol was notably sluggished, an in methanol it failed completely. After 1 h, 89% conversion to cyclohexanol was observed with 2-propanol as hydrogen source in the presence of NaOH, whereas with ethanol after 4 h only 28% conversion was reached. The presence of hydroxide ions seems obligatory for the formation of alkoxyde ions bound to Ru in the complex, and slower reaction with primary alcohols was ascribed to deactivation of the complex by CO.

The mechanism of this reaction was assumed to be similar to that described by Morton and Cole-Hamilton [36], and also proposed by Mestroni et al. for transfer hydrogenation of ketones by some Rh complexes with bisnitrogen ligands [37], Scheme 4.

Much lower activity in transfer hydrogenation of aldehydes as compared to ketones was demonstrated for $IrHCl_2(Me_2SO_4)_3$ complex in the presence of 2-propanol [38]. Hydrogenation of cyclohexanon after 2 h at 90°C reached 97%, whereas only 5% of butyraldehyde was reduced under the same conditions.

4. Homogeneous catalytic hydrogenation of aldehydes by molecular hydrogen in aqueous solution

Using water-soluble complex catalysts which are poorly soluble in organic media for the



chel=bisnitrogen ligand

Scheme 4.

reduction of substrates soluble in organic solvents combine the advantages of homogeneous and heterogeneous catalysis: simple and complete separation of the products from the catalyst, high reactivity and high selectivity. Such catalytic reactions are performed in two-phase systems, and industrial applications in the field of hydrogenation [39,40] and hydroformylation [41,42] have already indicated the wide scope of this type of catalysis.

However, with water-soluble organic substrates lake sugars, homogeneous catalysis with water-soluble complexes is obligatory, though their separation from the catalyst usually is not trivial and requires specific chromatographic techniques. In order to effectively perform this reaction, ligands which form water-soluble transition metal complexes are required. To this aim triaryl phosphines are modified to hydrophilic ligands by introduction of polar, ionized groups. Water soluble phosphine complexes are usually prepared from hydroxylated, carboxylated, amminated, and sulphonated phosphines [43–45]. Sodium salt of tri(*meta*-sulphonylphenyl)phosphine, $P(C_6H_4SO_3Na)_3$, TPPTS, represents one of the best water-soluble ligands (1200 g/l). A series of its Ru complexes **14–20** has been examined in hydrogenation of propanal in water at 100°C and 50 bar hydrogen pressure [46,47].

$1/2[RuCl_2L_2]_2$ (14)

$[RuHClL_3]$ (15)

$[RuH(OAc)L_3]$ (16)

$[RuH_2L_4]$ (17)

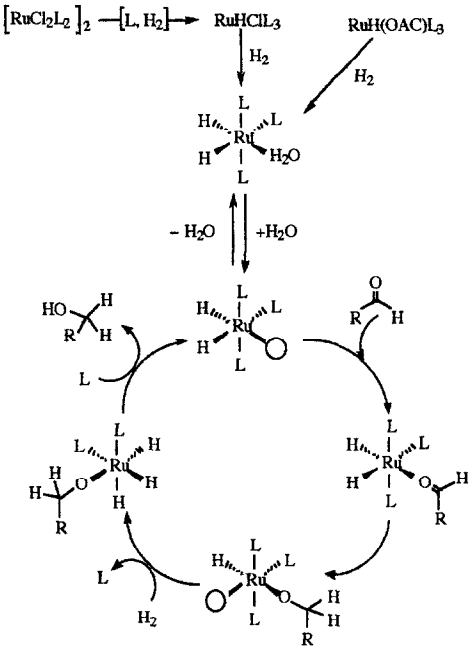
$[RuHIL_3]$ (18)

$[RuCL_2(CO)_2L_2]$ (19)

$[Ru(OAc)(CO)_2L]_2$

[L = tri(*meta*-sulphonylphenyl)phosphine)] (20)

Fast and quantitative reduction to propanol was achieved with all complexes, though IR spectra of the reaction solution indicated formation of carbonylated Ru species. Repeated hydrogenation of the fresh quantities of propanal



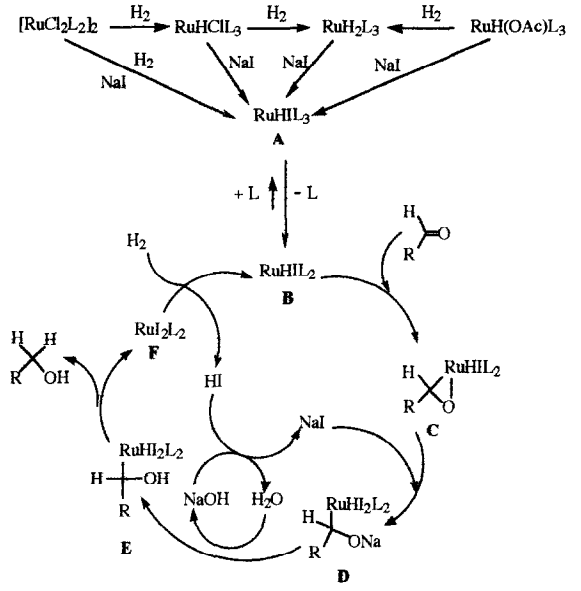
L=TPPTS; TPPTS=tris(*meta*-sulphonylphenyl)phosphine; R = CH_3CH_2

Scheme 5.

revealed after three cycles nearly unaltered activity of the catalyst, indicating very slow decarbonylation of the aldehyde. It was also demonstrated that catalytic activity of the complexes **14–17** is promoted by the inorganic salts [47]. Hydrogenation of propanal in the presence of NaI was faster at 30°C than at 100°C in the absence of this salt. Activity of the catalyst is dependent on both, anion and cation of the added salt. Hydrogenation rate was enhanced by the anions in the order $HCl:SbF_6 \leq NO_3 \leq Cl \leq Br \leq J$, and by the cations of the order of $Li^+ \leq K^+ \leq Na^+ \geq Mg^{2+} \leq Ca^{2+}$.

The same authors proposed catalytic cycles in aqueous solution initiated by $RuH_2(TPPTS)_3$, as outlined in the Scheme 5, corresponding to that proposed for hydrogenation of aldehydes in organic solvents [48].

Iodide ion enters into coordination sphere of the complexes **1–4**, as confirmed by ^1H-, ^{13}C-, and ^{31}P-NMR spectra [46]. A series of precatalytic equilibria with NaI afford three catalytic species **A**, which release one molecule of the



Scheme 6.

ligand forming complex **B** that coordinates aldehyde as η_2 ligand in the complex **C**, Scheme 6.

Subsequent interaction with the electrophilic centre, as e.g. sodium cation, changes coordination from η_2 to η_1, precluding hydrogen transfer to the carbon atom, and promoting formation of the complex **D**. In the next step complex **D** hydrolyses into **E** which undergoes reductive elimination to n-propanol and complex **F**. This latter complex regenerates starting complex **A** by oxidative addition of hydrogen. One mole of HI is formed in the last step, which is neutralized by the base formed in the hydrolysis of **C**, and regeneration of the salt is completed.

Joó et al. [49] have studied hydrogenation of the carbonyl group in the oxoacids by water soluble Ru complexes **21** and **22**, and compared the data with the rate of reduction of the C=C bond in analogous unsaturated acids.

Table 2
Comparision of the catalytic activity of $HRu(CH_3COO)(Dpm)_3$ (**21**) and $HRuCl(Dpm)_3$ (**22**), as expressed in mol H_2/mol catalyst [a] [49]

Substrate	**21**	**22**
	0.1 M acetate buffer, pH 4.8	0.1 M Cl, pH 1
CH_3–CO–COOH	46	175
C_6H_5–CO–COOH	46 [b]	115
CH_3–$(CH_2)_2$–CO–COOH	74 [b]	70
CH_3–CO–$(CH_2)_2$–COOH	25 [b]	13
CH_3–$(CH_2)_5$–CO–COOH	74 [b]	
CH_3–$(CH_2)_7$–CO–COOH	48 [b]	
HOOC–$(CH_2)_2$–CO–COOH	67 [b]	95
trans–CH_3–CH=CH–COOH	198	23
trans–C_6H_5–CH=CH–COOH	92	30
cis–HOOC–CH=CH–COOH	92	23
trans–HOOC–CH=CH–COOH	92	49
CH_2=C(COOH)–CH_2–COOH		84
CH_2=CH–CH=CH–COOH [c]	175	
OH–CH_2–CO–CH_2–OH		60

[a] 2×10^{-4} mol substrate, 1×10^{-5} mol (**21**) or 5×10^{-6} mol (**23**); Dpm/Ru = 5:1; p_{H_2} = 610 mm Hg, at 1 atm total pressure, $T = 60.0\pm0.1$°C.
[b] As before, but 5×10^{-4} mol substrate.
[c] As before, but 2×10^{-3} mol substrate and 5×10^{-5} mol catalyst.

$$[RuH(OOCCH_3)(Dpm)_3] \quad (21)$$

$$[RuHCl(Dpm)_3]$$

(Dpm = diphenylphosphinebenzene-*m*-sulphonyl) (22)

The effect of pH was particularly interesting, Table 2.

Complex **21** was the most effective in hydro-

Table 3
Kinetic data for hydrogenation of D-glucose in *N,N*-Dimethylacetamide [50]

Run	Substrate conc. (M)	$RuCl_2(PPh_3)_3$ conc. (M)	p_{H_2} (lb.in.$^{-2}$)	$t_{1/2}$ (min)	$k'\times10^3$ (min^{-1})	T (°C)
1	0.5	0.01	50	20	0.35	75
2	0.5	0.005	50	42	0.17	75
3	0.5	0.01	10	27	0.26	75
4	0.5	0.01	30	20	0.35	75
5	0.5	0.01	50	225	0.031	50
6	0.5	0.01	50	76	0.092	60
7	0.5	0.01	50	8	0.84	90

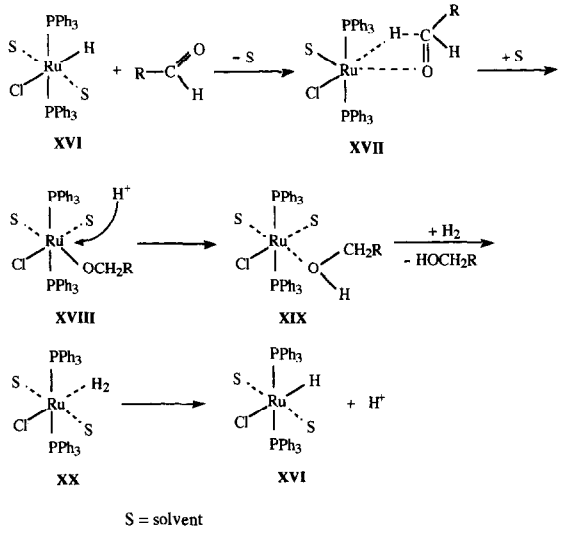
genation of unsaturated acids, whereas complex **22** was more effective in the hydrogenation of oxoacids, in particular at low and high pH values. At neutral pH **22** was inactive, by formation of its stable complex with oxoacid, as explained by the authors.

5. Homogeneous hydrogenation of aldoses

Kruse et al [50] studied hydrogenation of D-glucose by $RuCl_2(PPh_3)_3$ in various solvents at 75°C and 3 bar hydrogen pressure. Kinetic measurements in dimethylacetamide (DMA) revealed no enhancement of the rate at hydrogen pressures over 3 bar. The rate was of the first order in concentration of aldose and the catalyst, and was dependent on the solvent used, Table 3.

D-Fructose was hydrogenated in DMA at approximate the same rate as D-glucose, affording a 58:42 mixture of D-mannitol/D-sorbitol. Based on the kinetic data the authors proposed the mechanism outlined in Scheme 7.

Coordination of aldoses to the solvated complex **XVI** results in aldehyde-Ru complex **XVII** wherein hydrogen transfer from Ru atom to carbonyl carbon leads to alkoxy-Ru complex **XVIII**. Second, hydrogen transfer takes place in the next step, and Ru–O bond cleaves affording alkoxyde **XIX**. Dissociation of alcohol generates complex **XX**, which regenerates **X** on heterolytic activation of hydrogen.



Scheme 7.

Rajagopal et al. [51,52] described the first transfer hydrogenation of aldose, D–glucose catalyzed by $RuCl_2(PPh_3)_3$ in the presence of various alcohols as hydrogen donors in the mixtures of organic solvents and water, Table 4.

In the absence of an effective hydrogen donor D-glucose disproportionates into D-sorbitol and 1,5-gluconolactone [53]. This process is significantly slower when secondary alcohol is used as the solvent and hydrogen donor. In some pri-

Table 4
Transfer hydrogenation of D-glucose by $[RuCl_2(PPh_3)_3]$ [55]

Hydrogen donors and solvents	[H-donor]/[D-glucose]	Conv. of D-glucose (%)	Selectivity (%)
2-Propanol–DMF–water (18:4:3) [b]	47.0	36	75
2-Propanol–DMA–water (18:4:3)	47.0	85	85
2-Butanol–DMF–water (18:4:3)	39.2	47	75
2-Butanol–DMA–water (18:4:3)	39.2	95	85
1-phenylethanol–dioxane–water (10:12:3)	16.6	58	90
benzyi alchohol–dioxane–water (10:12:3)	19.3	52	90
cyclohexanol–toluene [c]–dioxane–water (10:2:10:3)	19.2	33	90
benzhydrol–dioxane–water (6:22:3)	6.5	25	90
2-methoxyethanol–toluene [c]–water (17:5:3)	43.1	34	65
tetrahydrofurfuryl alchohol–toluene [c]–water (17:5:3)	35.1	45	65

[a] [D-glucose]: 0.2 M; $[RuCl_2(PPh_3)_3]$: 1.67×10^{-3} M; [D-glucose]/$[RuCl_2(PPh_3)_3]$: 120; *T*: 100°C; time: 10 h.
[b] The numbers in parentheses give volume in ml of the solvents, except benzhydrol which is expressed in g.
[c] Added to increase the solubility of the catalyst.

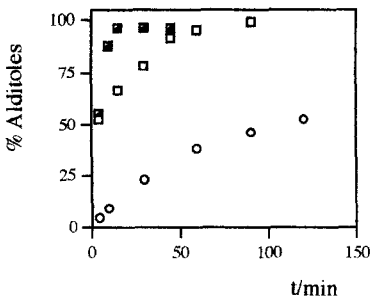


Fig. 1. Progress curve for the hydrogenation of D-Glc and D-Man catalysed by [Ru–TPPTS] complex in water at 100°C and 50 atm; □ D-mannitol, □ D-sorbitol, and hydrogenation of D-Man in the absence of NaI: □ D-mannitol [9].

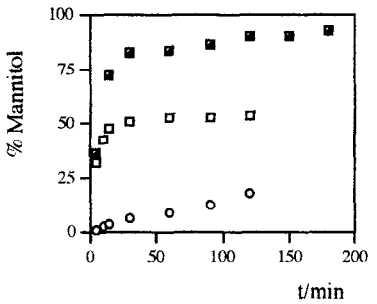


Fig. 2. Progress curve for the transfer hydrogenation of D-Man catalysed by [Ru-TPPTS] complex in water at 100°C with □ NEt_3/formic acid (2:5), □ Na-formate, ○ NH_4-formate [9].

mary alcohols, like 2-methoxyethanol or tetrahydrofurfurol, $RuCl_2(PPh_3)_3$ forms hydridochloro-carbonylic complex $RuClH(CO)(PPh_3)_3$ which is catalytically inactive for hydrogenation, but retains catalytic activity for disproportionation reaction according to Scheme 8.

During hydrogenation in solvents like DMF or DMA deactivation of the catalytic complex and formation of inactive complexes $RuCl_2(CO)(PPh_3)_2(DMF)$, $RuCl_2(CO)(PPh_3)_2(DMA)$, and *cis*-$RuCl_2(CO)_2(PPh_3)_2$ takes place. All these species have been isolated from the reaction solution and spectroscopically identified; their formation from the open form of D-glucose was postulated [54,55].

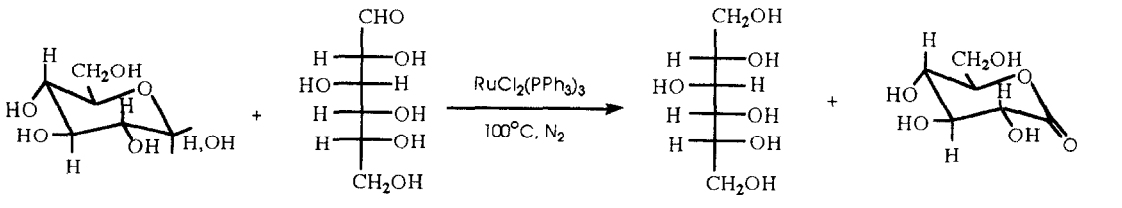
D-Fructose was also hydrogenated in the presence of $RuCl_2(PPh_3)_3$, and propanol-2 or butanol-2 as hydrogen donors [56]. At 100°C conversion was complete, and ca. 1:1 mixture of D-mannitol/D-sorbitol was obtained.

In our recent study [9], we have compared relative rates of hydrogenation of epimeric aldoses, D-glucose and D-mannose, with molecular hydrogen and by transfer hydrogenation, both catalyzed by Ru(TPPTS). Both methods proved effective, transfer hydrogenation was pH and temperature dependent, and D-mannose proved more reactive isomer. Fig. 1 shows much faster hydrogenation of D-mannose at hydrogen pressure of 50 bar, and also promoting effect of sodium iodide, as already discussed in the Section 4.

Fig. 2 reveals that transfer hydrogenation with formiate strongly depends on the counterion. Azeotropic mixture of formic acid and triethylamine (5:2) was much more effective than sodium or ammonium formiate. The former reagent was successfully used by Brunner and co-workers in transfer hydrogenation of α,β-unsaturated carboxylic acids [57,58].

6. Conclusion

Homogeneous catalytic hydrogenation of aldehydes and aldoses differs from analogous



Scheme 8.

reaction with ketones in extreme easy with which the catalytic complex rises decarbonylation of these substrates. Though this side reaction usually leads to self-deactivation of the catalyst, conditions are presently known where hydrogenation could be safely performed with high regioselectivity and in good yields. Future development is expected in the field of homogeneous catalytic hydrogenation in aqueous solution, where significantly lower hydrogen pressures, or the use of inorganic salts as hydrogen donors put no special demand on the equipment, and thus outweighs the eventual need for chromatographic separation of the complex homogeneous catalyst.

References

[1] T. Tanase, F. Shimizu, M. Kuse, S. Yano, M. Hidai and S. Yoshikawa, Inorg. Chem. 27 (1988) 4085.
[2] R.S. Dickson, Homogenous Catalysis with Compounds of Rhodium and Iridium (Kluwer, Dordrecht, 1985) pp. 40–86.
[3] P.A. Chaloner, Handbook of Coordination Catalysis in Organic Solvents (Butterworths, London, 1986) pp. 11–63.
[4] H. Takaya, T. Ohta and R. Noyori, in: Catalytic Asymmetric Synthesis, ed. I. Ojima (VCH, Weinheim, 1993) pp. 1–39.
[5] H. Brunner and W. Zetlmeier, Handbook of Enantioselective Catalysis, Vols. I and II (VCH, Weinheim, 1993).
[6] M. Kruse, US Pat. 4295451 (1981).
[7] M. Makkee, A.P.G. Kieboom and H. van Bekkum, Carbohydr. Res. 138 (1985) 225.
[8] A.P.G. Kieboom and H. van Bekkum, in: Starch Conversion Technology, eds. G.M.A. Van Beynum and J.A. Roels (Marcel Dekker, New York, 1985) pp. 278–284.
[9] S. Kolarić and V. Šunjić, J. Mol. Catal., 110 (1996) in press.
[10] J. Tsui and H. Suzuki, Chem. Lett. (1977) 1085.
[11] J.F. Knifton, Tetrahedron Lett. (1975) 2163.
[12] J.F. Knifton, J. Org. Chem. 40 (1975) 519.
[13] J.F. Knifton, J. Org. Chem. 41 (1976) 1200.
[14] W. Strohmeier and L. Weigelt, J. Organometal. Chem. 145 (1978) 189.
[15] J.A. Osborn, F.M. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A (1966) 1711.
[16] M.C. Baird, C.J. Nyman and G. Wilkinson, J. Chem. Soc. A (1968) 348.
[17] .K. Ohno and J. Tsuji, J. Am. Chem. Soc. 90 (1968) 99.
[18] H. Fujitsu, E. Matsumura, K. Takeshita and I. Mochida, J. Org. Chem. 46 (1981) 5353.
[19] R.S. Coffey, J. Chem. Soc., Chem. Comm. (1967) 923.
[20] M. Angoletta and M. Araneo, Gazzeta Chim. It. 93 (1963) 1343.
[21] H. Imai, T. Nishiguchi and K. Fukuzumi, J. Org. Chem. 41 (1976) 665.
[22] H.M. Walborsky and L.E. Allen, J. Am. Chem. Soc. 93 (1971) 5465.
[23] R.E. Ireland and G. Pfister, Tetrahedron Lett. (1969) 2145.
[24] T. Okamato and S. Oka, Bull. Chem. Soc. Jpn. 45 (1981) 1265.
[25] J.R. Weir, B.A. Patel and R.F. Heck, J. Org. Chem. 45 (1980) 4926.
[26] J.D. Entwistte, A.J. Jackson, R.A.W. Johnstone and R.P. Telford, J. Chem. Soc., Perkin Trans. 1 (1977) 443.
[27] T. Nishiguchi, J. Mol. Catal. 41 (1976) 249.
[28] M.P. Terpko and R.F. Heck, J. Org. Chem. 45 (1980) 4992.
[29] P. Helquist, Tetrahedron Lett. (1978) 1913.
[30] E.V. Dehmlow and S.S. Dehmlow, Phase Transfer Catalysis (Verlag Chemie, 1980).
[31] R. Bar and Y. Sasson, J. Mol. Catal. 26 (1984) 327.
[32] Y. Sasson and J. Blum, J. Org. Chem. 40 (1975) 1887.
[33] S.R. Patil, D.N. Sen and R.V. Caudhari, J. Mol. Catal. 19 (1983) 233.
[34] S.M. Pillai, S. Vancheesan, J. Rajaram and J.C. Kuriacose, J. Mol. Catal. 16 (1982) 349.
[35] R.L. Chowdhury and J.E. Bäckvall, J. Chem. Soc., Chem. Commun. (1991) 1063.
[36] D. Morton and D.J. Cole-Hamilton, J. Chem. Soc., Chem. Commun. (1988) 1154.
[37] G. Mestroni, G. Zassinovich, E. Alessio and M. Tornatore, J. Mol. Catal. 49 (1989) 175.
[38] M. Gullotti, R. Ugo and S. Colonna, J. Chem. Soc. C (1971) 2652.
[39] C. Larpent, R. Dabard and H. Patin, Tetrahedron Lett. 28 (1987) 2507.
[40] C. Larpent and H.J. Patin, Mol. Catal. 61 (1990) 65.
[41] P. Eschoffre, A. Thorez and P. Kalck, J. Chem. Soc., Chem. Commun. (1987) 146.
[42] W.A. Hermann, J. Kellner and H. Riepl, J. Organomet. Chem. 389 (1990) 103.
[43] D. Sinou, Bull. Soc. Chem. Fr. 3 (1986) 480.
[44] W.A. Herrmann and J.A. Kulpe, J. Organometal. Chem. 389 (1990) 85.
[45] W.A. Herrmann, J.A. Kulpe and H. Riepl, J. Organometall. Chem. 389 (1990) 103.
[46] E. Fache, C. Santini, F. Senocq and J.M. Basset, J. Mol. Catal. 72 (1992) 331.
[47] E. Fache, C. Santini, F. Senocq and J.M. Basset, J. Mol. Catal. 72 (1992) 337.
[48] R.A. Sanchez-Delgado, N. Valencia, R.L. Marqvez-Silva, A. Andriollo and M. Medina, Inorg. Chem. 25 (1986) 1106.
[49] F. Joó, Z. Zóth and M.T. Beck, Inorg. Chim. Acta. 25 (1977) L61.
[50] W.M. Kruse and L.W. Wright, Carbohydr. Res. 64 (1978) 293.
[51] S. Rajagopal, S. Vancheesan, J. Rajaram, C. Kuriacose, Proc. 4 th Natl. Sym. Catal., Bombaj (1978) 380.
[52] S. Rajagopal, S. Vancheesan, J. Rajaram, J.C. Kuriacose, Indian J. Chem. *18 B* (1979) 293.
[53] S. Rajagopal, S. Vancheesan, J. Rajaram, J.C. Kuriacose, J. Mol. Catal. *22* (1983) 137.

[54] S. Rajagopal, S. Vancheesan, J. Rajaram, J.C. Kuriacose, J. Mol. Catal. *22* (1983) 131.
[55] S. Rajagopal, S. Vancheesan, J. Rajaram, J.C. Kuriacose, J. Mol. Catal. *75* (1992) 199.
[56] S. Rajagopal, S. Vancheesan, J. Rajaram, J.C. Kuriacose, J. Mol. Catal. *81* (1993) 185.
[57] H. Brunner, E. Graf, W. Leitner, K. Wutz, Synthesis, *115* (1989) 743.
[58] W. Leitner, J.M. Brown, H. Brunner, J. Am. Chem. Soc. *115* (1993) 152.