ORGANOMETALLIC CATALYSIS IN AQUEOUS SOLUTIONS: THE BIPHASIC TRANSFER HYDROGENATION OF ALDEHYDES CATALYZED BY WATER-SOLUBLE PHOSPHINE COMPLEXES OF RUTHENIUM, RHODIUM AND IRIDIUM

ATTILA BÉNYEI and FERENC JOÓ*

Institute of Physical Chemistry, Kossuth Lajos University, Debrecen 10, P.O. Box 7, H-4010 (Hungary)

(Received January 15, 1989; accepted April 27, 1989)

Summary

Aromatic and aliphatic aldehydes can be reduced to the corresponding alcohols by hydrogen transfer from formate using, as catalysts, water-soluble complexes of Ru(II), Rh(I) and Ir(I) with monosulphonated triphenylphosphine ($mSP\phi$)$_2$, in aqueous/organic biphasic systems *without* phase transfer catalysts. $HRu(O_2CH)(mSP\phi_2)_3$ was identified as the key intermediate in the processes catalyzed by $RuCl_2(mSP\phi_2)_2$ in an excess of phosphine. Olefinic double bonds (including those in α,β-unsaturated aldehydes), as well as substitutents of the aromatic ring, are not affected.

Attempted catalysis of the transfer of benzaldehyde *from* the organic *to* the aqueous phase by β-cyclodextrin resulted in inhibition of the metal complex-catalyzed transfer hydrogenation.

Introduction

Catalyzed organic transformations under two-phase conditions are most often coupled with the catalysis of the transfer of hydrophilic reactants to the organic phase by quaternary ammonium salts or other phase transfer (PT) agents. This method of combined organometallic and PT catalysis has proved extremely powerful in synthesis (for a review, see [1]). On the other hand, there are but a few examples of complex-catalyzed reactions of lipophilic substrates in aqueous solutions, the landmark being the Ruhrchemie/Rhone Poulenc process for the very low pressure hydroformylation of propylene [2]. Reasons for this relative scarcity include the rather limited, though steadily growing, number of water-soluble organometallic catalysts [3, 4], and the

*Author to whom correspondence should be addressed.

0304-5102/90/$3.50

solubility problems encountered using lipophilic substrates in aqueous solutions. Consequently, it is hard to find a biphasic reaction where a systematic comparison of the performance of the same catalyst (made water soluble with only a slight modification, and without changing its essential chemical properties) in the different phases can be made.

Aqueous sodium formate can be used under phase transfer conditions for the hydrogenation of various substrates [5, 6], including aldehydes [7]. Bar *et al.* performed a detailed kinetic study of the reduction of *p*-tolualdehyde catalyzed by $RuCl_2(P\phi_3)_3$ in the presence of quaternary ammonium salts [8]. We report here that the biphasic reaction:

$$ArCHO_{(org)} + HCOONa_{(aq)} + H_2O_{(l)} \rightarrow ArCH_2OH_{(org)} + NaHCO_{3(aq)} \quad (1)$$

is efficiently catalyzed by complexes of Ru, Rh and Ir with monosulphonated triphenylphosphine ($mSP\phi_2$ = *m*-sulphophenyldiphenylphosphine) in the *absence* of phase transfer agents. Kinetics of the transfer hydrogenation of benzaldehyde catalyzed by $RuCl_2(mSP\phi_2)_2$ is also presented. This method of performing the reaction widens its scope and offers advantages in product isolation and catalyst recycling.

Experimental

Reagents and solvents of analytical grade were commercial products and were purified by recrystallization or distillation. Monosulphonated triphenylphosphine [9], $RuCl_2(mSP\phi_2)_2$ [10], $HRuCl(CO)(mSP\phi_2)_3$ [10], $RuCl_2(CO)_2(mSP\phi_2)_2$ [10], $[Ru(CO)(H_2O)Cl_2]_n$ [11] and $RhCl(mSP\phi_2)_3$ [12] were prepared according to published procedures. *Trans*-$IrCl(CO)(mSP\phi_2)_2$ [13] was obtained as follows (under N_2 where appropriate). A solution of 0.5 g H_2IrCl_6·aq (38% Ir, 1 mmol) and 0.21 g anhydrous Na_2CO_3 (2 mmol) in 25 ml 2-methoxyethanol was refluxed under CO for 5 h, giving a brownish-yellow solution which was dried on Na_2SO_4. On addition of 0.8 g (2 mmol) *m*-sulphophenyldiphenylphosphine, sodium salt dihydrate, a greenish-yellow solution was obtained, which was slowly added to 100 ml diethyl ether. The pale yellow precipitate which formed was filtered and washed several times with ether, then dried *in vacuo* at 70 °C. Yield of $IrCl(CO)(mSP\phi_2)_2$: 86%, ν(CO): 1960 cm^{-1}. The product may contain as an impurity the O_2 adduct, $O_2IrCl(CO)(mSP\phi_2)_2$, ν(CO): 2010 cm^{-1}, ν(OO): 850 cm^{-1} (KBr).

NMR spectra were run on a Bruker WP 200 SY spectrometer. Gas chromatographic analyses were made with a Chrom 5 gas chromatograph, equipped with a flame ionization detector, using a 2.4 m long glass column packed with 3% OV-17 on Anachrome (90–100 mesh) or with 3% Carbowax 20M–2% NaOH on Diatomite CQ (80–100 mesh).

Kinetic measurements were run with benzaldehyde as substrate and $RuCl_2(mSP\phi_2)_2$ as catalyst. Reproducibility of the conversions at different reaction times was within 3%. In a representative run, 3 ml of 5 M aqueous

HCOONa solution, 0.1 mmol of mSPϕ_2, 2.5 mmol of benzaldehyde, and 2.2 mmol of naphthalene (internal standard) in 5 ml of chlorobenzene was charged into a thermostatted (80 ± 1 °C) Schlenk-type flask equipped with a reflux condenser and a magnetic stirrer. Slow N_2 flow was passed through the flask during the reaction, which was initiated by adding the catalyst $RuCl_2(mSP\phi_2)_2$ (0.01 mmol). Samples removed periodically from the organic phase were subjected to GC analysis. Under these conditions, the conversion of benzaldehyde into benzyl alcohol was practically complete in 30 min.

Preparative experiments with various aldehydes were run using a pre-formed catalyst solution: 5 ml of 1 M aqueous sodium formate solution containing 75 mg $RuCl_2(mSP\phi_2)_2$ and 30 mg mSPϕ_2 was heated to 60 °C until a bright yellow solution formed (several minutes), followed by cooling to room temperature. This solution is stable in air (excess formate!) and can be stored for days in the refrigerator. To a mixture of 1 mmol of neat aldehyde and 2 ml 5 M HCOONa solution at 80 °C was added 1 ml of the above catalyst solution, and the mixture was stirred at this temperature for the time indicated in Table 1. The resulting mixture was cooled and extracted with chloroform; the organic layer was separated, washed with water, dried ($MgSO_4$) and evaporated to give the desired alcohol. Products were identified by ^1H NMR spectroscopy.

TABLE 1

Reduction of aldehydes by $RuCl_2(mSP\phi_2)$-catalyzed hydrogen transfer from formate[a]

No.	Substrate	Time (h)	Conv. (%)	Yield (%)
1	C_6H_5—CHO	1.5	99.7	94
2	4-CH_3—C_6H_4—CHO	1.5	99.5	99
3	4-$OCH_3C_6H_4$—CHO	1.5	98.8	90
4	4-Br—C_6H_4—CHO	1.5	99.8	94
5	2,6-di-Cl—C_6H_3—CHO	1.5	100	96
6	3,4,5-tri-OCH_3—C_6H_2—CHO	8	98.6	91
7	4-$N(CH_3)_2$—C_6H_4—CHO	1.5	98.9	98
8	2-NO_2—C_6H_4—CHO	2	100	90
9	C_6H_5—CH=CH—CHO	2	98	92
10	CH_3—CH=CH—CHO[b]	2.5	—	78
11	$(CH_3)_2C$=$CHCH_2CH_2C(CH_3)$=CH—CHO[c]	7	98	95
12	$(CH_3)_2C$=$CHCH_2CH_2CH(CH_3)CH_2$—CHO	4	93	90
13	2-naphthaldehyde	3.5	100	98
14	pyrrole-2-carboxaldehyde	5	99.8	66
15	2-OH-1-naphthaldehyde	3	0	98[d]
16	2-OH—C_6H_4—CHO	3	0	63[d]

[a] Conditions: 0.01 mmol $RuCl_2(mSP\phi_2)_2$, 0.1 mmol mSPϕ_2, 1 mmol aldehyde (neat), 3 ml 5 M HCOONa in water, 80 °C.

[b] 30 °C; side reactions at 80 °C.

[c] Mixture of geranial and neral (2:1). No isomerization was observed.

[d] Only the starting material could be recovered.

Results and discussion

The biphasic reduction by hydrogen transfer from formate is applicable for various aldehydes. It can be seen from Table 1 that neither hydrogenation nor hydrogenolysis of substituents on the aromatic rings was observed, and the isolated yields of the product alcohols were in most cases close to quantitative. Note the very pronounced selectivity for unsaturated aldehydes, resulting in the exclusive formation of unsaturated alcohols. However, a strongly coordinating substituent in the *ortho*-position to the aldehyde function inhibits the reaction completely, and only starting material could be recovered.

$RuCl_2(mSP\phi_2)_2$ is by far the most useful catalyst for the transfer of hydrogen from formate to aldehydes (Table 2.) $RhCl(mSP\phi_2)_3$ is much less active, and $IrCl(CO)(mSP\phi_2)_2$ loses its catalytic activity during the first 25 cycles. Some of the ruthenium carbonyl complexes may give useful conversions in reasonable time; however, $RuCl_2(CO)_2(mSP\phi_2)_2$ is completely inactive at this temperature (80 °C). It is appropriate to mention here that $RuCl_2(CO)_2(PPh_3)_2$ was very successfully applied to catalyze the hydrogenation of aldehydes between 160 and 200 °C, under 15 bar H_2 pressure [14].

Kinetics of benzaldehyde reduction

The reduction catalyzed by $RuCl_2(mSP\phi_2)_2$ was studied in considerable detail. The effect of the concentrations of the catalyst, formate, aldehyde and $mSP\phi_2$ is illustrated in Figs. 1–4, respectively. In the studied concentration range, the reaction is of first order with respect to catalyst (Fig. 1). Following a sharp rise as a function of formate concentration in the <0.25 M range, the reaction rate levels off, and a slow decrease in rate with increasing [HCOONa] can even be observed above 5 M (Fig. 2). Since it is highly probable that the reaction involves the aldehyde dissolved in the bulk aqueous phase, this decrease can well be the consequence of a salting-out effect of the high electrolyte concentration. In the related PTC system [8],

TABLE 2

Reduction of benzaldehyde by formate in the presence of different catalysts[a]

Catalyst	r_0 (mM/min)	Time (min)	Conv. (%)
$RuCl_2(mSP\phi_2)_2$	90	20	100
$HRuCl(CO)(mSP\phi_2)_3$	29	60	80
$[Ru(CO)(H_2O)Cl_2]_n$	18	30	41
		120	62
$RuCl_2(CO)_2(mSP\phi_2)_2$	0	60	0
$IrCl(CO)(mSP\phi_2)_2$	16	10	9
		130	11
$RhCl(mSP\phi_2)_3$	1.3	72	22

[a] Conditions: 0.01 mmol catalyst, 0.1 mmol $mSP\phi_2$, 5 ml of 0.5 M benzaldehyde in chlorobenzene, 3 ml 5 M HCOONa in water, 80 °C.

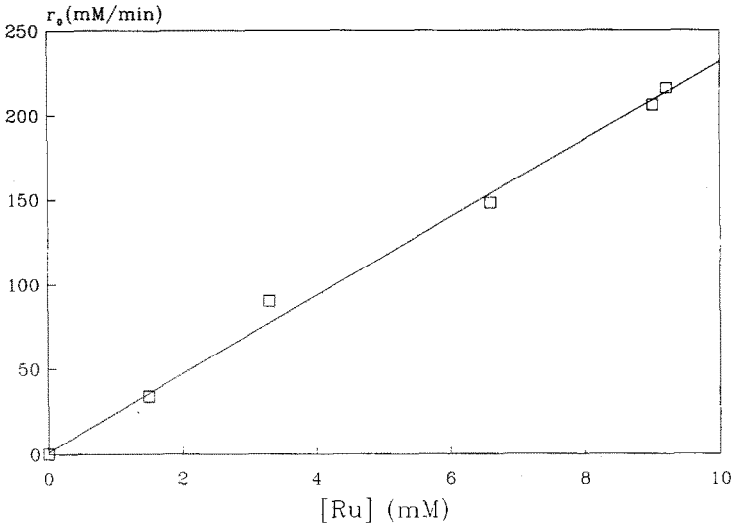


Fig. 1. Dependence of the initial rate on the catalyst concentration. Conditions: $RuCl_2(mSP\phi_2)_2$ (0–0.03 mmol) in 3 cm^3 of 5 M aqueous sodium formate; [P]/[Ru] = 10; 5 cm^3 of 0.5 M benzaldehyde in chlorobenzene; 80 °C.

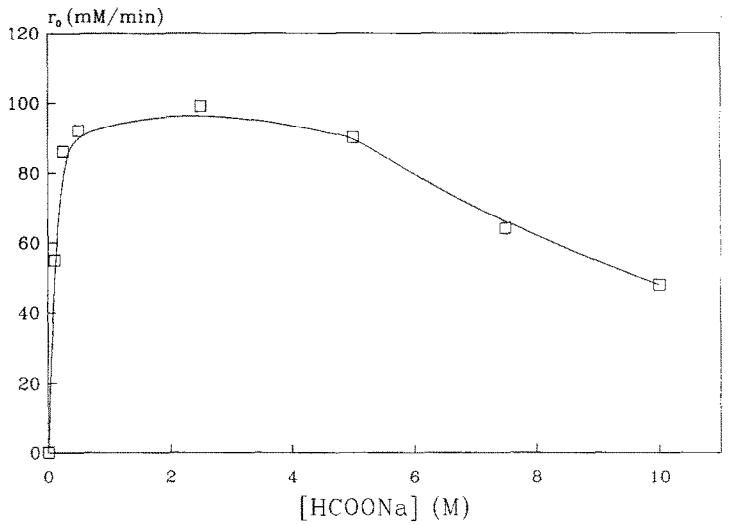


Fig. 2. Dependence of the initial rate on the concentration of HCOONa. Conditions: 0.01 mmol of $RuCl_2(mSP\phi_2)_2$ and 0.1 mmol of $mSP\phi_2$ in 3 cm^3 of aqueous sodium formate solution; 5 cm^3 of 0.5 M benzaldehyde in chlorobenzene; 80 °C.

the initial reaction rate reached its saturation value at ~5 M formate concentration in the aqueous phase, using Aliquat® 336 as phase transfer catalyst.

A remarkable feature of reaction (1) is that it does not require a phase transfer agent. Indeed, quaternary ammonium salts transfer $RuCl_2(mSP\phi_2)_2$

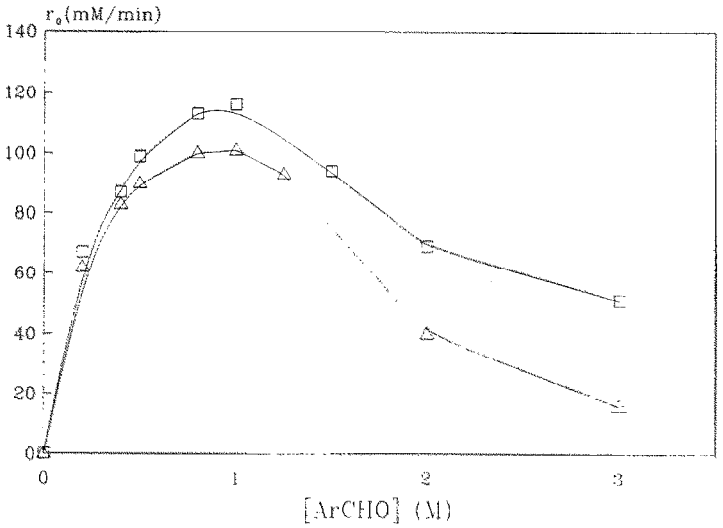


Fig. 3. Dependence of the initial rate on the concentration of benzaldehyde. Conditions: 0.01 mmol of $RuCl_2(mSP\phi_2)_2$ and $mSP\phi_2$ (Δ) 0.1 mmol, (□) 0.2 mmol, in 3 cm^3 of 5 M aqueous sodium formate solution; solvent chlorobenzene; 80 °C.

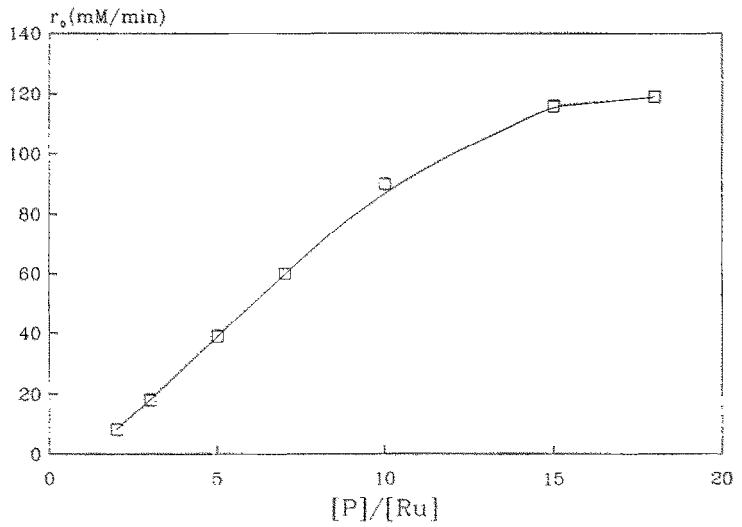


Fig. 4. Dependence of the initial rate on the [P]/[Ru] ratio. Conditions: 0.01 mmol of $RuCl_2(mSP\phi_2)_2$ and $mSP\phi_2$ in 3 cm^3 of 5 M aqueous sodium formate solution; 5 cm^3 of 0.5 M benzaldehyde in chlorobenzene; 80 °C.

and its derivatives to the organic phase (changing its colour to orange), and by doing so they decrease the rate of the transfer hydrogenation. The rate does not depend on the shape of the vessel or on the stirring rate above 500 rpm. In all cases the reaction mixtures were stirred at 1175 rpm. The effect of the ratio of the volumes of the two liquid phases was not studied.

Use of various organic solvents (toluene, dibutyl ether, or chlorobenzene) resulted in the same initial rates. It can be concluded from these findings that most probably the reaction takes place in the bulk aqueous phase or at the interface of the two liquid phases, the rate being chemically controlled at the high stirring rates applied. An important practical consequence of working without a PT agent is that there is no need to remove or recover it from the product.

The initial rate of the reaction as a function of aldehyde concentration shows a pronounced maximum (Fig. 3). This behaviour is again analogous to that observed in [8], however, the maximum is shifted to 1 M from 0.1 M aldehyde concentration. In this case, it is the aldehyde which is partitioned between the two immiscible phases, and the highest concentration in the aqueous phase can be reached by using a neat aldehyde phase. Indeed, this is how the preparative experiments were carried out (Table 1), showing that substrate inhibition does not hinder the process completely.

A crucial factor for obtaining high rates and conversions is the excess of the phosphine ligand, $mSP\phi_2$, as illustrated in Fig. 4. For $C_{mSP\phi_2}/C_{Ru} = 2$ (*i.e.* in the absence of excess phosphine), not only is the initial rate slow but the conversion is also limited (20%). Adding $mSP\phi_2$ equimolar to Ru results in an only slightly higher rate, but in an almost quantitative conversion (90%, under the conditions of Fig. 4). This finding leads to the assumption that the catalytically active ruthenium species contains at least three phosphine ligands. A further increase in $mSP\phi_2$ concentration results in a steady increase in the reaction rate up to the solubility limit of the phosphine. However, it should be remembered that sulphonated phosphines are strongly surface-active substances, and the rate-increasing effect may reflect their role in the reaction mechanism as well as the acceleration of transfer of the substrate from the organic to the aqueous phase.

It is often assumed [10, 13] that in $HRuClP_3$ ($P = PPh_3$ or $mSP\phi_2$) catalyzed hydrogenations, the dissociation of one phosphine ligand is a prerequisite for high catalytic activity. This assumption is also contained in the reaction mechanism suggested in [8] for the PTC reduction of tolualdehyde by formate with $RuCl_2(PPh_3)_3$, although no investigation of the effect of added PPh_3 is reported. However, there are reports [10, 19] of a beneficial effect of added phosphine on the rate of hydrogenation of carbonyl groups. This rate-increasing effect was shown quantitatively [10] to originate from an inhibition of the formation of a catalytically inactive Ru species, namely, an increase in the substrate inhibition. In the present reaction the situation may be identical, but without further studies it is not possible to say which intermediate(s) of the catalytic cycle is (are) prone to form the inactive bis(aldehydo) complex(es) with concomitant loss of a phosphine ligand. All our attempts to detect the latter complexes by UV–Vis spectrophotometry met with no success.

During the process, the catalyst gradually becomes irreversibly deactivated. This is evidenced by the observation that while a conversion of 92% could be reached using 5 mmol benzaldehyde in one batch, however under

identical conditions two consecutive 2.5 mmol batches of substrate gave only 3.6 mmol benzyl alcohol (an overall conversion of 72%). In any case reduction of the aldehyde is much faster than catalyst deactivation, since if in dilute solutions there is an excess of aldehyde over sodium formate, a 100% yield of alcohol (based on HCOONa) can be observed.

The absolute turnover of the catalyst in a given run also depends on the actual concentrations of aldehyde, formate and phosphine. All these substances compete for the coordination sites around ruthenium, and the formation of a bis(aldehydo) complex results in an efficient substrate inhibition (Fig. 3). Therefore, if during a run the concentration ratios vary in favour of this inhibition, the catalyst becomes reversibly deactivated before the complete conversion of formate or aldehyde. It was observed, on the other hand, that an excess of phosphine not only accelerates aldehyde reduction, but at the same time prevents catalyst deactivation (Fig. 3). For high absolute turnovers carefully chosen initial conditions are required; for example, stirring 2 ml of benzaldehyde and 5 ml of 5 M aqueous HCOONa solution at 80 °C together with 15 mg $RuCl_2(mSP\phi_2)_2$ gave maximum conversions of 42% and 98% in the presence of 60 mg and 120 mg $mSP\phi_2$, respectively. This latter conversion corresponds to 1250 catalytic cycles per Ru.

During the reaction there is a slight increase in the pH, from 7.8 to 9.2. However, in this range the rate of benzaldehyde reduction is independent of pH (Fig. 5).

Determination of the rate as a function of temperature yielded a *formal* activation energy of 98 kJ mol^{-1} (Fig. 6), which is considerably higher than the value reported by Bar *et al.* (70 kJ mol^{-1}). This temperature quotient also contains the term originating from the temperature dependence of aldehyde solubility in the concentrated (5 M) aqueous sodium formate solution, and therefore the true activation energy could not be worked out. However, it seems likely that, as in the case of the phase-transfer catalyzed reaction [8], the rate is governed by chemical factors, and not by phase transfer or diffusion.

A key observation concerning the mechanism of aldehyde reduction arises from the investigation of the reaction of $RuCl_2(mSP\phi_2)_2$ with formate in the *absence* of aldehydes. Above 50 °C, a bright yellow solution is formed when $RuCl_2(mSP\phi_2)_2$ and 1 equiv of $mSP\phi_2$ are dissolved in aqueous formate solutions. The resulting compound is characterized by $\lambda_{max} = 365$ nm and $\varepsilon = 3860\ M^{-1}\ cm^{-1}$, and is active for hydrogen transfer from formate to aldehydes. In the absence of the latter, at room temperature, the colour and catalytic activity are long retained even in the presence of air, although slow catalytic decomposition of formate occurs. The yellow compound can be extracted into $CHCl_3$ or CH_2Cl_2 by adding a stoichiometric amount of $Bu_4N^+HSO_4^-$. ^1H NMR in $CDCl_3$ showed a multiplet at −18.3 ppm characteristic of a ruthenium hydride. In the IR spectrum of CH_2Cl_2 solutions ν(Ru—H) could be detected at 2000 cm^{-1}, and the two carboxylate vibrations, *i.e.* ν(OCO, asym) at 1553 cm^{-1} and ν(OCO, sym) at 1315 cm^{-1} refer to

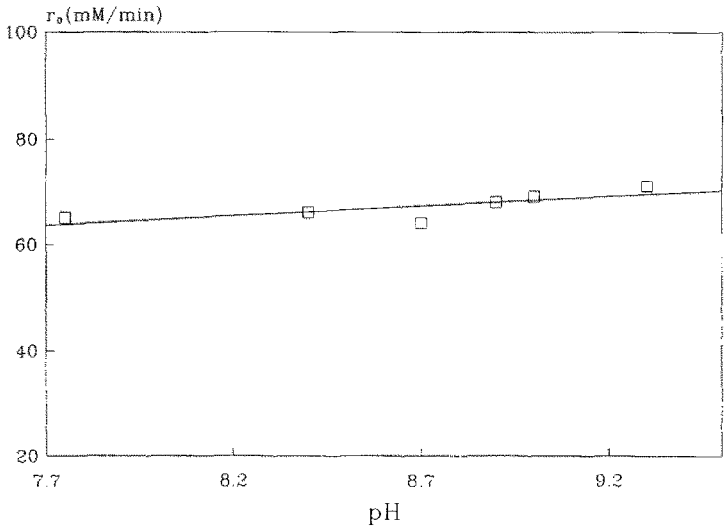


Fig. 5. Dependence of the initial rate on pH of the aqueous phase. Conditions: 0.009 mmol of $RuCl_2(mSP\phi_2)_2$ and 0.09 mmol of $mSP\phi_2$ in 3 cm^3 of buffered aqueous solution of appropriate starting pH, 1.6 M HCOONa in 0.26 M borate buffer; 5 cm^3 of 0.5 M benzaldehyde in chlorobenzene; 80 °C.

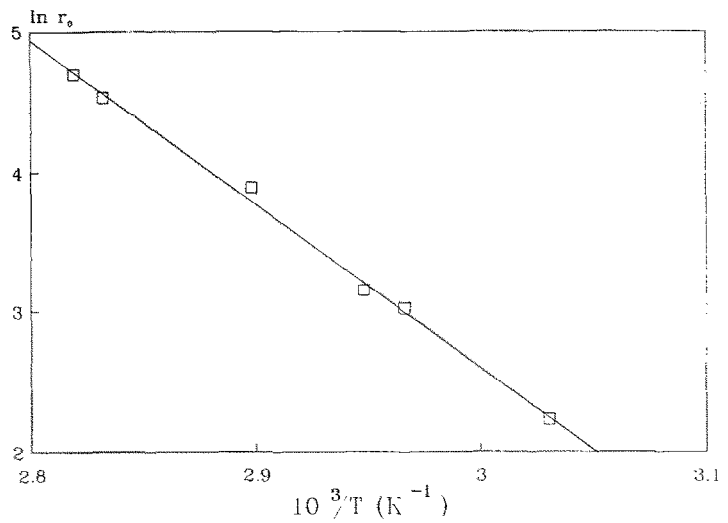


Fig. 6. Dependence of the initial rate on the temperature. Conditions: 0.01 mmol of $RuCl_2(mSP\phi_2)_2$ and 0.1 mmol of $mSP\phi_2$ in 3 cm^3 of 5 M aqueous sodium formate solution; 5 cm^3 of 0.5 M benzaldehyde in chlorobenzene.

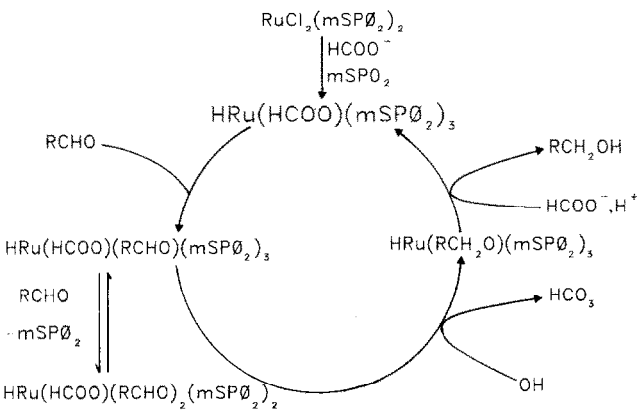
a bidentate carboxylate ligand. Therefore the compound can be assumed to be $HRu(O_2CH)(mSP\phi_2)_3$, and, indeed, the IR data are in agreement with those of $HRu(O_2CH)(PPh_3)_3$ [15, 16]. (It is worth mentioning that this latter compound was prepared in the reaction of $H_2Ru(PPh_3)_4$ or other ruthenium

hydrides with CO_2, and that the usual methods for the preparation of carboxylate complexes [17, 20] are not readily applicable due to solubility problems or fast HCOOH decomposition.) Addition of benzaldehyde to a chloroform solution of $HRu(O_2CH)(mSP\phi_2)_3$ (as Bu_4N^+ salt), leads to the formation of a stoichiometric amount of benzyl alcohol, as detected by gas chromatography.

Based on these findings, a possible mechanism for aldehyde reduction of $RuCl_2(mSP\phi_2)_2$-catalyzed hydrogen transfer from formate is suggested, as outlined in Scheme 1. Accordingly, in the presence of $mSP\phi_2$, $RuCl_2(mSP\phi_2)_2$ gives $HRu(O_2CH)(mSP\phi_2)_3$ on the action of formate. The hydridoformate would then react with the aldehyde dissolved in the aqueous phase. Rearrangement and reaction with another formate ion afford the product alcohol.

It is known from earlier studies [10] that an excess of phosphine efficiently inhibits the hydrogenation of olefins by $RuCl_2(mSP\phi_2)_2$ or $HRu(O_2CCH_3)(mSP\phi_2)_3$. This may explain the very high selectivity in formation of unsaturated alcohols from unsaturated aldehydes, as well as the complete inactivity of the complex in attempted reduction of olefins (*e.g.* cyclohexene and decene-1).

The *reported* possibility to reduce olefins in this system [21] deserves some comment. It is well known that formic acid can be decomposed either to $H_2 + CO_2$ or to $H_2O + CO$. By gas chromatography we have established that the rapid decomposition of HCOOH or 1:1 HCOOH:HCOONa mixtures, catalyzed by $RuCl_2(mSP\phi_2)_2$, yielded H_2 and CO_2 together with minute traces of CO. On the other hand, in HCOONa solutions formate decomposition is slow and stops almost completely during reduction of aldehydes. Since our reactions were always run under a slow stream of N_2, there was no



Scheme 1. Proposed mechanism of aldehyde reduction by catalyzed hydrogen transfer from formate.

possibility of H_2 accumulation in the gas phase. However, it cannot be ruled out, and indeed, was found in certain cases [22], that in *closed* systems the catalyst activates the *molecular* H_2 originating from formate decomposition.

Effect of cyclodextrins

Cyclodextrins can be successfully applied to facilitate transfer of lipophilic compounds from an organic to an aqueous phase [23], and in certain cases even their chirality can be used to induce enantioselectivity [24, 25].

We have found, however, that β-cyclodextrin (CD) inhibits the reduction of benzaldehyde; *e.g.* under the conditions of Fig. 7, 45% conversion in 1 h is obtained in the presence of the cyclodextrin instead of 74%. Since the Ru:CD:aldehyde ratio is 1:2:36, this great decrease in the rate cannot be the consequence of sequestering of the aldehyde by the cyclodextrin, but should arise from an interaction between cyclodextrin and the catalyst. Similar inhibition phenomena were observed with different cyclodextrins in the hydrogenation of acetophenone catalyzed by $RhCl(mSP\phi_2)_3$ [26] or $RhCl(P\phi_3)_3$ [27]. It follows, therefore, that in reactions catalyzed by transition metal complexes bearing phosphine ligands with unsubstituted phenyl groups, cyclodextrins cannot be used as phase transfer agents or chiral inductors.

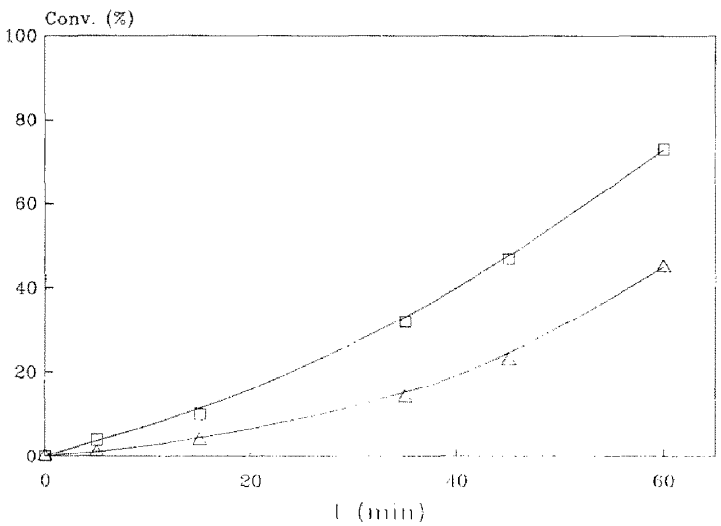


Fig. 7. Effect of β-cyclodextrin on the conversion–time profile of the reaction. Conditions: 0.56 mmol benzaldehyde; 19 cm^3 of 1 M HCOONa solution; 1 cm^3 of catalyst solution containing 0.015 mmol of $RuCl_2(mSP\phi_2)_2$ and 0.015 mmol of $mSP\phi_2$ in 1 M HCOONa, previously heated to 60 °C then cooled; room temperature; (□) without cyclodextrin, (△) with 0.03 mmol cyclodextrin.

Conclusions

Using a *water-soluble catalyst,* $RuCl_2(mSP\phi_2)_2$, aqueous solutions of HCOONa can be efficiently used for reduction of aldehydes to alcohols *without* a phase transfer agent. The solution of the catalyst is stable to air in the presence of $HCOO^-$, the execution and workup of the reaction are facile. It is concluded that the use of water-soluble complexes may offer considerable advantages in accomplishing biphasic reactions, as compared to the more conventional lipophilic catalysts.

Acknowledgements

This study was supported by the Hungarian National Foundation for Scientific Research OTKA through Grant No. 133/86 to F.J., and by the Hungarian Academy of Sciences through a fellowship to A.B. A generous loan of $RuCl_3$ by Johnson Matthey Ltd. is also gratefully acknowledged.

References

1 H. Alper, in M. Graziani and M. Giongo *Fundamental Research in Homogeneous Catalysis,* Vol. 4, Plenum Press, New York, 1984, p. 79.
2 E. G. Kuntz, *Chemtech, 17* (1987) 570.
3 F. Joó and Z. Tóth, *J. Mol. Catal., 8* (1980) 369.
4 D. Sinou, *Bull. Soc. Chim. Fr.,* (1987) 480.
5 R. Bar and Y. Sasson, *Tetrahedron Lett., 22* (1981) 1709.
6 R. Bar, Y. Sasson and J. Blum, *J. Mol. Catal., 16* (1982) 175.
7 R. Bar, Y. Sasson and J. Blum, *J. Mol. Catal., 26* (1984) 327.
8 R. Bar, L. K. Bar, Y. Sasson and J. Blum, *J. Mol. Catal., 33* (1985) 161.
9 S. Ahrland, J. Chatt, N. R. Davies and A. A. Williams, *J. Chem. Soc.,* (1958) 276.
10 Z. Tóth, F. Joó and M. T. Beck, *Inorg. Chim. Acta, 42* (1980) 153.
11 R. Colton and R. H. Farthing, *Aust. J. Chem., 22* (1969) 2011.
12 F. Joó and M. T. Beck, *J. Mol. Catal., 24* (1984) 135.
13 F. Joó, Z. Tóth and M. T. Beck, *Proc. 19th ICCC,* Prague, Czechoslovakia, 1978, Vol. 2, D62; I. Végvári, *M.S. Thesis,* Debrecen, 1974.
14 W. Strohmeier and L. Weigelt, *J. Organometall. Chem., 145* (1978) 189.
15 I. S. Kolomnikov, A. I. Gusev, G. G. Aleksandrov, T. S. Lobeeva, Yu. T. Struchkov and M. E. Vol'pin, *J. Organometall. Chem., 59* (1973) 349.
16 S. Komiya and A. Yamamoto, *J. Organometall. Chem., 46* (1972) C58.
17 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.,* (1973) 1912.
18 B. R. James, *Homogeneous Hydrogenation,* Wiley, New York, 1972, p. 83.
19 R. A. Sanchez-Delgado, A. Andriollo, O. L. De Ochoa, T. Suarez and N. Valencia, *J. Organometall. Chem., 209* (1981) 77.
20 R. A. Sanchez-Delgado, U. Thewalt, N. Valencia, A. Andriollo, R-L. Marquez-Silva, J. Puga, H. Schöllhorn, H-P. Klein and B. Fontal, *Inorg. Chem., 25* (1986) 1097.
21 J. A. Chukhajian, V. P. Kukolev, V. A. Matossian and N. A. Balyushina, Abstracts *4th ISHC,* Leningrad, USSR, 1984, Vol. 4, p. 138.
22 Y. Watanabe, T. Ohta, Y. Tsuji, T. Hiyoshi and Y. Tsuji, *Bull. Chem. Soc. Jpn, 57* (1984) 2440.

23 A. Harada, Y. Hu and S. Takahashi, *Chem. Lett.*, (1986) 2083.
24 R. Fornasier, F. Reniero, P. Scrimin and U. Tonellato, *J. Org. Chem.*, *50* (1985) 3209.
25 H. Gountzos, W. R. Jackson and K. J. Harrington, *Aust. J. Chem.*, *39* (1986) 1135.
26 F. Joó and A. Romhányi, unpublished observations.
27 H. A. Zahalka and H. Alper, *Organometallics*, *5* (1986) 1909.