The triphasic transfer hydrogenation of aromatic aldehydes by aqueous sodium formate in the presence of heterogenized ruthenium(II) complexes bound to swellable polymer matrices

Z.S. Liu *, G.L. Rempel **

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Abstract

Aromatic aldehydes can be reduced to the corresponding alcohols by hydrogen transfer from HCO_2Na in the presence of Ru(II) complexes bound to swellable polymer matrices and a quaternary ammonium salt. The reaction kinetics have been measured between 50 and 80 °C. The process was shown to depend on the structure of the aldehyde acceptor, on the concentrations of formate donor and phase-transfer agent, on the amount of the catalyst and also to be sensitive to the polarity of the organic solvent. The observed activation energy, $E_a = 20.80$ kcal mol^{-1}, suggests that process is a predominantly chemically controlled reaction. A general reaction mechanism and rate equation have been proposed.
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Keywords: Ruthenium; Transfer hydrogenation; Swellable polymer support catalyst; Aromatic aldehyde; Sodium formate

1. Introduction

Reduction of ketones and aldehydes to the corresponding alcohols is a class of reactions that are valuable in the pharmaceutical and chemical industry. Among the method used, transfer hydrogenation is an elegant strategy that can be accomplished with homogeneous, heterogeneous and water-soluble catalysts using different hydrogen sources such as isopropanol, formic acid derivatives and so on. Naskar and Bhattacharjee [1] reported the transfer hydrogenation of aldehydes to alcohols catalyzed by two cationic ruthenium(II) complexes, $[(PPh_3)_2Ru(CH_3CN)_3Cl][BPh_4]$ and $[(PPh_3)_2Ru(CH_3CN)_3Cl][ClO_4]$. They found that these two compounds are catalytically active at 90 °C using 2-propanol as the source of hydrogen in the presence of K_2CO_3. Ajjou and Pinet [2] investigated the biphasic transfer hydrogena-

tion of aldehydes and ketones with isopropanol catalyzed by water-soluble rhodium complexes, which generated in situ from $[Rh(COD)Cl]_2$ and triphenylphosphine trisulfonate (P(*m*-$C_6H_4SO_3Na)_3$, TPPTS) under basic conditions. The various aliphatic and aromatic aldehydes and ketones were selectively converted to the corresponding alcohols. The catalytic system can be recycled and reused with only negligible loss of catalytic activity. Recently, Naskar and Bhattacharjee [3] reported the selectively transfer hydrogenation of α,β-unsaturated carbonyl compounds with $[(PPh_3)_2Ru(CH_3CN)_3Cl][BPh_4]$ catalyst with high conversions when formic acid is the hydrogen donor. The transfer hydrogenation of aldehydes can be catalyzed by other metallic catalysts. Baidossi et al. used Pd/C heterogeneous catalyst in transfer hydrogenation of benzaldehydes to benzyl alcohols using potassium formate as the selective hydrogen donor [4]. The ketones did not react under these conditions. This method would be used into separate aldehydes selectively from a mixture of aldehydes and ketones.

One of the major developments in organic chemistry during the past few decades has been the application of phase-transfer catalysis in organic synthesis. These reactions are often effected in an aqueous base-organic two-phase system with an ammonium or phosphonium salt or crown ether as the catalyst. Some of the more attractive features of phase-transfer catalytic

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* Corresponding author. Current address: Food and Industrial Oil Research, National Center for Agricultural Utilization Research, Agricultural Research Service/U.S. Department of Agriculture, 1815 North University Street, Peoria, IL 61604, USA.
** Corresponding author.
E-mail addresses: kevin.liu@ars.usda.gov (Z.S. Liu), grempel@cape.uwaterloo.ca (G.L. Rempel).

reactions are that they are effective under mild conditions, rapid, and usually simple to work up. It is also a technique of considerable industrial importance.

The synthetic advantage of the phase-transfer technique in transition metal-catalyzed processes has been well demonstrated and reviewed by Cassar and Alper [5,6]. This method combined organometallic and phase-transfer catalysis has proved to be extremely powerful in organic synthesis. The ruthenium complex, $RuCl_2(PPh_3)_3$, was used to catalyze transfer reduction of aromatic aldehydes by aqueous sodium formate and catalytic amounts of quaternary ammonium salts under phase-transfer conditions [7,8]. This reaction has been shown to be of considerable synthetic importance. In this catalytic system, the transition metal catalysts dissolve in either the organic or aqueous phase, therefore they are monophasic homogeneous catalysts. These monophasic homogeneous catalysts suffer from some of the same disadvantages as more conventional homogeneous catalysts, i.e., separation and recovery. Especially when expensive transition metals are used on a large scale, recovery of the catalysts is a major consideration. These difficulties could be overcome by attaching the metal complexes to an insoluble polymeric support. These supported catalysts now function in a triphasic environment in either a liquid–solid–liquid or solid–liquid–solid reaction mixture. They are easily separated from the products at the end of the reaction and can be reused.

Recently Normura and Kuromatsu [9] reported the preparation of various pyridine and 2,2′-bipyridyl ligands attached to the polymer chain end of ring-opened poly(norbornene) by living ring-opening metathesis polymerization (ROMP) using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(O^tBu)_2$. The prepared pyridine and 2,2′-bipyridyl derivatives were used as ligands for catalytic hydrogen transfer reduction of cyclohexanone in the presence of $Ru(acac)_3$ (in toluene/^iPrOH in the presence of NaO^iPr, at 50 °C, acac: acetylacetonato). The catalytic activity increased upon addition of the above polymer as the ligand, and the prepared catalyst could be recovered by filtration as the precipitate, by pouring the reaction mixture into methanol. The recovered catalyst could be reused without decrease in the activity.

It has been reported that the activity of the catalysts supported on the polymer depends on the swellability and porosity of the polymer, as well as polymer–solvent interactions. Highly active catalysts require a large surface area of active component on the supports. Wang et al. [10] reported development of a polymer gel supported catalyst system. The catalytic activity of this system can be switched-on and -off abruptly when the solvent composition is changed. This accomplishment is a step forward in developing artificial enzymes with activity that can be tightly regulated. The swellable polymer supported catalysts are found to offer advantages over non-swellable polymer supported catalysts. The polymer contained some units having a better affinity for the liquid phase as the support might render the active sites to be readily available to the substrate and reduce, or eliminate diffusion control. Che and coworker developed soluble polymer, poly(ethylene glycol), supported ruthenium porphyrin catalysts [11]. They tried to combine the

best futures of both homogeneous and heterogeneous ruthenium catalysts. These catalysts exhibited high-reactivity and selectivity toward alkene epoxidation with 2,6-dichloropyridin-*N*-oxide and alkene cyclopropanation with diazo compounds. The catalysts are easily separated from organic products after reaction. In our previous study [12], we have reported on the preparation of swellable polymer (CCPAA absorbent) supported ruthenium(II) complexes, referred to as CCPAARu, and their catalytic applications in the transfer hydrogenation of aldehydes. Oga et al. [13] reported the transfer hydrogenation of ketones with HCO_2Na as a hydrogen donor, catalyzed by achiral Ru(II) complexes. Canivet et al. [14] studied transfer hydrogenation of aromatic ketones to give the corresponding chiral secondary alcohol with sodium formate with arene ruthenium complexes. In the present work, a detailed investigation of the transfer hydrogenation of aromatic aldehydes by aqueous sodium formate catalyzed by CCPAARu, which contains 4.93% Ru, is reported. This reaction is described in Eq. (1). Kinetic measurements have also been performed for this reaction.

$$ArCHO_{(org)} + HCOONa_{(aq)}$$

$$+ H_2O \xrightarrow[CCPAARu]{Q^+Z^-} ArCH_2OH_{(org)} + NaHCO_{3(aq)} \qquad (1)$$
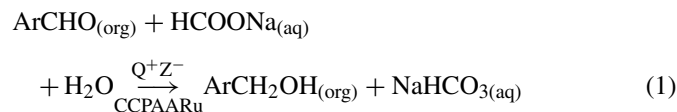
Q^+Z^- is the quaternary ammonium salt, Aliquat® 336 (phase-transfer catalyst).

2. Experimental

2.1. Materials

The solvents, bromobenzene, chlorobenzene, 1,2-dichlorobenzene, *p*-xylene and toluene (Aldrich, Milwaukee, WI, USA) were distilled before use. The reagents, benzaldehyde, 4-nitrobenzaldehyde, *p*-tolualdehyde, 4-bromobenzaldehyde and *p*-anisaldehyde (Aldrich, Milwaukee, WI, USA) were used as received. Ruthenium atomic absorption standard solution (990 ppm) (Aldrich, Milwaukee, WI, USA) and Aliquat® 336 (Aldrich, Milwaukee, WI, USA) were used as received.

2.2. Synthesis of catalyst

Details for the synthesis of the catalyst, CCPAARu, (4.93% Ru) are given in Ref. [12]. The particle size of CCPAARu is less than 250 μm.

2.3. Gas chromatography (GC) analysis

A Perkin-Elmer AutoSystem Gas Chromatograph coupled with a 1020 PC Plus data acquisition system was used for the analysis of transfer hydrogenation products, using a FID detector. The separations were accomplished with a 30 m × 0.322 cm column which was packed with DB-1 (100% polymethyl siloxane, 0.3 μm film).

2.4. Direct current plasma (DCP) analysis

The ruthenium content of the CCPAA supported ruthenium complexes before and after reaction was determined by atomic emission spectrometer using a SpectraSpan 7 Plasma Emission Spectrometer (SS-7) by ARL Fisons. Standards and polymeric samples for the DCP analysis were prepared according to the procedure described in Ref. [12].

2.5. Gas chromatography–mass spectroscopy (GC–MS) analysis

The transfer hydrogenation products were also identified by GC–MS with a VG TRIO-1 Benchtop instrument. The separations were accomplished with a 30 m × 0.322 cm column packed with DB-1 (100% polymethyl siloxane, 0.3 μm film).

2.6. Kinetic measurements

Kinetic measurements were carried out by following the conversion of 2,6-dichlorobenzaldehyde to the corresponding 2,6-dichlorobenzyl alcohol using GC. For a typical experiment, a nitrogen-flushed 50 ml flask equipped with a reflux condenser, two neoprene-capped side arms and a magnetic stirrer bar was immersed in an oil bath thermostated at $80 \pm 1\,^{\circ}$C. It was found that reaction rate of the aromatic aldehydes reduction depends strongly on the stirring velocity at lower stirring speed, but at higher stirring speed (over 600 rpm) the reaction rate is independent of stirring speed. In order to eliminate the stirring rate effect, all the experiments were carried out at a constant stirring rate of 800 rpm. 0.213 g (0.12 M) 2,6-dichlorobenzaldehyde, 0.13 g (32.20 mM) Aliquat® 336, $(CH_3)(C_8H_{17})_3N^+Cl^-$, 0.025 g ($1.22 \times 10^{-2}$ mmol Ru) CCPAARu and 10 ml chlorobenzene were added to the flask, and after temperature equilibration, 2 ml of 5 M sodium formate solution was added to the system. 0.4 μl samples were withdrawn periodically with the aid of a syringe and the organic phase was subjected to gas chromatographic analysis. Naphthalene (0.1000 g) was used as an internal standard.

Like some other transition metal catalysts [15], the CCPAARu catalyst decomposes aqueous sodium formate into H_2, CO_2 and Na_2CO_3. However, this takes place only in the absence of an external hydrogen acceptor [16]. Therefore, care should be taken to add the sodium formate as the last component to the reaction mixture.

3. Results and discussion

The products of the transfer hydrogenation were identified by GC–MS. The spectra of the products fit well with the known compounds. It should be noted however that the product of the substituted benzyl alcohol, like benzyl alcohol, has hydrogen donor ability [17]. Reaction (2) does not take place in the reverse direction. This result is interpreted by the explanation that the carbonyl group is stabilized through resonance with the benzene ring, and the hydrogen donating ability of primary alcohols is not strong enough to reduce the aromatic aldehy-
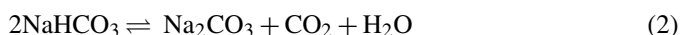
Table 1
Rate constants of transfer hydrogenation of some substituted benzaldehydes, ArCHO, by sodium formate in a bicatalytic system

Aldehyde	Temperature (°C)	k' ($\times 10^{-3}$ min^{-1})
2,6-Dichlorobenzaldehyde	80	16.9
4-Nitrobenzaldehyde	80	6.46
4-Bromobenzaldehyde	80	4.44
4-Anisaldehyde	80	3.14
4-Tolualdehyde	80	1.91

des. Therefore, full conversions of the substrate are usually obtained.

In spite of the fact that the basicity of the reaction mixture increases gradually as the result of the formation of both $NaHCO_3$ (see Eq. (1)) and Na_2CO_3 (Eq. (2)), no Cannizzaro reaction of the substrate could be traced by GC:

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + CO_2 + H_2O \qquad (2)$$

3.1. Effect of the structure of the aldehyde

The effect of the structure of the aldehyde on the reaction rate constant was studied. The results are summarized in Table 1 and indicate a rate constant dependence on the electronic nature of the aldehyde. It is to be noted that electron-withdrawing groups, Cl, Br, and NO_2, enhance hydrogen transfer hydrogenation, while electron-donating groups, CH_3O and CH_3, have a negative effect on the reaction rate. As aldehyde with an electron-donating group has strong coordinating ability, it may act as a poison towards the catalyst and make the coordination of the hydrogen donor difficult. The aliphatic aldehydes are generally reduced much more slowly than the aromatic aldehydes reported by Bar et al. [8]. For example, the initial reduction rates of *n*-heptanal and *n*-hexanal under the same reaction conditions as aromatic aldehydes in a two-phase system generally are 10–100 times lower than that of aromatic aldehydes. The 2,6-dichlorobenzaldehyde was chosen for kinetic study because of a higher reaction rate constant.

3.2. Effect of solvent

The effect of the solvent on the reaction rate constant was studied. The reactants dissolved well in these solvents at the reaction temperature used. The results are shown in Table 2. Table 2 shows the solvent effect of some halogenated and non-halogenated aromatic hydrocarbons on the transfer hydrogenation reaction. The dielectric constants of organic solvents

Table 2
Correlation between the dielectric constant of organic solvents and the rate constant reaction

Solvent	Dielectric constant (T, °C)	k' ($\times 10^{-3}$ min^{-1})
1,2-Dichlorobenzene	9.93 (25)	33.38
Chlorobenzene	5.62 (25)	16.9
Bromobenzene	5.40 (25)	11.52
Toluene	2.38 (25)	9.56
p-Xylene	2.27 (25)	1.89

Table 3
Effect of particle size on reaction rate constant

Particle size (μm)	k' ($\times 10^{-3}$ min^{-1})
300–250	15.6
250–125	17.1
125–45	19.1

in Table 2 have been reported by Weast [18]. The results indicate a moderate rate constant dependence on the polarity of the medium. The halogenated compounds with higher dielectric constants were found to be the most efficient solvents. Chlorobenzene was used in subsequent kinetic studies.

3.3. Effect of particle size

Various particle sizes of the CCPAARu catalyst were obtained by sieving dry samples. The effect of particle size on the reaction rate constant for the transfer hydrogenation of 2,6-dichlorobenzaldehyde with sodium formate was then investigated. The results are summarized in Table 3. The results show that the particle size of the CCPAARu catalyst has a slight effect on the reaction rate constant over the range of between 300 and 45 μm. This may be explained in that the CCPAA absorbent has a good swellability in the aqueous phase, and therefore it might make the active sites readily available to the substrate and reduce diffusion control problems.

3.4. Metal leaching

The metal leaching of the CCPAARu catalyst after reaction was investigated by DCP analysis. The analysis showed that only 1.83% of the Ru metal leached from the CCPAARu catalyst during the first catalytic run. The conversions of 2,6-dichlorobenzaldehyde to 2,6-dichlorobenzyl alcohol catalyzed by fresh and reused CCPAARu are presented in Table 4. It is to be noted that the catalyst can be reused, the activity of the catalyst being only slightly decreased. The main reason probably is that after the first catalytic run, the polyacrylic acid chain, which is an electrolyte, shrunk a little bit in the presence of the high electrolyte solution of formate. When the catalyst is reused, it probably takes a longer time to swell the support. At a lower swelling ratio of the support the substrate has a more difficulty to move toward the active metal centre within the polymer chain. It can be seen that the reaction rate decreased in the second run, but 100% conversion of 2,6-dichlorobenzaldehyde to 2,6-dichlorobenzyl alcohol can still be obtained with a reaction time of 8 h.

Table 4
Conversion of 2,6-dichlorobenzaldehyde catalyzed by CCPAARu

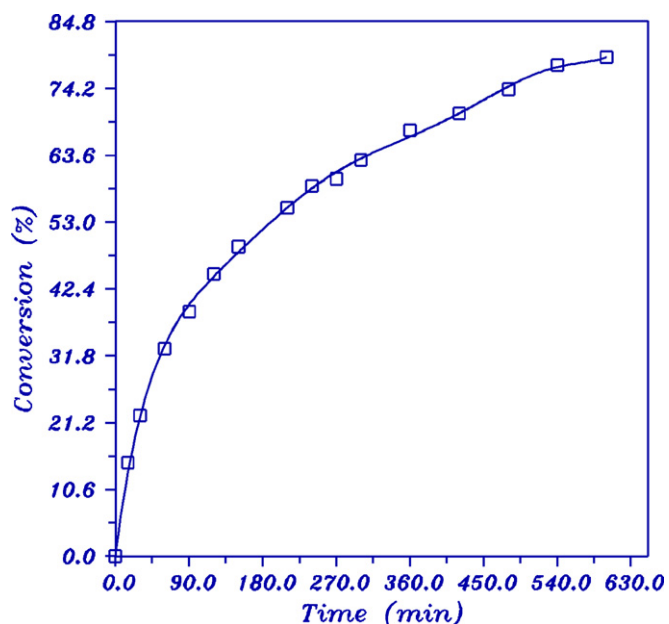| Use of catalyst (cycle)	Initial Ru%	Reaction time (h)	Conversion (%)
1	4.93	4	100
2	4.84	8	100
3	4.75	8	77.7

Fig. 1. Representative transfer hydrogenation plot for the hydrogenation of 2,6-dichlorobenzadehyde.

3.5. Reaction kinetics

A representative conversion–time plot for the transfer hydrogenation of 2,6-dichlorobenzaldehyde by sodium formate catalyzed by CCPAARu is shown in Fig. 1. It seems that the reaction exhibits an apparent first-order dependence on the aldehyde concentration in the earlier stage of the reaction. Good linear plots of ln[aldehyde] versus reaction time such as shown in Fig. 2 are obtained by using the data points from the transfer hydrogenation plots of Fig. 1 with up to 79% completion of the reaction. The slopes of such plots provided values for the pseudo-
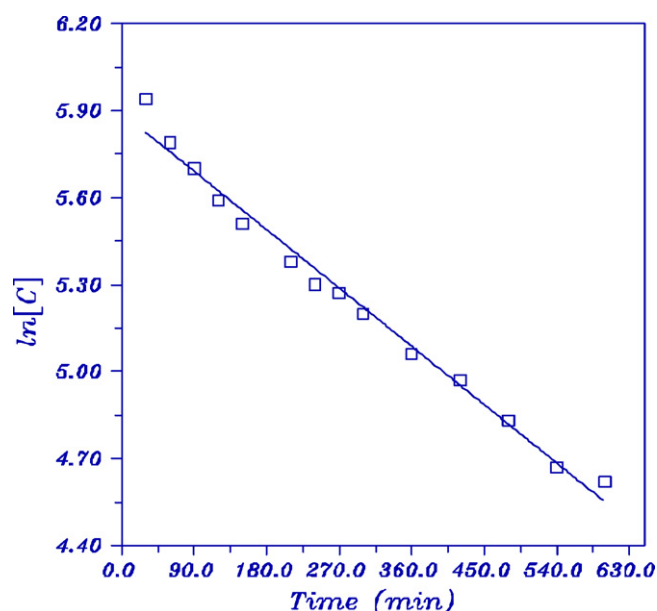

Fig. 2. Logarithmic plot of ln[aldehyde] vs. time for the transfer hydrogenation of 2,6-dichlorobenzaldehyde.

Table 5
Kinetic data for transfer hydrogenation of 2,6-dichlorobenzaldehyde by sodium formate

Ru ($\times 10^{-2}$ mmol)	[PTC] (mM)	[Aldehyde] (M)	[HCOONa], 2 ml (M)	T (°C)	k' ($\times 10^{-3}$ min^{-1})
1.22	32.20	0.12	5	80	16.90
1.22	32.20	0.24	5	80	11.35
1.22	32.20	0.37	5	80	8.59
1.22	32.20	0.37	5	80	9.14
1.22	32.20	0.49	5	80	6.44
1.22	32.20	0.61	5	80	2.69
1.22	32.20	0.12	5	50	1.26
1.22	32.20	0.12	5	60	3.58
1.22	32.20	0.12	5	65	5.19
1.22	32.20	0.12	5	70	10.25
1.22	32.20	0.12	5	80	16.90
1.22	32.20	0.12	1	80	6.92
1.22	32.20	0.12	3	80	9.65
1.22	32.20	0.12	3	80	8.49
1.22	32.20	0.12	4	80	14.20
1.22	32.20	0.12	5	80	16.90
1.22	32.20	0.12	6	80	10.08
1.22	32.20	0.12	8	80	6.94
0.24	32.20	0.12	5	80	2.49
0.24	32.20	0.12	5	80	3.20
0.49	32.20	0.12	5	80	4.07
0.49	32.20	0.12	5	80	3.94
0.73	32.20	0.12	5	80	9.96
0.98	32.20	0.12	5	80	13.20
1.22	32.20	0.12	5	80	16.90
1.22	8.16	0.12	5	80	3.04
1.22	16.10	0.12	5	80	9.04
1.22	24.20	0.12	5	80	12.86
1.22	32.20	0.12	5	80	16.90

first-order rate constant k'. In Table 5 a summary of the results for a series of experiments showing the effect of the reaction variables on k' is provided. Notably, these effects include aldehyde concentration, reaction temperature, formate concentration, catalyst amount and PTC concentration. For individual study of these effects is discussed in the following sections. Replicates of many experiments were carried out to study the reproducibility of the catalysis. The error in rate constants was found to be within ±5%. For example, the duplicated experiments of benzaldehyde hydrogenation using catalyst concentration at 0.49×10^{-2} mmol, k' values obtained (Table 5) are 4.07 and 3.94×10^{-3} min^{-1}.

3.6. Effect of formate concentration

The dependence of the initial rate on the concentration of the sodium formate in the aqueous phase was studied. The results are shown in Fig. 3. An increase in initial rate was found when the formate concentration is lower than about 5 M. A slow decrease in initial rate can be observed above 5 M. Firstly, an explanation for this is that of the high probability 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. It was reported that the increase in formate concentration from 5 to 10.3 M is associated with a decrease in

the concentration of the water from 46.6 to 36.1 M [8]. Secondly, it is probable that the polyacrylic acid chain, which is a high electrolyte, shrunk at higher concentration of the formate electrolyte, therefore, the substrate has difficulty to diffuse into the active
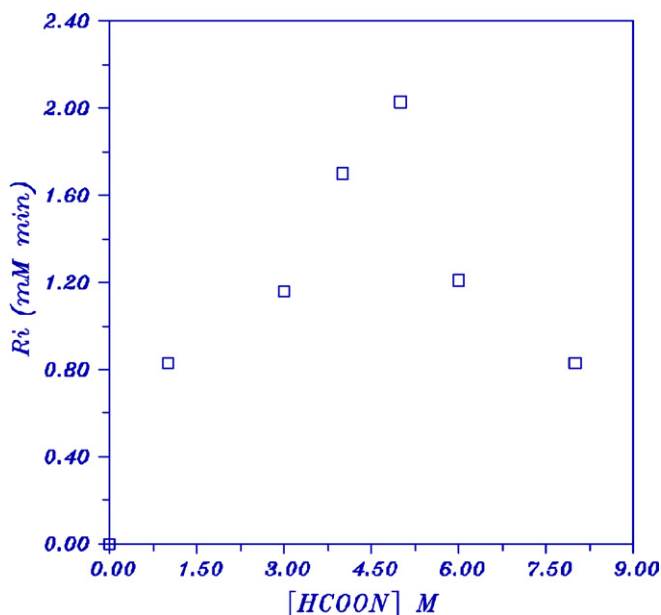

Fig. 3. Dependence of the initial rate on the concentration of HCOONa.

centre and consequently the reaction rate is suppressed. In the related phase-transfer catalysis system, the initial rate reached its highest value at around 5 M formate concentration in the aqueous phase using Aliquat® 336 as the phase-transfer catalyst according to Bar's report [8]. Here, our experimental result is in full agreement with his results, the reaction rate reached its highest value at 5 M formate concentration as shown in Fig. 3.

3.7. Effect of PTC concentration

It is reported that in the absence of the phase-transfer catalyst or in the presence of the more hydrophillic onium salts (tetramethyl- or tetraethylammonium bromide), the reaction of the transfer hydrogenation of aldehyde was found to proceed very slowly [8]. A considerable rate enhancement was observed when the chain length of the alkyl groups of the ammonium salt $(C_nH_{2n+1})_4N^+Br^-$, was increased from 3 to 5 carbon atoms. When $n > 5$, the initial rate levelled off and did not change. Based on this experimental data, Aliquat® 336, $(CH_3)(C_8H_{17})_3N^+Cl^-$, was chosen as phase-transfer catalyst. The initial rate dependence on the concentrations of the phase-transfer catalyst over the range of 8.16–32.20 mM was investigated. The initial rate dependence of the PTC concentration is shown in Fig. 4. It is found that it exhibits a linear relationship between the initial rate and phase-transfer catalyst concentration ranging from 0 to 32.20 mM. It is reported that the onium salt was found to have an effect on the interfacial tension of the water–chlorobenzene layers opposite from that on the initial rate [8]. While the interfacial tension decreased from 21 to 8 dyn cm^{-1} by increasing the concentrations from 0 to 14.4 mM, the initial rate increased from 0.3 to 15.8 mM min^{-1}. In our case, by increasing the concentration from 8.16 to 32.20 mM, the initial rate increased from 0.35 to 2.03 mM min^{-1}. It has been reported that at a relative high
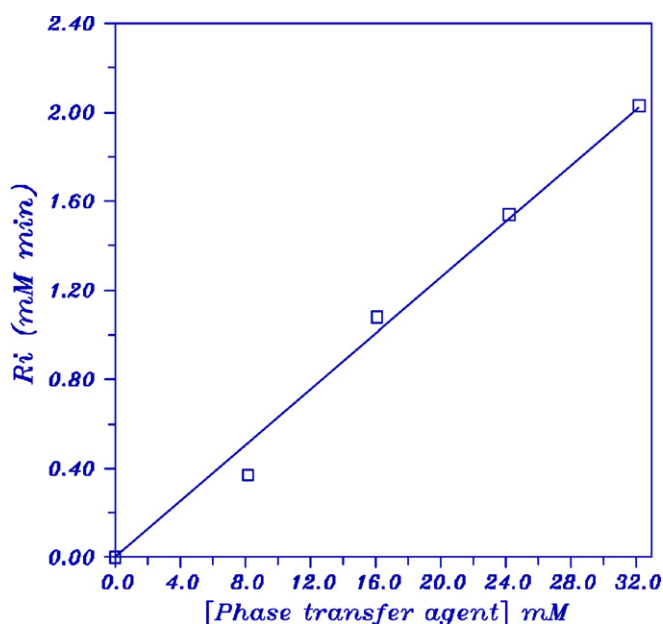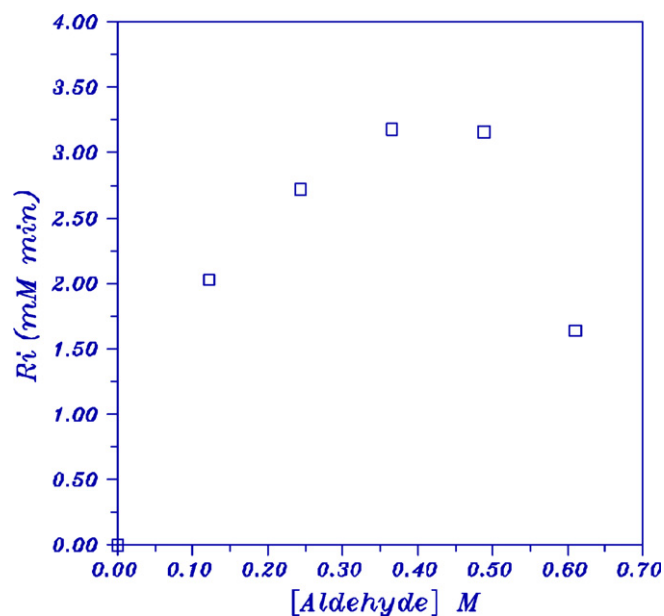

Fig. 5. Dependence of the initial rate on the concentration of 2,6-dichlorobenzaldehyde.

concentration the phase-transfer catalyst has hardly any effect on the rate, because of the interface saturation [19].

3.8. Effect of aldehyde concentration

The initial rate dependence on the aldehyde concentration was studied over the range of 0.12–0.61 M. The results are shown in Table 5. A plot of the initial rate against 2,6-dichlorobenzaldehyde concentration is presented in Fig. 5. A first to zero order relationship is observed up to about 0.49 mM of the substrate and then the rate decreases above 0.49 mM. A probable explanation is that the aldehyde molecule has a very strong coordination ability, which has been shown by spectroscopic study [20] and by the effect of addition of triphenylphosphine and olefins [21]. We also studied the effect of the addition of the triphenylphosphine on the transfer hydrogenations [17]. It shows that the rate of reduction of aldehydes was not changed at all. At higher concentrations of aldehyde, it is thought that a considerable amount of two aldehyde molecules coordinated on ruthenium metal exists and may inhibit transfer hydrogenation. Such rate dependence has also been reported in some other related hydrogen transfer processes [8,22,23]. If, however, the aldehydes were left out, fast decomposition of the formate into molecular hydrogen and sodium bicarbonate started right away [24]. This undesired reaction stopped immediately when the aldehyde was added [24]. Therefore, we took care that in all experiments the aqueous formate was the last component added to the reaction mixture.

3.9. Effect of the amount of the catalyst

The effect of total ruthenium amount on the initial rate of transfer hydrogenation was investigated. The source of ruthenium CCPAARu (4.93% Ru) was present in varying amounts
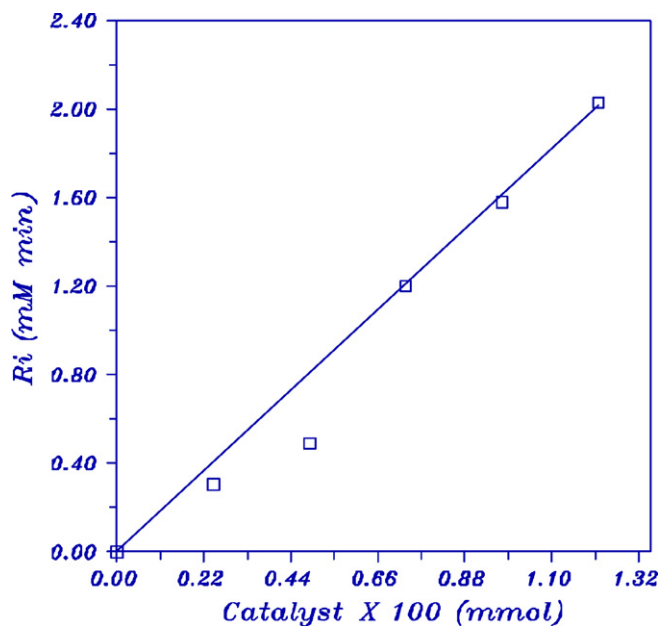

Fig. 4. Dependence of the initial rate on the concentration of phase-transfer catalyst.

Fig. 6. Dependence of the initial rate on the catalyst amount.

ranging from 0.24×10^{-2} to 1.22×10^{-2} mmol. A plot of the initial rate against catalyst concentration is presented in Fig. 6. The results indicate a linear dependence of initial rate on catalyst amount ranging from 0.24×10^{-2} to 1.22×10^{-2} mmol.

3.10. Effect of temperature

The effect of temperature on the reaction rate constant is shown in an Arrhenius plot. A number of kinetic runs listed in Table 5 were carried out at several temperatures ranging from 50 to 80 °C. Fig. 7 shows an Arrhenius plot of $\ln(k)$ versus $1/T$. A good linear plot was obtained. The apparent activation energy, E_a, obtained from the least squares slope of the
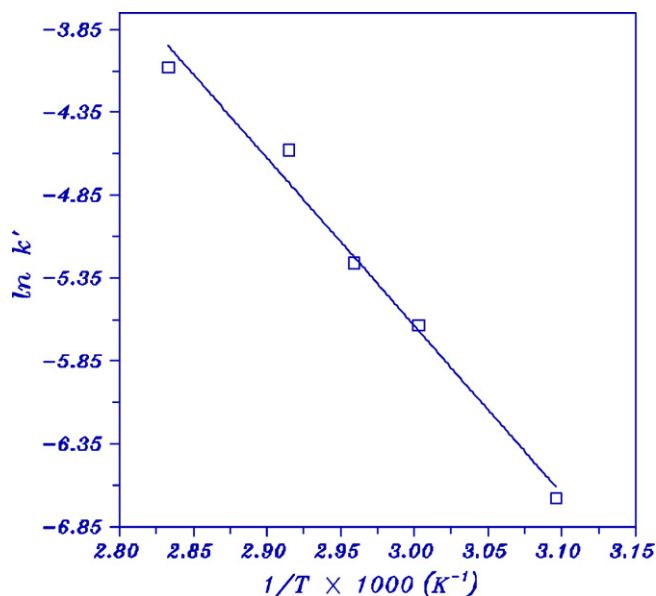

Fig. 7. Dependence of the rate constant on the temperature.

plot is 20.80 kcal mol^{-1}. Which is typical of a chemically controlled transfer hydrogenation reaction (20–25 kcal mol^{-1}) [24]. Since the kinetic studies were carried out at 80 °C, they are predominantly under chemical control, and do not involve a phase-transfer or diffusion controlled reaction.

3.11. Mechanistic consideration and rate equation

Inspection of the overall behaviour of this triphasic system led to the conclusion that the rate is controlled by both mass transfer and a chemical reaction, but predominantly by a chemical reaction. The effect of the mass transfer could be deduced from the observed slight influence of the particle size (Table 3). While the effect of the chemical reaction was demonstrated by the rate dependence on the concentration of the aldehyde (Fig. 5) and on the amount of the CCPAARu catalyst (Fig. 6), as well as by the electronic nature of the substrate (Table 1). The combination of the two effects may be understood in terms of a model of the triphasic system, i.e., liquid–solid–liquid. In this triphasic system, there are organic and aqueous boundary layers separated by an interface [25]. It is assumed that the diffusion of the ion pair Q^+HCOO^- formed at the interface through the boundary layer (film diffusion) [25] is faster than the diffusion through the solid polymer support to the metal active sites. In this case if the diffusion were fast, consequently the reaction would be chemically controlled. If the chemical reaction were very fast, it would be controlled by the diffusion rate of Q^+HCOO^- through polymer support. In our case, because CCPAA absorbent has very good swellability in water, the diffusion through the polymer support becomes easier. Consequently the reaction appears to be chemically controlled. This assumption was supported by observing only a slight influence of particle size on the rate. The value of the activation energy, 20.80 kcal mol^{-1}, also supports that this system is predominantly a chemically controlled reaction.

A mechanism of hydrogen transfer hydrogenation of the aldehyde by sodium formate can be proposed utilizing results from the above kinetic studies and product characterization, as well as information from literature sources. The initial rate dependence on the concentration of the aldehyde (Fig. 5) suggests a mechanism which involves catalyst deactivation by the substrate. The first step of this transfer hydrogenation is presumed to be complexation of aldehyde A with catalyst M to form the active centre MA. The latter species can either react irreversibly to yield the products or add reversibly a second aldehyde molecule to give

$$M + A \underset{}{\overset{K_1}{\rightleftharpoons}} MA + A \rightleftharpoons MA_2$$

(I)   (II)   (III)

$$k \downarrow Q^+HCOO^-nH_2O$$

products
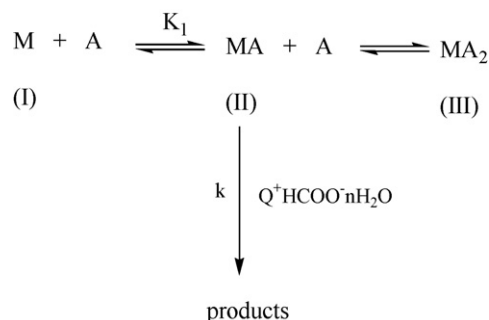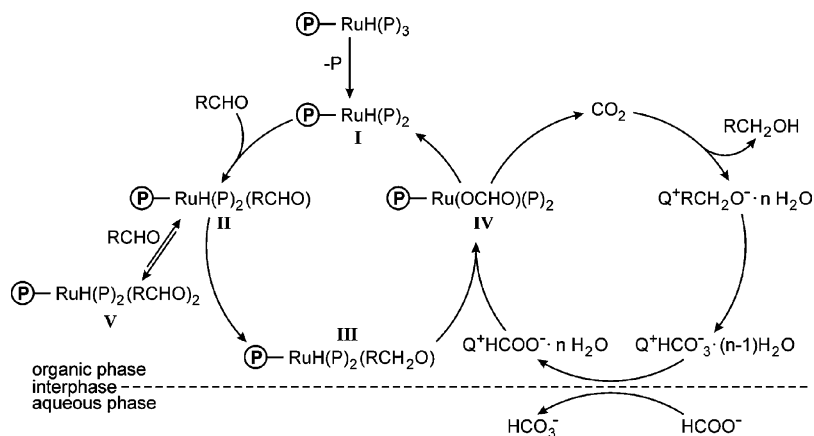
Scheme 1.

Scheme 2. A proposed mechanism of the triphasic transfer hydrogenation of aldehydes.

an inactive species MA_2. This sequence can be demonstrated as shown in Scheme 1

Based on Scheme 1, the following rate law is obtained

$$R = k[Q^+HCOO^-][II] \tag{3}$$

The total concentration of metal catalyst $[M_0]$ is given by the following equation:

$$[M_0] = [I] + [II] + [III] \tag{4}$$

The equilibrium constants K_1 and K_2 shown in Scheme 1 can be used to describe the following ratios in Eqs. (5) and (6).

$$K_1 = \frac{[II]}{[I][A]} \tag{5}$$

$$K_2 = \frac{[III]}{[II][A]} \tag{6}$$

Rearrangement of Eqs. (5) and (6), followed by substitution into Eq. (4) results in the following equation:

$$[II] = \frac{K_1[A][M_0]}{1 + K_1[A] + K_1K_2[A]^2} \tag{7}$$

Finally substituting Eq. (7) into Eq. (3) gives the final rate expression (8):

$$R = \frac{k_1[Q^+HCCO^-]K_1[M_0][A]}{1 + K_1[A] + K_1K_2[A]^2} \tag{8}$$

This expression accommodates all the experimental results. For example, the rate equation implies a linear dependence on the initial concentration of the catalyst, which is in full agreement with the experimental results (Fig. 6). It also explains the rate concentration of aldehyde profile shown in Fig. 5, which ascends in the low substrate concentration region but descends above 0.488 mM. Derivation of the rate equation reveals that rate reaches its highest value when

$$[A] = \frac{1}{(K_1K_2)^{1/2}} \tag{9}$$

The rate equation expresses a linear dependence on the concentration of ion pair Q^+HCOO^-, which should be proportional

to the concentrations of phase-transfer catalyst and sodium formate. The experimental data show the first-order dependence on the PTC concentration (Fig. 4) and first-order dependence on the sodium formate at a concentration of less than 5 M (Fig. 3). At higher sodium concentration, the reaction rate decreased because of a salting out effect and limiting swellability of the CCPAA support.

A proposed mechanism of reaction (1) which is compatible with our results is summarized in Scheme 2. Scheme 2 includes both the phase-transfer and the metal-catalyzed cycles. The dissociation of the PPh_3 should be complete and fast under those reaction conditions. The quaternary ammonium cation in the organic solution is assumed to extract hydrated formate anions via the interface.

Activation of the CCPAA–ruthenium(II) complex by loss of one PPh_3 is expected to give the active ruthenium hydride I. Complexation of it with an aldehyde molecule is assumed to form II which can rearrange via intramolecular hydride transfer to a metal alkoxide III. Anion exchange with Q^+COO^- results in formation of a quaternary ammonium alcoholate, $Q^+RCH_2O^-$ and the generation of the initial hydride I via complex IV. The carbon dioxide formed by decarboxylation of IV may react with the basic intermediate $Q^+RCH_2O^-$ to give an ammonium hydrogen carbonate, $Q^+HCO_3^-$ and the alcoholic product RCH_2OH. When complex II reacts with a second aldehyde molecule, an inactive species $P\text{-}HRu(RCHO)_2(PPh_3)_2$ V is formed.

4. Conclusion

The CCPAARu catalyst and an aqueous solution of HCOONa can be efficiently used for reduction of aromatic aldehydes to alcohols using the phase-transfer agent, Aliquat® 336. A kinetic study has been carried out in chlorobenzene at 80 °C. A general rate law derived from the proposed reaction mechanism is consistent with the observed kinetic data. The observed activation energy, $E_a = 20.80 \text{ kcal mol}^{-1}$, suggested the reaction is a predominantly chemically controlled reaction.

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