Catalysis Today 247 (2015) 14–19

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Unexpectedly fast catalytic transfer hydrogenation of aldehydes by formate in 2-propanol–water mixtures under mild conditions

Imre Szatmári [a], Gábor Papp [b], Ferenc Joó [a,b,*], Ágnes Kathó [a,1]

[a] University of Debrecen, Department of Physical Chemistry, P.O. Box 7, H-4010 Debrecen 10, Hungary
[b] MTA-DE Homogeneous Catalysis and Reaction Mechanisms Research Group, P.O. Box 7, H-4010 Debrecen 10, Hungary

ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form 24 May 2014
Accepted 18 June 2014
Available online 11 July 2014

Keywords:
Unsaturated aldehyde
Transfer hydrogenation
Ruthenium-phosphine catalyst
Sodium formate
Water
2-Propanol

ABSTRACT

Unsaturated aldehydes were efficiently reduced by transfer hydrogenation from sodium formate in water–2-propanol mixtures using a water-soluble Ru(II)-tertiary phosphine catalyst. The reaction yielded unsaturated alcohols with complete selectivity and without hydrogenation or isomerization of C=C bonds of the substrates. Very high reaction rate was observed in the transfer hydrogenation of cinnamaldehyde already at 30 °C with turnover frequency of 160 h^{-1} and this increased to 3800 h^{-1} at 70 °C. Consequently, the method is applicable to the synthesis of unsaturated alcohols in case of heat sensitive or highly volatile aldehydes, too. Based on multinuclear NMR investigations, *trans*-$[RuH_2(H_2O)(m\text{tppms})_3]$ is suggested as the key catalytic species.

1. Introduction

Hydrogenation of aldehydes is a synthetically important reaction and has attracted much interest both from the heterogeneous and homogeneous catalysis community. Selective hydrogenation of α,β-unsaturated aldehydes is a particularly challenging problem because the reaction may yield three products all of which have their important applications as starting materials for flavor and fragrance substances. A specific example (Scheme 1) is the reduction of cinnamaldehyde (*trans*-3-phenyl-2-propenal, A) which supplies cinnamyl alcohol (3-phenyl-2-propenol, B), 3-phenyl-propanal (C) and 3-phenyl-propanol (D).

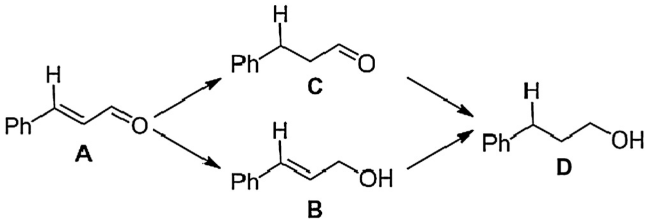
Several homogeneous catalytic hydrogenation processes were reported in the literature for the reduction of aldehydes [1–30], however, in most cases catalyst recovery and product isolation were cumbersome. Limited solubility of aldehydes in water allows the use of aqueous–organic biphasic systems with the use of water-soluble catalysts. In such systems, the catalyst resides in the aqueous phase while the substrate is found in the organic phase so they can be separated upon completion of the reaction. Most often the water-soluble catalysts contain sulfonated phosphine ligands such as *m*tppms (sodium 3-diphenylphosphinobenzenesulfonate) [31], *m*tppts (trisodium 3,3′,3″-phosphinetriylbenzensulfonate) [32] or pta (1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane or 1,3,5-triaza-7-phosphaadamantane) [33]. Typical catalysts are $[\{RuCl_2(m\text{tppms})_2\}_2]$ [7], $[RhCl(m\text{tppts})_3]$ [7] or the in situ prepared Rh(I)-complexes with water-soluble thioligands, such as (L)-cysteine or (S)-captopril [20]. Hydrogenation of allylic alcohols may proceed via isomerization to aldehydes or ketones and in such cases the catalyst should be able to facilitate the hydrogenation of the C=O function [34–36]. In general, it can be stated that the rhodium(I)-based catalysts are more active in hydrogenation of the C=C bond, while the Ru(II)-complexes prefer hydrogenation of the C=O bond. Nevertheless, this can be regarded only as a vague rule of orientation because the actual selectivity may depend on many factors such as, e.g. the pH of the aqueous phase or the hydrogen pressure. Hydrogenation of aldehydes in aqueous–organic biphasic systems has been reviewed recently [4].

Transfer hydrogenation is a highly efficient and versatile tool for reducing various unsaturated compounds. Although several hydrogen donors have been found useful for this purpose, the two most extensively investigated are 2-propanol and formic acid/formate salts. In most cases, 2-propanol is used in the presence of a strong base (*t*-BuOH, KOH, etc.) very often applying Ru(II)-based homogeneous catalysts. Excellent rates and selectivities were achieved by Noyori [37], Bäckvall [8], Xiao [38] and others in synthesis of secondary alcohols. In general, water is not well tolerated in such processes [38], and several studies showed that both the rates and

---

[*] Corresponding author at: University of Debrecen, Department of Physical Chemistry, P.O. Box 7, H-4010 Debrecen 10, Hungary. Tel.: +36 52 512900x22382.
E-mail addresses: joo.ferenc@science.unideb.hu, joofer49@yahoo.com (F. Joó).
[1] Author for further information.

http://dx.doi.org/10.1016/j.cattod.2014.06.023
0920-5861/



Scheme 1. Hydrogenation of *trans*-cinnamaldehyde.

selectivities decrease substantially with increasing water content of the 2-propanol–water mixtures even in those cases when water-soluble catalysts were applied. Notable exceptions are the transfer hydrogenations of ketones studied by Williams et al. [39,40] and by Ajjou and Pinet [11] where up to 51% (v/v) water could be applied beneficially. Xiao applied a water-insoluble catalyst in aqueous–organic biphasic system for transfer hydrogenation of ketones from formate and observed an accelerating effect of water (on water reaction) [41].

In contrast to 2-propanol, the most suitable solvent for formic acid/formate salts is water and the insolubility of many of the aldehyde or ketone substrates in water allows to run transfer hydrogenations in aqueous–organic biphasic systems. Both aldehydes and ketones were successfully hydrogenated by H-transfer from aqueous formate using Ru(II)-complexes as catalysts [42–47]. Rh(I)- and Ir(I)-complexes are also known to act as catalysts in such reactions [48,49], in fact, Ir(I)-complexes with monotosylated ethylenediamine ligands [9,10] showed outstanding catalytic activities up to turnover frequencies, TOF = $3.0 \times 10^5\ h^{-1}$ (TOF = mol reacted aldehyde × $(\text{mol catalyst})^{-1} \times h^{-1}$) [10].

Interestingly, in the first biphasic transfer hydrogenation of aldehydes both the $[RuCl_2(PPh_3)_3]$ catalyst and the substrates were dissolved in the same (organic) phase and the aqueous phase served only as a reservoir of the H-donor (Na-formate) [42,43]. Consequently, a phase transfer catalyst (Aliquat 336) had to be used in order to attain reasonably high reaction rates. In addition, due to substrate inhibition [42], the aldehyde concentration in the organic phase had to be kept low. For substrate-catalyst separation and catalyst recycling a better arrangement is to dissolve the catalyst together with HCOONa in the aqueous phase and contact it with an organic phase of the aldehyde (neat or dissolved in a suitable solvent, such as, e.g. toluene). In such an aqueous–organic biphasic system, we achieved 100% selective transfer hydrogenation of unsaturated aldehydes to unsaturated alcohols at 80 °C by using $[\{RuCl_2(m\text{tppms})_2\}_2] + n m\text{tppms}$ or $[RuCl_2(\text{pta})_4]$ catalysts and 5 M aq. HCOONa as H-donor [44–47].

Catalytic hydrogenations and transfer hydrogenations in aqueous–organic biphasic systems can be influenced by several factors which may be belong to one of the following groups: (1) effects connected to the presence of water, (2) effects of phase transfer and solubilities. Water may influence the actual molecular form of the catalyst by promoting hydrolysis (formation of hydroxo-complexes) [50]; preferring heterolytic activation of H_2 [50]; allowing formation of several hydrido- and molecular hydrogen complexes from the same catalyst precursor depending on the pH of the aqueous phase and on H_2 pressure [23,24,50]; protonation/deprotonation equilibria, etc. Concerning phase transfer and solubility effects the chemical reaction may proceed either in the catalyst-containing bulk aqueous phase, or at the interphase of the two bulk phases. The most important factor is perhaps the transfer of substrates to the interphase and their dissolution into the aqueous phase and this can limit the overall rate of the hydrogenation process. Another rate-decreasing factor is the lower solubility of H_2 in water, compared to the usual organic solvents. On the other hand, limited solubility of the substrate (e.g. an aldehyde) in the aqueous phase may eliminate substrate inhibition even in cases when the aldehyde concentration in the organic phase is high (or when the neat substrate is applied without any added organic solvent) [45]. Solubility of inorganic salts in the aqueous phase can be beneficial, too. For example, significant rate increasing effects of various cations were observed in aqueous–organic biphasic hydrogenation of aldehydes with several Ru(II)-mtppts catalysts [25,26]. Finally, mutual solubility of water in the organic phase and vice versa should also be considered.

In case of substrates with very low aqueous solubility a straightforward way to speed up the reaction is the use of co-solvents. Nevertheless, a co-solvent can always increase leaching of the water-soluble catalyst into the organic phase. For example, Monflier et al. investigated the hydrogenation of water-insoluble aldehydes in the presence of various co-solvents (with Ru(II)-*m*tppts catalysts) with beneficial effects on the reaction rate, however, the amount of co-solvents had to be kept below 5% (w/w) of the aqueous phase due to increased leaching [51]. In other cases, the reaction was found faster in the co-solvent alone than in the water-aldehyde-co-solvent mixtures. For example, Paganelli et al. found that hydrogenation of unsaturated aldehydes such as cinnamaldehyde and 3-(1,3-benzodioxol-5-yil)-2-methylpropenal (the saturated aldehyde is the precursor of the fragrance Helional®) was accelerated by addition of ethylene glycol to the mixture of the aldehyde and water [20]. Furthermore, the highest rate was observed by running the reaction in ethylene glycol (in what the Rh(I)-(L)-cysteine or Rh(I)-(S)-captopril were soluble under conditions of the reaction).

Similarly, Ajjou and Pinet investigated transfer hydrogenation of aldehydes (and ketones) in water/2-propanol 10/3 (v/v) mixtures with Na_2CO_3 as base and $[\{RhCl(COD)\}_2] + 15\ m\text{tppts}$ catalyst. High conversions were obtained in 2 h at 80 °C (e.g. benzaldehyde 98%, 2-thiophenecarboxaldehyde 72%) [11]. Obviously, in this system 2-propanol had the dual role of H-donor and cosolvent. Under the applied conditions, the reaction mixtures were homogeneous and the product was isolated by extraction with diethyl ether. No unsaturated aldehydes were studied therefore no data are available from this work on the selectivity of the catalyst in basic aqueous 2-propanol.

In our earlier investigations, we have already used HCOONa as base in transfer hydrogenation of unsaturated aldehydes and ketones from 2-propanol catalyzed by chiral Rh(I)-, Ru(II) and Ir(I)-aminoacidate complexes [52,53]. It was established that presence of water in the H-donor solvent up to 4% (v/v) was neither beneficial nor detrimental on the reaction rate and selectivity. Based on our experience in aqueous–organic transfer hydrogenation of aldehydes catalyzed by $[\{RuCl_2(m\text{tppms})_2\}_2] + n\ m\text{tppms}$ we initiated a study of transfer hydrogenation of aldehydes from aq. HCOONa in water–2-propanol mixtures. A particularly interesting question was whether both formate and 2-propanol act as H-donors and whether the water/2-propanol ratio effects the selectivity in the case of unsaturated aldehydes. These investigations led to the discovery of an exceedingly fast transfer hydrogenation of aldehydes under mild condition as described in the following.

2. Experimental

Aldehydes (Aldrich) and other reagents and solvents were commercially available and used as received. The water-soluble phosphine ligand *m*tppms [31] and $[\{RuCl_2(m\text{tppms})_2\}_2]$ [31] were prepared by published procedures.

All reactions and manipulations were carried out under argon atmosphere. Reaction mixtures were analyzed by gas chromatography (HP5890 Series II; Chrompack WCOT Fused Silica 30 m × 32 mm CP WAX52CB; FID; carrier gas: argon). The products