

# An unusual enhancement of catalytic activity in biphasic catalysis: The rhodium catalyzed hydroformylation of acrylic esters

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Received 13 February 1997; accepted 9 June 1997

## Abstract

The hydroformylation of various acrylic esters in a two-phase system using a water soluble rhodium complex of trisulfonated triphenylphosphine as catalyst was investigated. The hydroformylation rates of acrylates relatively soluble in water are surprisingly higher in a biphasic system than those observed in a homogenous single-phase system; rate enhancement by a factor of 2–14 can be reached. The role of water on the enhancement of catalytic activity is discussed. © 1998 Elsevier Science B.V.

*Keywords:* Acrylate; Hydroformylation; Biphasic system; Rhodium; Water-soluble phosphine

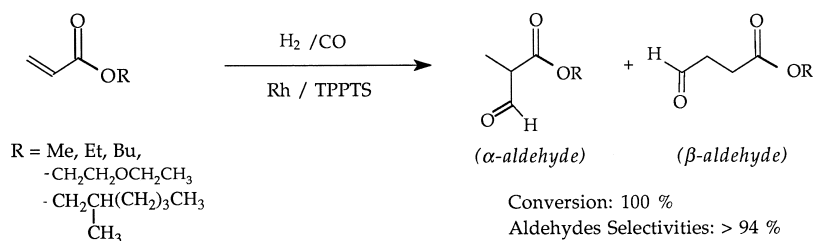
## 1. Introduction

Since the discovery of the water-soluble ligand tris(sodium-*m*-sulfonatophenyl) phosphine (TPPTS), catalysis in a aqueous–organic two-phase system has emerged as an important method for achieving easier separation of homogeneous metal catalysts [1,2]. By using this

concept, numerous reactions such as hydroformylation [3,4], hydrogenation [5–9], carbonylation [10–13], oligomerization [14] and carbon–carbon coupling [15–17] have been carried out successfully. A biphasic literature survey shows that the immobilization of the catalyst in an aqueous solvent affects generally the regio, the stereoselectivity and the rate of the reaction. So, except the hydroxycarbonylation of allylic chloride [18], catalytic activities of biphasic systems are identical or lower than analogous reactions in the homogeneous phase due to slow mass transfer between aqueous and organic phases [1,2].

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Scheme 1. Hydroformylation of various acrylates in biphasic medium.

In our ongoing work on the rhodium-catalyzed hydroformylation of methyl acrylate into methyl 2-formylpropanoate [19,20], we have investigated the hydroformylation of various acrylic esters in biphasic medium. In this paper, we report that the hydroformylation rates of acrylic esters having high solubility in water are in a biphasic system much higher than those observed under comparable homogeneous conditions (Scheme 1).

## 2. Experimental

Acrylic esters and rhodium(I) dicarbonylacetylacetonate ( $\text{Rh}(\text{acac})(\text{CO})_2$ ) were purchased in their highest purity available from Aldrich Chemical and were used as received without further purification. Trisodium tris(*m*-sulfonatophenyl) phosphine (TPPTS) was synthesized as reported by Gärtner et al. [21]. The purity of TPPTS was carefully controlled. In particular,  $^{31}\text{P}$  solution NMR indicated that the product was a mixture of TPPTS (ca. 98%) and oxide of TPPTS (ca. 2%).

Preparations of the reaction mixtures were carried out as following: (i) *homogeneous systems*: under a nitrogen atmosphere, the rhodium precursor  $\text{Rh}(\text{acac})(\text{CO})_2$  (0.2 mmol), triphenylphosphine (TPP, 2 mmol) and substrate (100 mmol) were dissolved in 40 ml of toluene. (ii) *biphasic systems*:  $\text{Rh}(\text{acac})(\text{CO})_2$  (0.2 mmol) and TPPTS (2 mmol) were stirred in 30 ml of

water until total dissolution, and then 100 mmol of substrate were added in 40 ml of toluene.

A 100 ml stainless steel autoclave was charged under a nitrogen atmosphere with the reaction mixture, then heated at 50°C, and pressurized with 50 atm of  $\text{CO}/\text{H}_2$  (1:1). Mechanical stirring (1000 rpm) was then started. The pressure was kept constant throughout the whole reaction by using a gas reservoir along with a pressure regulator. The reaction was monitored by quantitative gas chromatographic analyses. Products were identified by comparison of GLC retention times and spectral characteristics with authentic samples.

## 3. Results

Catalytic activities for the hydroformylation of methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), 2-ethoxyethyl acrylate (EEA) and 2-ethylhexyl acrylate (EHA) were determined under standard reaction conditions (50°C, 50 bar  $\text{CO}/\text{H}_2$ : 1/1) for both homogeneous ( $\text{Rh}/\text{TPP}$ , toluene) and biphasic ( $\text{Rh}/\text{TPPTS}$ , toluene water) systems. Initial and average catalytic activities, i.e. mol of substrate transformed per mol of catalyst per minute at 10–20% conversion for initial activity and over the whole reaction time for average activity, are presented in Fig. 1.

Under homogeneous conditions, hydroformylation rates appeared to be rather slightly af-

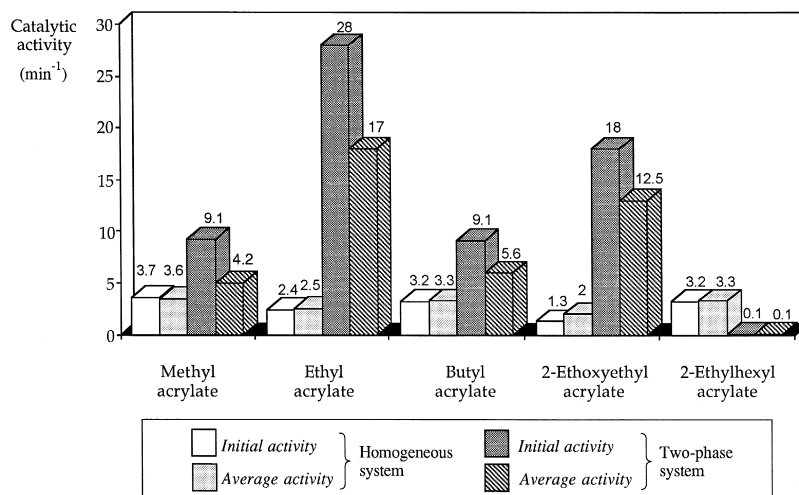


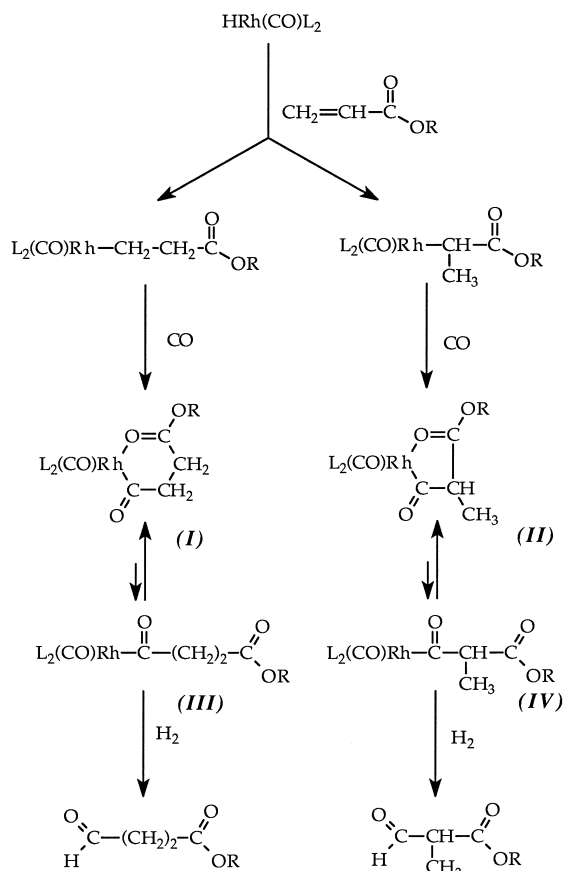
Fig. 1. Initial and average activities for the hydroformylation of various acrylates in homogeneous and biphasic systems.

affected by the nature of the substrate as all acrylates were hydroformylated with a moderate initial activity of ca. 2–3 min<sup>-1</sup>. The results obtained in biphasic medium are quite surprising. Indeed, except 2-ethylhexyl acrylate, the catalytic activities were higher than those observed in the homogeneous single-phase system. As a matter of fact, the initial rate was increased by a factor of 2.4, 12, 2.8 and 14 for methyl, ethyl, butyl and 2-ethoxyethyl acrylate, respectively. Although the enhancement of activity was less marked, a similar trend was found considering the average hydroformylation rate<sup>2</sup>. Indeed, the latter was increased by a factor of 1.5, 7.2, 1.7 and 10 for methyl, ethyl, butyl and 2-ethoxyethyl acrylate, respectively. The catalytic activity for 2-ethylhexyl acrylate dropped from 3.3 min<sup>-1</sup> in the homogeneous system to 0.1 min<sup>-1</sup> in the two-phase system. Such a decrease in activity can be attributed most probably to low mass transfer between aqueous and organic phases, due to the very poor solubility

of this acrylate in water (0.1 g/l at 20°C) [22–24]. One of the most intriguing features is that the hydroformylation rates for ethyl and butyl acrylate in the biphasic medium were respectively higher or comparable to those observed with methyl acrylate. Actually, the water solubilities of ethyl and butyl acrylate (18.3 and 2.0 g/l at 20°C, respectively [25]) are lower than that of methyl acrylate (59.3 g/l at 20°C).

From an aldehyde selectivity point of view, the biphasic system Rh/TPPTS proved to be slightly better than the homogeneous system Rh/TPP: 96.6 versus 95.4% for MA, 96.6 versus 93.5% for EA, 98.2 versus 95.6% for BA, 94.0 versus 86.5% for EEA and 97.1 versus 93.4% for EHA. The only side-product observed in both cases was the hydrogenated acrylate. Acrylate polymerization or formation of adducts between acrylate and phosphine [26,27] were not observed in our experimental conditions. Regioselectivity of both homogeneous and biphasic systems was almost exclusively directed towards the formation of the branched aldehyde, as expected from this type of functionalized olefin [28–32]. Only, slight variations of the branched to linear aldehydes ratio were observed in going from the homogeneous to the biphasic system (128 versus 160 for

<sup>2</sup> Noteworthy, in contrast with the homogeneous system which exhibited an apparent zero-order with respect to the substrate, a decrease of the catalytic activity was observed in the course of biphasic reactions, thus indicating a non-zero order under such conditions.



Scheme 2. Proposed catalytic cycle for the acrylate hydroformylation in homogeneous medium.

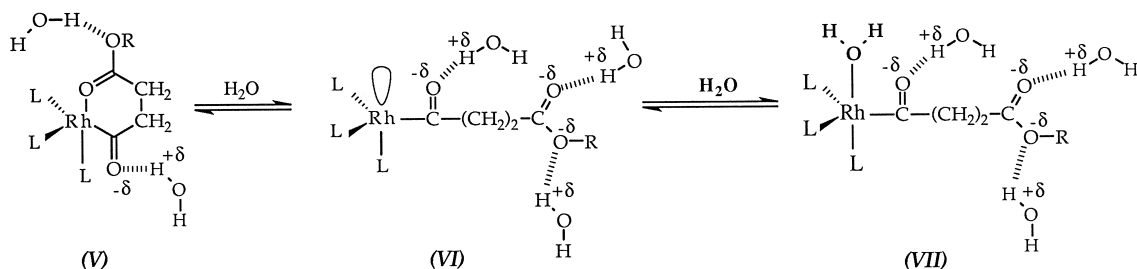
MA, 121 versus 137 for EA, 123 versus 140 for BA, 72 versus 62 for EEA and 59 versus 63 for EHA).

#### 4. Discussion

As the hydrophobic complex  $\text{HRh}(\text{CO})(\text{TPP})_3$  and the water-soluble complex  $\text{HRh}(\text{CO})(\text{TPPTS})_3$  generally exhibit a similar behavior in hydroformylation reactions [1,2], we think that the peculiar enhancement of the catalytic activity in biphasic medium for the acrylates hydroformylation is brought about by the protic, polar aqueous solvent and not by the sulfonation of the TPP ligand.

The key intermediates generally accepted for the mechanism of acrylates hydroformylation in homogeneous medium are acyl–rhodium complexes (I) and (II) depicted in Scheme 2 [33].

These complexes are formed by insertion of acrylate into the rhodium–hydride bond of the complex  $\text{HRh}(\text{CO})(\text{PR}_3)_2$ , followed by carbon monoxide insertion into the alkyl–rhodium bond. In complexes (I) and (II), carbonyl group coordination allows the formation of thermodynamically stable six- and five-membered rings. It is assumed that these coordinatively saturated complexes are not reactive toward dihydrogen and that such oxidative addition requires the transformation of chelated rhodium complexes (I) and (II) into coordinatively unsaturated complexes (III) and (IV), which are thermodynamically unstable active catalytic species [33]. So, numerous authors have proposed that the most probable rate determining step for the hydroformylation of acrylates in homogeneous



Scheme 3. Possible interactions between water and catalytic species in biphasic medium.

medium is the dissociation of the carbonyl group from rhodium complexes. This hypothesis is consistent with the apparent zero order we observed for kinetics of acrylates hydroformylation under homogeneous conditions.

Considering the equilibrium between chelated and non-chelated rhodium species, the difference in the reactivity observed in aqueous and organic medium can be reasonably explained. Indeed, in water, it is expected that the acyl group of water-soluble complexes analogues of complexes (III) and (IV) will hydrogen bond to water as presented in Scheme 3.

In such a hypothesis, it is assumed that water fills the vacant coordination site of complex (VI) and that hydrogen bondings stabilize non-chelated rhodium species (VI) and (VII). Consequently, we think that, in water, the equilibrium between chelated and non-chelated rhodium complexes is shifted towards the non-chelated species, that obviously makes oxidative addition of hydrogen easier. Unfortunately, we did not succeed in obtaining spectroscopic evidence for the presence of the hydrosoluble complexes (V), (VI) and (VII). Indeed,  $^{31}\text{P}$  NMR spectra of catalytic solutions sampled in the reaction course (10–100% conversion) showed only the presence of  $\text{HRh}(\text{CO})(\text{TPPTS})_3$  ( $\delta$ : 43 ppm, d,  $J_{(\text{Rh}-\text{P})} = 156$  Hz [34]) as the resting state. This observation and the change in kinetics in going from homogeneous (apparent zero-order) to biphasic system (non-zero order) is consistent with the appearance of another rate determining step in place of the dissociation of carbonyl group from rhodium species (most probably substrate transfer into the aqueous phase as hydroformylation rates can be significantly improved by using supported aqueous phase catalysts [35] or inverse phase transfer catalysts like dimethyl- $\beta$ -cyclodextrin [22,23]).

A literature survey shows that enhancement of catalytic activities by use of polar and coordinating solvents is a well-known phenomenon in homogeneous catalysis [24]. An interesting example which is consistent with our hypothesis is the beneficial effect of polar and coordinating

solvents like dimethylformamide on the hydroformylation rate of vinyl acetate [33,36,37]. In this case, it was assumed that the polar solvents avoid the formation of chelated structures by being coordinated onto rhodium complexes and stabilizing non-chelated species. Finally, it is also worth mentioning that the coordinating ability of water has already been described in the biphasic related literature. For instance, Basset et al. reported that water allows the dissociation of complex  $\text{RuH}_2(\text{TPPTS})_4$  into complex  $\text{RuH}_2(\text{TPPTS})_3(\text{H}_2\text{O})$  [38] and that the decrease of the catalytic activity during the hydrogenation of propionaldehyde was due to the coordination of water on the catalyst [39].

## 5. Conclusion

We have demonstrated that the aqueous–organic biphasic catalysis is an efficient approach to achieve the hydroformylation of acrylates having adequate solubility in water which combines catalyst recovery and high productivity and selectivity. The few examples described in the literature on water-soluble complexes affected by the presence of water [40–42] and this work support, so far, the idea that water must not only be considered as an inert solvent but also as a reactant or a coordinating solvent which can modify elementary steps of the catalytic cycle. Consequently, care should be taken about predictions of catalytic performances under biphasic catalysis.

## Acknowledgements

Financial support from the Centre National de la Recherche Scientifique (C.N.R.S.) and Elf-Atochem company is gratefully acknowledged.

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