



## Hydroformylation of Higher Olefins in Aqueous Biphasic Medium Using Rhodium-Sulfoxantphos Catalyst: Activity and Selectivity Study

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Hydroformylation of higher olefins such as 1-hexene, 1-octene, 1-decene and 1-dodecene has been studied in an aqueous biphasic medium using water-soluble Rh-sulfoxantphos complex catalyst. The effect of temperature, presence of various co-solvents and concentration of co-solvent on the reaction rate and chemo and regioselectivity was investigated. *N*-Methyl pyrrolidone (NMP) was found to be the best co-solvent, which enhances the rate dramatically (4-96 fold) as compared to the reactions in aqueous-organic biphasic medium for hydroformylation of higher olefins. Catalyst recycle study was performed to check the leaching of metal in organic phase.

**Keywords:** Aqueous biphasic, Hydroformylation, Rh-Sulfoxantphos, Co-solvent, Recycle.

### INTRODUCTION

Hydroformylation of olefins is an important commercial process for the production of aldehydes and alcohols for which homogeneous Rh and Co catalysts are widely used in commercial production depending on the olefin types [1,2]. A major drawback of this process is the difficulty in separating the products (being non-volatile) from the catalyst by conventional methods. Therefore, the use of a heterogeneous catalyst would be most desirable way to overcome this limitation. Different attempts were made to heterogenize the homogeneous catalysts to achieve catalytic activity and selectivity similar to the homogeneous ones and also achieve easy catalyst-product separation [3,4]. Two approaches have been mainly used, biphasic catalysis wherein water soluble catalyst is used as an immiscible liquid phase to that of reactants and products and solid state supported or anchored catalysts. The aqueous biphasic catalysis is commercially implemented [5-9], while the heterogenized solid state catalysts have not yet found major commercial applications due to the problem of lower activity, catalyst leaching and deactivation [10,11].

Even though biphasic catalysis is a commercial success for propylene hydroformylation to butyraldehyde [5] (300 000

TPA), the wider application of these catalysts for higher olefins has been limited. One of the major limitations of the aqueous biphasic catalysis is their lower reaction rate for the hydroformylation of higher olefins like hexene, octene, decene, *etc.* due to their poor solubility in the aqueous (catalyst) phase [12]. Attempts to increase the solubility of higher olefins in water (catalyst phase) by incorporation of various additives such as co-solvents [13-19], surfactants [20,21], phase transfer agents [22-26] and promoter ligands [27,28] to the reaction mixture resulted in significant improvements in the rates; however it also led to other issues like lower regio-selectivity, separation of the catalyst, formation of side products, *etc.*

Van Leeween and coworkers [29] have shown that hydroformylation of propylene and hexene using Rh-sulfoxantphos catalyst in aqueous biphasic system gives a high *n/i* ratio of 30-35. However, only attempt made on further improvement of the rates for the hydroformylation of higher olefins like 1-octene and 1-decene was by addition of randomly methylated  $\alpha$ - or  $\beta$ -cyclodextrin (Rame  $\alpha$ - or  $\beta$ -CD) as an inverse phase transfer catalyst [30]. They observed around 60-70% olefin conversion in 24 h (TOF = 15 h<sup>-1</sup>), which is rather poor for practical applications. In this article, we further investigated the effect of co-solvent on aqueous biphasic hydroformylation

of higher olefins to show that with a few combinations of co-solvents and reaction conditions, a significant rate enhancement can be achieved with improved selectivity towards *n*-aldehyde.

## EXPERIMENTAL

Rhodium trichloride ( $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ) (Arora Matthey, India), xantphos (**1**) (4,5-bis(diphenylphosphino)-9,9-dimethyl xanthene), triisooctylamine (Aldrich, USA) were used as received without further purification. Sulphuric acid, acetyl acetate, dimethyl formamide and sodium hydroxide (Loba Chemie, India) were used as received. Oleum of 25% (w/w of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$ ) strength was prepared. The solvents, toluene, *N*-methyl 2-pyrrolidone (NMP), ethanol, methanol, 1,4-dioxane and methyl ethyl ketone (MEK) were freshly distilled and degassed prior to use. Distilled degassed water was used in all operations. Carbon monoxide (> 99.8 % pure) from Matheson Gas Co., U.S.A. and hydrogen and nitrogen supplied by Indian Oxygen Ltd. Mumbai, were used directly from cylinders. The syn gas with 1:1 ratio of  $\text{H}_2$ :CO was prepared by mixing  $\text{H}_2$  and CO in a reservoir. All operations were performed under argon atmosphere.  $\text{Rh}(\text{CO})_2(\text{acac})$  was prepared according to reported procedure [31]. Sulfoxantphos (2,7-bis( $\text{SO}_3\text{Na}$ )-xantphos) (**2**) was synthesized by the procedure described by van Leeuwen *et al.* [29] (Scheme-I). The purity of the ligand was checked by  $^{31}\text{P}$  NMR (Fig. 1) and elemental analysis, which was consistent with the literature. [ $^{31}\text{P}$  { $^1\text{H}$ } NMR ( $\text{CD}_3\text{OD}$ ; ppm):  $\delta$  14.69. Elemental analysis calcd. (found) %: C 59.8 (58.8); H 3.9 (4.2); S 8.1 (8.2).

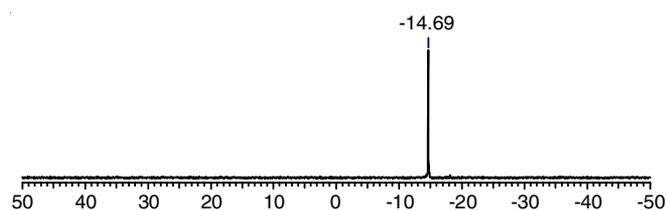


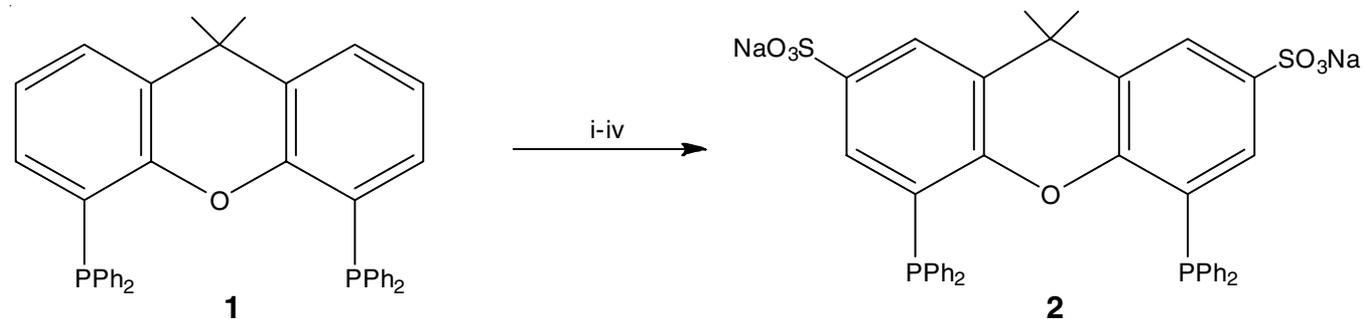
Fig. 1:  $^{31}\text{P}$  NMR spectrum of sulfoxantphos ligand

**Procedure:** All the hydroformylation experiments were carried out in a 50 mL ( $50 \times 10^{-5} \text{ m}^3$ ) micro reactor, made of stainless steel (maximum pressure capacity of 20.7 MPa at 548 K), supplied by Amar Instruments India Pvt. Ltd. The reactor is fitted with provisions for sampling of liquid and gaseous

contents, automated temperature control and variable agitation speed. The reactor was designed for a working pressure of 20.4 MPa and temperature up to 523 K. Consumption of CO and  $\text{H}_2$  at a constant pressure was controlled as a function of time by measuring the decrease in pressure in the gas reservoir. A schematic diagram of the experimental setup is identical to that of reported earlier [32].

In a typical experiment, sulfoxantphos and  $\text{Rh}(\text{CO})_2(\text{acac})$  were mixed in the desired ratio, in 10 mL degassed water under argon atmosphere. The resulting yellowish solution was transferred to the autoclave. The autoclave was then flushed three times with nitrogen and syngas, respectively. The autoclave was pressurized to 1.38 MPa with CO/ $\text{H}_2$  and heated to 393 K. The solution was stirred for 12 h at 393 K, then cooled to 25 °C and depressurized. Then the reactor was charged with the olefin and toluene ( $15 \times 10^{-6} \text{ m}^3$ ), which comprises the organic phase for the reaction. In the experimental work, co-solvent was added before the addition of organic phase. The contents were flushed with nitrogen and then with a mixture of CO and  $\text{H}_2$ . The autoclave was heated to reach the necessary temperature, then a mixture of CO and  $\text{H}_2$  (in an appropriate ratio, 1:1) was introduced into the autoclave to the desired pressure (4.14 MPa). A sample of the liquid mixture was withdrawn and the reaction began by switching the stirrer on. The reaction was then continued by supply of syngas from the reservoir vessel through a constant pressure regulator at a constant pressure of CO +  $\text{H}_2$  (1:1). Since the major product produced in this study was an aldehyde, the supply of CO +  $\text{H}_2$  at a ratio of 1:1 (as per stoichiometry) was sufficient to maintain a constant composition of  $\text{H}_2$  and CO in the reactor as initially introduced. The reactor was cooled after completion of the reaction and the final sample was taken for analysis. The aqueous phase was found to contain negligible quantity of the reactant and products.

**Analytical methods:** The reaction products were identified using GC-MS, (Agilent GC 6890N with 5973 mass selective detector instrument). Rhodium leaching analysis to the organic phase was analyzed using inductively coupled plasma with atomic emission spectra (ICP-AES), Perkin-Elmer 1200 instrument. The quantitative analysis of the reactant and hydroformylation products was performed using a gas chromatographic technique using external standard method. For this reason, a HP-5 capillary column (30 M  $\times$  320  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$  film thickness with a stationary phase of 5% diphenyl 95% dimethyl polysiloxane) fitted to HP 6890 gas chromatograph operated



**Scheme-I:** Synthesis of sulfonated xantphos (sulfoxantphos); **Reagents and conditions:** (i) 25%  $\text{SO}_3/\text{H}_2\text{SO}_4$ , 5 °C to room temperature; (ii) triisooctylamine, toluene; (iii) NaOH; (iv) neutralization, MeOH-extraction, EtOH

by the HP Chemstation program and equipped with an automatic sampler device was used.

## RESULTS AND DISCUSSION

**Hydroformylation of higher olefins using biphasic Rh-sulfoxantphos catalyst:** Hydroformylation of 1-hexene, 1-octene, 1-decene and 1-dodecene using  $\text{Rh}(\text{CO})_2(\text{acac})/\text{sulfoxantphos}$  catalyst in toluene-water biphasic system was studied at 393 K (Table-1). Under identical conditions the olefin conversion and activity was found to decrease drastically with increasing chain length of the olefin. This observation is expected as a result of the poor solubility of the substrates in the aqueous phase [33,34]. Besides, it is also known that hydroformylation activity decreases with increasing chain length even with homogeneous rhodium complex catalysts [35,36]. The major products formed were the corresponding linear aldehydes. The influence of bidentate phosphines on the regioselectivity in the Rh-catalyzed hydroformylation of olefins has been reported earlier [35-38]. A little amount of corresponding 2-methyl substituted aldehyde and isomerized olefin (1-5%) were also observed. No other aldehyde products were formed due hydroformylation of the isomerized olefin. An interesting observation was the increase in the  $n/i$  ratio with increase in chain length of olefin, which is similar to that reported for Rh-TPPTS system [34].

**Effect of co-solvent:** The addition of a co-solvent to the biphasic system improves the solubility of the higher olefins in the aqueous phase, while retaining the biphasic nature of the system [13-19,39-41]. In present study, the role of several co-solvents such as ethanol, 1,4-dioxane, methyl ethyl ketone and *N*-methyl 2-pyrrolidone was investigated for the hydroformylation of 1-decene (Scheme-II) and the results are shown in Fig. 2. Several fold rate enhancement was observed in the presence of these co-solvents. The rates were improved marginally in 1,4-dioxane and MEK, whereas significant enhancement of rates were observed when ethanol (13 times) and NMP (38 times) were used as co-solvents. The highest activity without any side products formation was observed using NMP as the

co-solvent. One more interesting observation was that the selectivity to undecanal was also improved in all the co-solvents as compared to reactions in their absence ( $n/i$  increased from 31.2 to 40.3 using ethanol as a co-solvent). The results in Fig. 2 indicate that NMP is a better co-solvent (rate enhancement 38 times) as compared to ethanol (13 times) for the hydroformylation of 1-decene. The products formed were undecanal and 2-methyldecenal along with a little amount of isomerized (2-decene and 3-decene)decene (1.5%). The ICP analysis showed negligible leaching (0.056 ppm) of rhodium metal to the organic phase. Further study was carried out using NMP as a co-solvent, which gave highest rate enhancement (38 times) and also retained the catalyst in the aqueous phase with negligible leaching of rhodium to the organic phase.

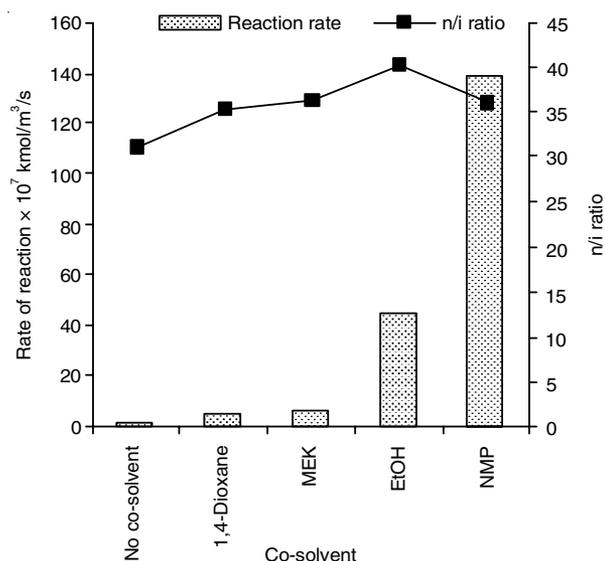
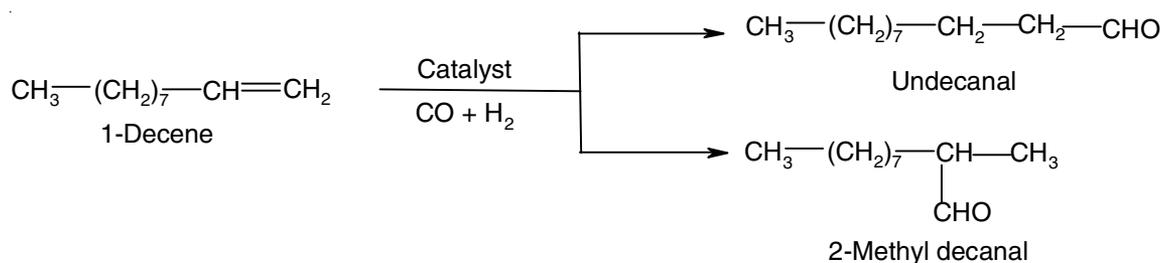


Fig. 2. Effect of co-solvent on rate and  $n/i$  ratio in aqueous biphasic hydroformylation of 1-decene; **Reaction conditions:** 1-decene:  $1.07 \text{ kmol/m}^3_{(\text{org})}$ ,  $[\text{Rh}(\text{CO})_2(\text{acac})]$ :  $3.85 \times 10^{-3} \text{ kmol/m}^3_{(\text{aq})}$ , sulfoxant-phos:  $1.93 \times 10^{-2} \text{ kmol/m}^3_{(\text{aq})}$  (Rh:L = 1:5), T: 393 K,  $P_{\text{CO}+\text{H}_2}$ : 4.14 MPa, agitation speed: 20 Hz, solvent: toluene-water-co-solvent, time: 8 h, total volume:  $2.5 \times 10^{-5} \text{ m}^3$

TABLE-1  
HYDROFORMYLATION OF HIGHER OLEFINS IN AQUEOUS BIPHASIC SYSTEM USING Rh-SULFOXANTPHOS CATALYST

Olefin	Conversion (%)	Aldehyde selectivity (%)	Isomerized olefin (%)	$n/i$	TOF ( $\text{h}^{-1}$ )
1-Hexene	55.3	95.5	4.5	27.8	13.7
1-Octene	13.4	98.1	1.9	28.3	2.8
1-Decene	7.5	98.2	1.8	31.2	0.8
1-Dodecene	2.9	98.4	1.6	34.8	0.2

**Reaction conditions:** Olefin:  $1.07 \text{ kmol/m}^3_{(\text{org})}$ ,  $[\text{Rh}(\text{CO})_2(\text{acac})]$ :  $3.85 \times 10^{-3} \text{ kmol/m}^3_{(\text{aq})}$ , Sulfoxantphos:  $1.93 \times 10^{-2} \text{ kmol/m}^3_{(\text{aq})}$  (Rh:L = 1:5), T: 393 K,  $P_{\text{CO}+\text{H}_2}$ : 4.14 MPa, agitation speed: 20 Hz, solvent: toluene and water  $\epsilon = 0.4$ , time: 24 h, total volume:  $2.5 \times 10^{-5} \text{ m}^3$



Scheme-II: Hydroformylation of 1-decene

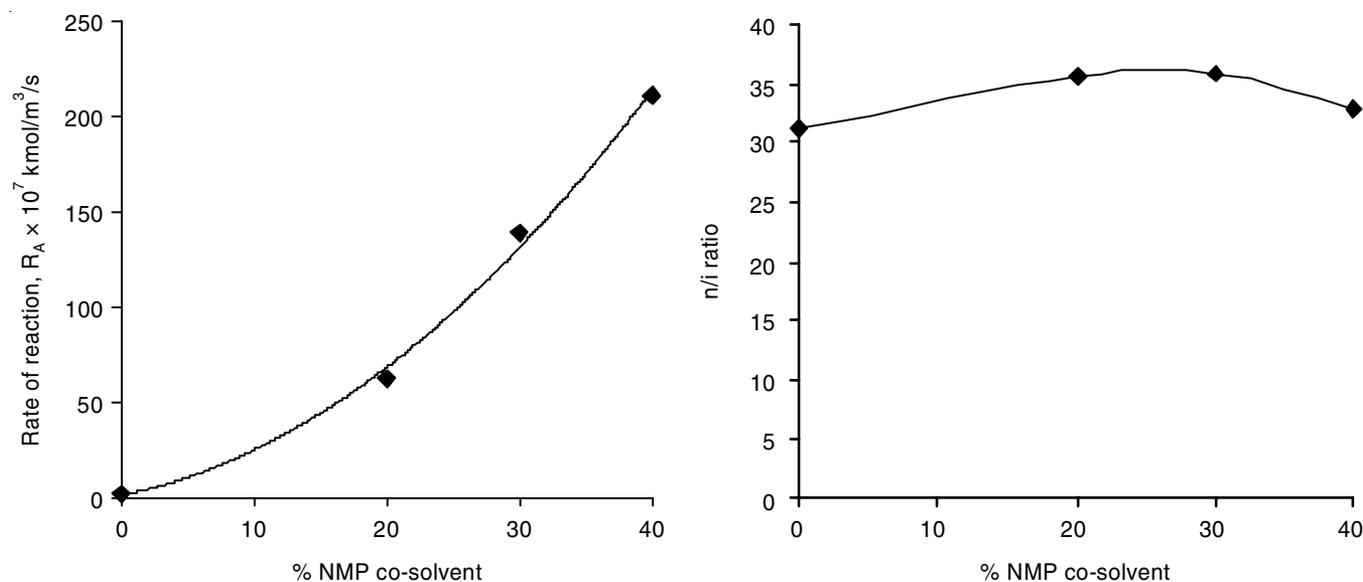


Fig. 3. Effect of % NMP co-solvent on rate and  $n/i$  ratio in aqueous biphasic hydroformylation of 1-decene; **Reaction conditions:** 1-decene:  $1.07 \text{ kmol/m}^3_{(\text{org.})}$ ,  $[\text{Rh}(\text{CO})_2(\text{acac})]$ :  $3.85 \times 10^{-3} \text{ kmol/m}^3_{(\text{aq.})}$ , sulfoxantphos:  $1.93 \times 10^{-2} \text{ kmol/m}^3_{(\text{aq.})}$  (Rh:L = 1:5), T: 393 K,  $P_{\text{CO}+\text{H}_2}$ : 4.14 MPa, agitation speed: 20 Hz, solvent: toluene ( $1.2 \times 10^{-5} \text{ m}^3$ ) water ( $0.7 \times 10^{-5} \text{ m}^3$ ) and NMP ( $0.3 \times 10^{-5} \text{ m}^3$ ), time: 8 h, total volume:  $2.5 \times 10^{-5} \text{ m}^3$

**Effect of NMP concentration:** To achieve the optimum ratio of the water to co-solvent, the effect of NMP content (0-40% (v/v) as a co-solvent) in the aqueous medium was studied for the hydroformylation of 1-decene using  $\text{Rh}(\text{CO})_2(\text{acac})/\text{sulfoxantphos}$  catalyst in the water-toluene biphasic medium at 393 K. The rate was found to vary linearly with increasing NMP content in the aqueous phase (Fig. 3). The maximum rates were observed at a water-NMP composition of 60:40 but the  $n/i$  ratio was found to reduce from 35.9 to 32.7. Therefore, the optimum ratio of water-NMP of 70:30 was chosen for further studies in order to maintain the advantage of high regioselectivity for the linear aldehyde, and high activity.

**Recycle study and rhodium leaching analysis:** The activity of  $\text{Rh}(\text{CO})_2(\text{acac})/\text{sulfoxantphos}$  catalyst on recycle was investigated in the presence of NMP co-solvent (30% v/v aqueous phase) at 393 K. The recycle experiments were performed by separating the aqueous catalyst phase from the organic phase at the end of reaction followed by addition of fresh organic phase along with 1-decene to the used aqueous catalyst phase. The NMP content in both the phases was analyzed and made up as required with addition of fresh NMP to the aqueous phase. The results are presented in Fig. 4. The aqueous catalytic phase was recycled for four times without a drop in activity. The selectivity to  $n$ -aldehyde was also retained on recycle. An interesting observation was the improvement in the activity for the first recycle over the virgin reaction. The enhancement of activity compared to the virgin reaction is due to the fact that the preformed active catalytic species is available for reaction on recycle. This enhanced activity then remained constant for all the subsequent recycles. The ICP analysis of the organic phase from each recycle showed negligible leaching (0.06, 0.03, 0.05, 0.08, 0.04 ppm, respectively) of rhodium to the organic phase. The recycle of organic phase with addition of fresh 1-decene showed no hydroformylation activity, which further confirmed

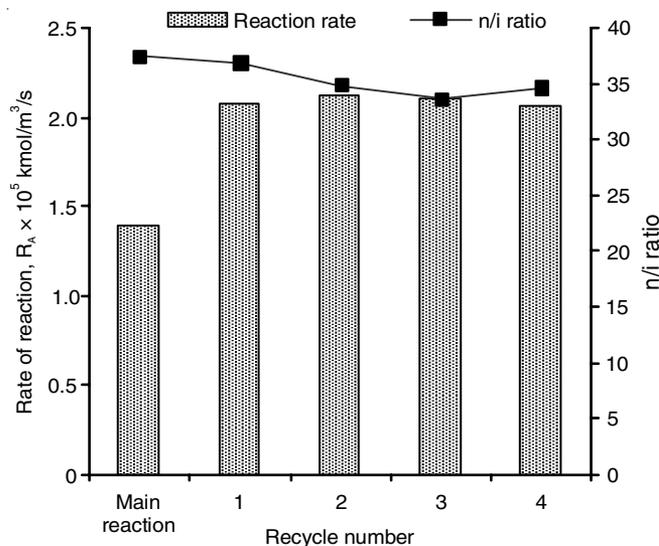


Fig. 4. Effect of catalyst phase recycles study on reaction rate and  $n/i$  ratio; **Reaction conditions:** 1-decene:  $1.07 \text{ kmol/m}^3_{(\text{org.})}$ ,  $[\text{Rh}(\text{CO})_2(\text{acac})]$ :  $3.85 \times 10^{-3} \text{ kmol/m}^3_{(\text{aq.})}$ , sulfoxantphos:  $1.93 \times 10^{-2} \text{ kmol/m}^3_{(\text{aq.})}$  (Rh:L = 1:5), T: 393 K,  $P_{\text{CO}+\text{H}_2}$ : 4.14 MPa, agitation speed: 20 Hz, solvent: toluene ( $1.2 \times 10^{-5} \text{ m}^3$ ), water ( $0.7 \times 10^{-5} \text{ m}^3$ ) and NMP ( $0.3 \times 10^{-5} \text{ m}^3$ ) time: 8 h, total volume:  $2.5 \times 10^{-5} \text{ m}^3$

that rhodium leaching was negligible and that activity observed was solely due to the aqueous phase catalyst.

**Effect of temperature:** The effect of temperature on hydroformylation of 1-decene has been investigated in a temperature range of 383-403K at  $[\text{Rh}(\text{CO})_2(\text{acac})]$ :  $2.89 \times 10^{-3} \text{ kmol/m}^3_{(\text{aq.})}$ , sulfoxantphos:  $1.44 \times 10^{-2} \text{ kmol/m}^3_{(\text{aq.})}$ , 1-decene:  $1.07 \text{ kmol/m}^3_{(\text{org.})}$  and  $P_{\text{CO}+\text{H}_2} = 4.14 \text{ MPa}$ . The results are shown in Fig. 5. The rate varies linearly with temperature at the same time aldehyde selectivity was also retained (> 97%). The  $n/i$  ratio decreased marginally from 37.5 to 31.3 with increase in temperature due to the increase in the formation of 2-methyl

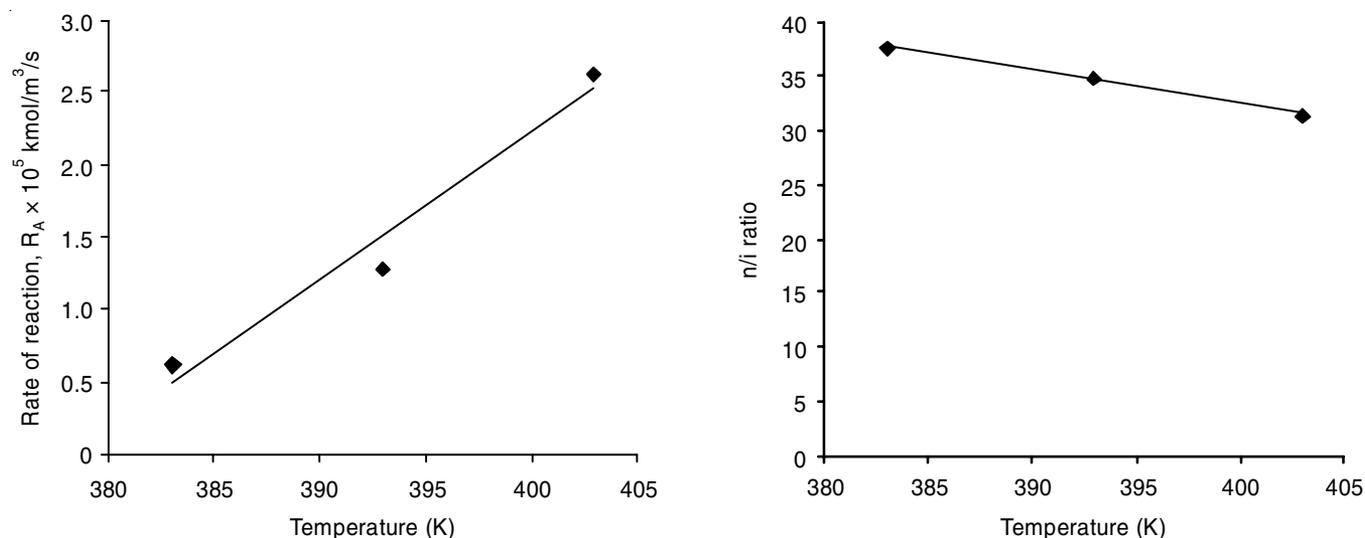


Fig. 5. Effect of reaction temperature on rate and n/i ratio in the biphasic hydroformylation of 1-decene; **Reaction conditions:** 1-decene: 1.07 kmol/m<sup>3</sup><sub>(org.)</sub>, [Rh(CO)<sub>2</sub>(acac)]: 2.89 × 10<sup>-3</sup> kmol/m<sup>3</sup><sub>(aq.)</sub>, sulfoxantphos: 1.44 × 10<sup>-2</sup> kmol/m<sup>3</sup><sub>(aq.)</sub> (Rh:L=1:5), T: 383-403 K, P<sub>CO+H<sub>2</sub></sub>: 4.14 MPa, total volume: 2.5 × 10<sup>-5</sup> m<sup>3</sup>, agitation speed: 20 Hz, solvent: toluene: water: NMP

decanal at higher temperatures. It has been reported in the literature [42-44] that in case of the some chelating (*e.g.* BISBI) ligand, aldehyde selectivity decreases drastically as the temperature increases. This is attributed due to the flexibility of BISBI backbone, which may result in monodentate binding of ligand by opening of chelate ring at elevated temperatures. But the rigidity of the xantphos structure (originating from the rigid xanthene backbone) results in stable chelated complex. It does not allow monodentate binding to the metal center in the reaction cycle and maintains its bidentate nature even at higher temperature [42,43] and hence only a marginal drop in n/i ratio was observed.

**Hydroformylation of higher olefins in the presence of NMP co-solvent:** An influence of NMP co-solvent was studied

on the hydroformylation of different higher olefin substrates using Rh-sulfoxantphos catalyst in aqueous biphasic medium. The results in Fig. 6 show a several fold enhancement in the rates for all the higher olefins studied. The rate improvement for 1-hexene (4-fold), 1-octene (15-fold), 1-decene (38-fold) and 1-dodecene (96-fold) shows that the magnitude of rate enhancement is higher for the higher olefins like 1-decene and dodecene where the development of biphasic catalysis always remains a challenge. The presence of NMP enhances the solubility of olefins in the aqueous phase leading to enhancement of rate. Compared to the reaction in aqueous biphasic medium, in absence of co-solvent, the n/i ratio also improved [for 1-hexene (26 to 32.4), 1-octene (28.2 to 35.6), 1-decene (31.2 to 35.9) and 1-dodecene (32 to 36.8)]

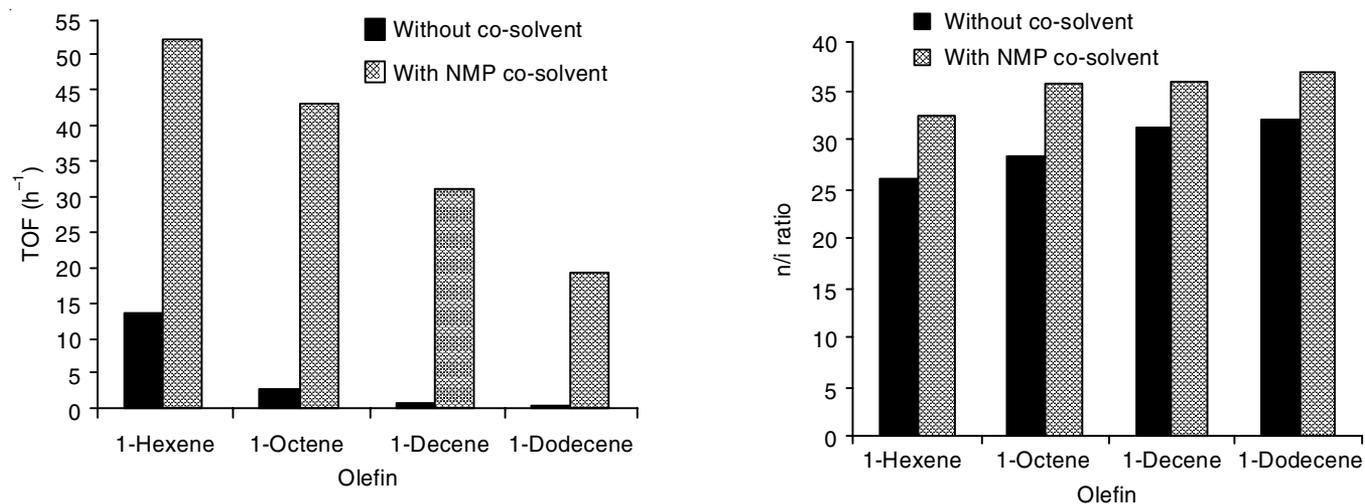


Fig. 6. Comparison of rates and n/i ratio on hydroformylation of higher olefins in biphasic reaction with and without co-solvent; **Reaction conditions:** olefin: 1.07 kmol/m<sup>3</sup><sub>(org.)</sub>, [Rh(CO)<sub>2</sub>(acac)]: 3.85 × 10<sup>-3</sup> kmol/m<sup>3</sup><sub>(aq.)</sub>, sulfoxantphos: 1.93 × 10<sup>-2</sup> kmol/m<sup>3</sup><sub>(aq.)</sub> (Rh:L=1:5), T: 393 K, P<sub>CO+H<sub>2</sub></sub>: 4.14 MPa, agitation speed: 20 Hz, solvent: toluene (1.2 × 10<sup>-5</sup> m<sup>3</sup>), water (0.7 × 10<sup>-5</sup> m<sup>3</sup>) and NMP (0.3 × 10<sup>-5</sup> m<sup>3</sup>), time: 8 h, total volume: 2.5 × 10<sup>-5</sup> m<sup>3</sup>

## Conclusion

Hydroformylation of higher olefins using rhodium-sulfoxanthphos water soluble catalyst in a aqueous biphasic medium has been studied to show that NMP as a co-solvent increases the rates significantly. Importantly the high regioselectivity towards linear aldehydes was retained with this unique complex catalyst. The rate enhancement is more prominent for 1-decene and 1-dodecene hydroformylation. The water:NMP ratio of 7:3 was found to be the optimum ratio to ensure high activity. ICP analysis showed negligible leaching of rhodium to organic phase indicates the true biphasic nature of the reactions. The aqueous catalyst phase was recycled several times with an interesting observation of increased activity during first recycle.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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