

Biphasic hydroformylation of olefins using a novel water soluble rhodium polyethylene glycolate catalyst

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Dedicated to Professor D. Walther on the occasion of his 60th birthday

Abstract

The highly reactive water-soluble hydroformylation catalyst, rhodium polyethylene glycolate ($\text{Rh}(\text{PEG})_x$), prepared by the reaction of polyethylene glycol and rhodium trichloride hydrate, was used as a catalyst for hydroformylation reactions of olefins, such as dodec-1-ene, 2,4,4-trimethylpent-1-ene and styrene, in biphasic systems. The reactions were done in a broad temperature range and at a pressure range from 7 to 12 MPa. Turnover frequency for the catalytic reaction of the low reactive 2,4,4-trimethylpent-1-ene is 450 (mol aldehyde/mol $\text{Rh} \times \text{h}$), which is 3 times higher than in comparable homogeneous rhodium systems. The selectivity for aldehydes is excellent (> 98%). The dependence of the conversion vs. time was monitored for different partial pressures, pH values, temperatures and catalyst concentrations. Activation parameters have been calculated for the hydroformylation of the olefins in water and polyethylene glycol with rhodium polyethylene glycolate as a precatalyst. The activation energy in water is calculated for the hydroformylation of various olefins (dodec-1-ene E_a 95 kJ/mol, 2,4,4-trimethylpent-1-ene E_a 30 kJ/mol and styrene E_a 34.1 kJ/mol). The hydroformylation reaction with rhodium polyethylene glycolate as a precatalyst is first-order for dodec-1-ene and 2,4,4-trimethylpent-1-ene and zero-order for styrene. © 2000 Elsevier Science B.V. All rights reserved.

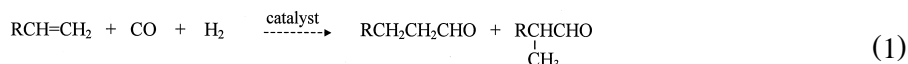
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The synthesis of products by means of catalytic procedures plays an important role in the chemical industry. But the demand for economically and environmentally friendly systems is growing rapidly. Due to the use of highly sophisticated and therefore expensive catalysts, the recovery of the catalysts is one of the main targets in catalytic science today. Use of standard techniques for recovery of homogeneous catalysts from high boiling hydroformylation products is still an unsolved problem. Two-phase catalysis is one of the most challenging fields in catalytic science. Usually, the catalyst resides and operates in polar phases, which is one of the phases in a two-phase system. Aqueous media are now viewed as excellent means to effect nearly complete catalyst separation and recovery, but the poor ability of water to dissolve most of the organic substrates is of potential limitation.

The hydroformylation of terminal olefins is a well-known industrial process for the large scale preparation of aldehydes involving homogeneous catalytic systems (Eq. 1). The classical Roelen

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process employed cobalt metal as the catalyst and the catalytically active species in this homogeneous process was believed to be $\text{HCo}(\text{CO})_4/\text{HCo}(\text{CO})_3$ [1–3]. However, the major disadvantage in using this so-called first generation catalyst is the remarkably high volatility of the catalyst and the harsh reaction conditions. This leads to the cobalt–phosphine catalysts, which may be considered as the final step in the development of the first generation catalysts. The need for improvements in view of reaction conditions, selectivity and by-product formation shifted the interest to the rather more expensive rhodium based catalysts, which are called the second generation of hydroformylation catalysts.



The latest development in hydroformylation processes is the hydroformylation of short-chain olefins in a biphasic system. This process is well known since many years and has been developed by the Ruhrchemie AG and is now used to produce more than 300,000 t/year of C_4 aldehydes [4]. Modification of the Wilkinson catalyst $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ with the water-soluble ligand TPPTS [tris(3-sulfonatophenyl-phosphine)] leads to a catalytic system for the hydroformylation of propene and butene [5–9]. Activity and selectivity are very high, if the amount of water-soluble ligand is used in large excess (50–1000). Herrmann and coworkers developed a new method for the synthesis of sulfonated phosphines without oxidation of the phosphorus atom in a side reaction [10,11]. With this method, a broad variety of sulfonated phosphines are now accessible and rhodium catalysts with these phosphines show a high activity and selectivity in the hydroformylation of propene. The excess of phosphines conventionally used could be reduced dramatically. However, the activity of the water-soluble catalysts decreases rapidly with increasing chain length of the olefin. Extensive work has been undertaken to overcome these limitations. The use of immiscible phases other than water, such as fluoruous biphasic systems developed by Horváth et al., offers some advantages [12,13]. This system consists of a fluoruous phase containing a dissolved catalyst with partially fluorinated phosphine ligands and a second phase, which may be any organic or inorganic solvent with limited solubility in the fluoruous phase. However, it is not apparent whether the reaction proceeds in the fluoruous phase or at the interface of the two phases. This system has been tested for different catalytic reactions. Hydroformylation of dec-1-ene was reported with good results without leaching of the rhodium species into the product phase. However, for industrial applications, fluoruous phases are much too expensive.

The hydroformylation of long-chained and branched olefins is still a domain of homogeneous cobalt catalysts, though recycling of the cobalt catalyst is achieved by classical methods [14]. Two-phase catalysis would be the key to a new kind of environmentally clean processes for the formation of a broad range of products. An overview of the latest developments in aqueous catalysis and industrial aspects could be found in the literature [4,15–17]. Since higher olefins have nearly no solubility in water the use of additives, such as alcohols [18–22] or tensides [23–25], in the catalytic hydroformylation systems are described. The use of short-chain polyalkyl glycols is also described to prevent precipitation of the rhodium metal prior to formation of the catalyst complex [26]. Activation of the classical Ruhrchemie/Rhône-Poulenc catalyst (made from rhodium acetate and TPPTS under CO/H_2 atmosphere) by polyethylene glycol is possible, so that higher olefins (like dodec-1-ene) could be hydroformylated [27,28]. However, by adding polyethylene glycol to rhodium acetate, the rate for the formation of oxoproducts could be increased only by small amounts (see also Table 2).

The only commercial nonaqueous biphasic process which is known today is the *Shell Higher Olefin Process* (SHOP) developed by Keim et al., which uses butanediol as polar phase [29,30]. Use

of a rhodium-poly(enolate-*co*-vinyl alcohol-*co*-vinyl acetate) was reported by Chen and Alper [31]. This water-soluble rhodium catalyst shows a high activity for the hydroformylation of linear olefins at a low aldehyde selectivity. For the hydroformylation of styrene, the catalyst shows a good regioselectivity (branched/linear) at low conversion. The recently reported use of a PPA/DPPEA (poly(4-pentenoic acid)/bis[2-(diphenylphosphino)ethyl]amine) water soluble rhodium complex for the hydroformylation of aliphatic olefins increases the conversion of the olefins. The aldehyde selectivity for the hydroformylation of dodec-1-ene with this new complex could not be improved and is still in the range of 50% to 60% [32].

Recently, we described for the first time the use of polyethylene glycol as polar phase in a biphasic system for the hydroformylation of hex-1-ene. Use of polyethylene glycol as polar phase required new kinds of metal catalysts. In contrast to the well known water soluble catalyst with phosphine ligands, like TPPTS, we introduced a new cobalt catalyst with σ -bonded polyethylene glycol chains to the catalyst [33–35]. Hydroformylation of hex-1-ene shows a high conversion rate of the olefin, without loss of cobalt catalyst into the organic phase.

In this paper, we report on the hydroformylation of long-chained and branched olefins using a new biphasic rhodium system. The catalytic system consists of a rhodium precursor made from rhodium trichloride hydrate and polyethylene glycol. The resulting rhodium polyethylene glycolate complex ($\text{Rh}(\text{PEG})_x$) has the ability to work in polyethylene glycol or water as a hydroformylation catalyst. The result of these investigations along with kinetic studies on the hydroformylation reaction in two phase systems are reported in this paper.

1. Results and discussion

1.1. Synthesis and spectra

The reaction of rhodium trichloride hydrate with excess polyethylene glycol 400 (P 400)¹ afforded under HCl gas evolution rhodium polyethylene glycolate, in the form of a solution in excess of polyethylene glycol. The solution is free of chloride and highly soluble in water, alcohols and acetonitrile. With stoichiometric amounts of polyethylene glycol the reaction is slow and resulted in a dark red viscous oil which contains small amounts of chloride (< 200 ppm), probably due to traces of unreacted rhodium chlorine bonds. ¹H and ¹³C NMR spectra are not very characteristic due to the excess polyethylene glycol present in the samples. Polyethylene glycol with a higher molecular weight (up to 1000) leads to the isolation of similar products. Short-length polyethylene glycol (< 400) does not react completely with rhodium trichloride hydrate. The product contains at least one chlorine, which could not be removed even at higher temperature or longer reaction times. The removal of three chlorines by an alcohol from rhodium trichloride is not described so far. No reaction was observed of water free rhodium trichloride with dry polyethylene glycol. Water is essential for the formation of rhodium polyethylene glycolate. Therefore, we assume that rhodium aqua complexes play an important role as intermediates. The chemistry of rhodium aqua ions is very complex and not fully understood [36]. The rhodium polyethylene glycolate complex has not been characterized structurally due to the excess of P400, which was necessary for the preparation but finally it could not be removed from the product. However, our results indicate the presence of a rhodium(III) alkoxide species; this suggestion is based mainly on two points — the absence of chlorine in the product and

¹ 400 represents the average molecular weight of the polyethylene glycol.

from the following NMR experiments, which show that a reduction of Rh(III) to Rh(I) is possible. It may be noted that, to the best of our knowledge, no rhodium(III) alkoxides are known so far. Only rhodium(I) alkoxides, such as $\text{Rh}(\text{OCH}(\text{CF}_3)_2)(\text{PPh}_3)_3$, have been described [37,38]. Reduction of rhodium polyethylene glycolate in the presence of TPPTS is possible. TPPTS (4 equiv) and rhodium polyethylene glycolate (1 equiv) react in an oxygen free atmosphere. The ^{31}P NMR spectrum shows typically three signals, which may be assigned to phosphorus atoms in phosphine ligands standing trans to each other and trans to the OR-group and for the presence of $\text{O} = \text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})_3$. Analogue ^{31}P NMR spectra for the reduction of rhodium trichloride have been reported [39]. Different results could be obtained by treating a solution of rhodium polyethylene glycolate with CO/H_2 (100°C, 8 MPa, 3 h) following by addition of 3 equiv of TPPTS. The ^{31}P NMR spectrum shows only on phosphorus signal of coordinated TPPTS (35.2 ppm, $J_{\text{Rh-P}}$ 122 Hz) and a signal of phosphorus atoms of free TPPTS (−5.3 ppm). No signal of OTPPTS could be observed, indicating that the reduction of the rhodium(III) polyethylene glycolate to a rhodium(I) glycolate species has already occurred with the help of CO/H_2 .

Matthews et al. [40,41], and Yoshida et al. [42] could show that under the conditions of hydroformylation a dihydrido rhodium(II) complex was formed. Rhodium hydrides are supposed to be the active catalytic species [43]. The catalyst formed from rhodium polyethylene glycolate shows no signals in the ^1H NMR spectra for hydrogen atoms connected to the rhodium center. However, we can not exclude that such a species is formed as an intermediate during the catalysis. The infrared spectra of the catalyst formed during the catalytic reaction in the aqueous phase shows two strong absorptions of carbonyl ligands ($\nu = 2056, 2040 \text{ cm}^{-1}$). In comparison with the infrared spectra of the cluster compounds $\text{Rh}_4(\text{CO})_{12}$ ($\nu = 2056$ and 2026 cm^{-1}) [44] and $\text{Rh}_{12}\text{CO}_{30}^{2-}$ ($\nu = 2080, 2040$ and 2020 cm^{-1}) [45], the formation of cluster species is possible. Absorptions for carbonyl ligands from simple rhodium carbonyl species, like $\text{Rh}(\text{CO})_4^-$ ($\nu = 1895 \text{ cm}^{-1}$) [46], could not be detected. In the separated organic phase we were not able to detect absorptions of carbonyl species.

1.2. Catalytic hydroformylation of olefins using rhodium polyethylene glycolate

Rhodium polyethylene glycolate shows high catalytic activity in hydroformylation reactions of various olefins. Dodec-1-ene, diisobutylene, and styrene are the preferred olefins that are used in the experiments. The summary of the present hydroformylation investigation using these and some other olefins as substrates is presented in Table 1.

For most of the following experiments, we have used diisobutylene (mixture of 76% 2.4.4-trimethylpent-1-ene and 24% 2.4.4-trimethylpent-2-ene) as a technical product.² The low specific activity in hydroformylation reactions of this mixture [47] is a challenging problem, which has not been solved yet. Another technical product that was used is a C11-inner olefin cut, with approximately 30% inner olefins.³ Hydroformylation of long-chained linear olefins is very fast, even if the olefin is used as a mixture (like the C11-inner olefin). Branched olefins and mixtures of them could be hydroformylated fairly regioselectively on an optimum time scale. Styrene shows a very high regioselectivity and afforded 2-phenylpropionaldehyde. The reaction time has to be extended to 35 h for 99% conversion. Reuse of the aqueous phase for up to eight times did not change the activity or selectivity. The turnover frequency (TOF) is very high in these systems. The values for oct-1-ene (entry 8, Table 1) and dodec-1-ene (entry 4, Table 1) are 609 and 608 (mol aldehyde/mol rhodium \times h). Compared to

² Diisobutylene was purchased as a technical product from Hoechst.

³ C11-olefin was purchased as a technical product from Shell.

Table 1
Catalytic hydroformylation of various olefins with rhodium polyethylene glycolate as precatalyst

Exp. no ^a	Olefin	Init press, MPa	Rhodium conc, ppm	Reaction time, h	Conversion, mmol (%) ^b	Selectivity iso/n ^c	Turnover no (3 h) ^d	TOF ^e
1	C11-inner olefin ^f	8	85.48	5	91.5 (99)	3.64	1936	614
2	Cyclooctene	8	79.90	40	150.5 (99)	> 99	430	140
3	Diisobutylene ^g	10	85.95	15	121.5 (97)	> 99	1534	453
4	Dodec-1-ene	8	83.72	3	88.3 (99)	1.13	1824	608
5	Hept-1-en-4-ole	8	80.32	15	139.2 (98)	1.37	731	238
6	Hex-1-ene	8	87.51	3	105.7 (95)	1.08	2499	833
7	α -Methyl-styrene	8	77.34	10	146.4 (96)	> 99	1717	523
8	Oct-1-ene	8	85.48	3	124.5 (99)	1.15	1827	609
9	Styrene	10	77.34	35	154.0 (99)	31.13	604	192
10	2.4.4-Trimethyl-pent-1-ene	10	85.95	15	122.8 (98)	> 99	1487	447

^aConditions: reaction temperature 100°C (exception styrene 40°C); olefin 20 ml; water (polar phase) 20 ml; internal standard 2 ml *n*-nonane.

^bPercent conversion — mmol aldehyde/mmol olefin; material balance 97%–99% (exception styrene: 93%); loss of olefin occurs during charging and depressurization of the autoclave.

^cSelectivity of branched/linear aldehydes; GC analysis at different high temperature programs showed no high molecular weight products and only trace amounts of hydrogenated products like alkanes or alcohols.

^dTurnover no — mol aldehyde/mol rhodium.

^eTurnover frequency — mol aldehyde/(mol rhodium \times h), 5 h (exception dodec-1-ene, hex-1-ene, oct-1-ene: 3 h).

^fC11-inner olefin — technical cut.

^gDiisobutylene — technical product: 24% 2.4.4-trimethylpent-2-ene, 76% 2.4.4-trimethylpent-1-ene.

the TOF values of 2.9 for the hydroformylation of oct-1-ene with HRh(CO) (TPPTS)₃ as precatalyst at 100°C, the values for rhodium polyethylene glycolate are excellent. Even the measured TOF for styrene (after 5 h 192) is very high. Aldehyde selectivity is almost quantitative for hex-1-ene, oct-1-ene, dodec-1-ene, diisobutylene and styrene.⁴ Formation of side products in the hydroformylation with rhodium polyethylene glycolate as a precatalyst is nearly independent on the catalyst concentration and the temperature. For these experiments, the olefin was treated with an aqueous solution of rhodium polyethylene glycolate under the described conditions. The determination of the absolute amount of rhodium in the organic phase after catalytic runs by photometric analysis shows a leaching of rhodium (1.9 ppm).

Addition of TPPTS (4 equiv) could minimize the loss of rhodium into the organic phase, so that no measurable amounts of rhodium (detection sensitivity limit with this method is 2.5 μ g of rhodium) were found. Consequently, the reuse of the separated organic phase as catalyst for the hydroformylation of hex-1-ene shows no activity. Reducing the amount of TPPTS (1 equiv) leads to a rhodium content of less than 1.5 ppm in the organic phase. The effect of TPPTS concentration on the rate of hydroformylation of diisobutylene and styrene is shown in Figs. 1 and 2, respectively.

The conversion⁵ for the hydroformylation of diisobutylene varies with the concentration of TPPTS in the system. High concentrations of TPPTS presumably inhibit the system by blocking the rhodium

⁴ For diisobutylene, the formation of side products is negligible over a period of 3 h, but becomes detectable after 5 h. A complete analysis by GC/GC-MS of the products after 5 h shows the following items: 3.3.5-trimethyl-hexan-1-al (96%), 2.4.4-trimethyl-pent-1-ene (1.5%), 2.4.4-trimethyl-pentane (0.3%), 2-*t*-butyl-3-methyl-butan-1-al (0.9%), 2.4.4-trimethyl-pent-2-ene (0.6%), 3.5.5-trimethyl-hexan-1-ol (0.2%), unidentified compounds (0.5%).

⁵ The conversion of the olefin was calculated as follows: $100\% \times (1 - (c_{A_0} - c_{A_t}) / c_{A_0})$, where c_{A_0} is the initial concentration of olefin and c_{A_t} is the concentration at the time t . Under the conditions chosen for kinetic studies, no side reactions were found to occur and hence, these data would be representative of the overall hydroformylation of the olefin to the corresponding aldehyde. Since H₂ and CO were consumed in an 1:1 ratio, the concentration of the olefin c_A could be determined from the slope of H₂/CO consumed.

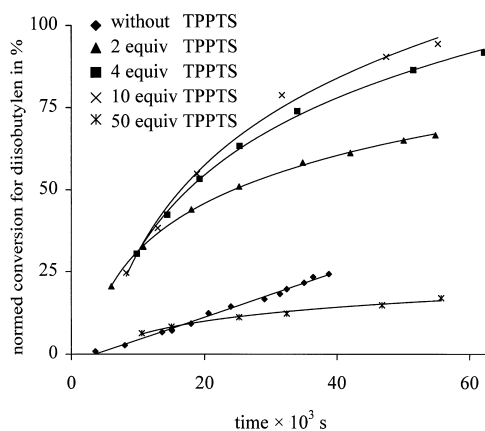


Fig. 1. Effect of the TPPTS concentration on the hydroformylation of diisobutylene with rhodium polyethylene glycolate as precatalyst. Reaction conditions: rhodium: (86.0 ppm); diisobutylene: (128 mmol); water: (19.75 ml); $P_{\text{CO}} = P_{\text{H}_2} = 4$ MPa; $T: 100^\circ\text{C}$.

center. In the range 2 to 10 equiv, TPPTS only slight variations in activity are observed with a maximum activity using 10 equiv TPPTS. The styrene hydroformylation is less dependent on the phosphine concentration. Highest activity was observed with 4 equiv TPPTS per rhodium center. The curves in Figs. 1 and 2 clearly indicate different kinetic behavior. This observation is fully supported by further kinetic studies, discussed *vide infra*.

1.3. Mechanistic studies

Mechanistic studies on the hydroformylation in two-phase systems for $\text{HRh}(\text{CO})(\text{TPPTS})_3$ as a catalyst are very limited and for higher olefins with chain length over 6 are not available so far. The reason is the decreased solubility of the olefins in water and the experimental difficulties to measure meaningful rates in these systems. The kinetics of oct-1-ene hydroformylation in water/ethanol-mixture was investigated recently [48]. Ethanol was used to increase the solubility of the olefin. Rate

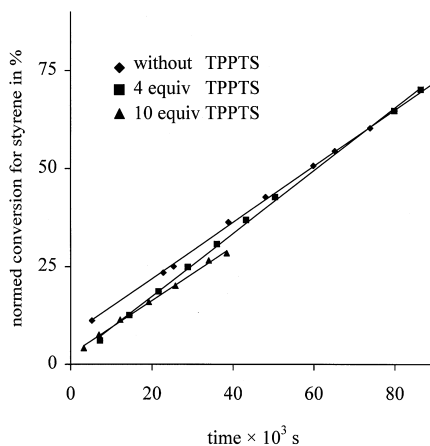


Fig. 2. Effect of the TPPTS concentration on the hydroformylation of styrene with rhodium polyethylene glycolate as precatalyst. Reaction conditions: rhodium: (77.3 ppm); styrene: (167 mmol); water: (19.75 ml); $P_{\text{CO}} = P_{\text{H}_2} = 5$ MPa; $T: 40^\circ\text{C}$.

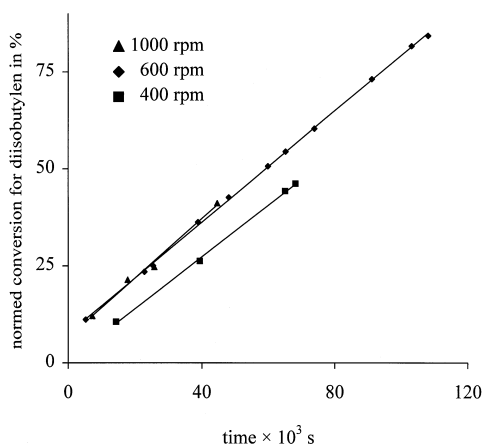


Fig. 3. Effect of agitation speed on the rate of reaction in the hydroformylation of diisobutylene. Reaction conditions: rhodium: (86.0 ppm); diisobutylene: (128 mmol); water: (19.75 ml); TPPTS: (4 equiv); $P_{\text{CO}} = P_{\text{H}_2} = 4$ MPa; T : 100°C.

constants, which are observed are first order in oct-1-ene and catalyst concentration, strongly depend on the H_2/CO pressure.

We have investigated kinetic parameters using rhodium polyethylene glycolate as a catalyst for the hydroformylation of various olefins in water and in polyethylene glycol as a polar phase. The consumption of H_2 and CO at a constant pressure was monitored by the pressure drop of a gas reservoir from which the gas mixture was supplied to the autoclave automatically. In addition, we took samples from the autoclave and analyzed the probes quantitatively by gas chromatography. To ensure that the monitored kinetic parameters are not dependent on the agitation speed, we carried out all reactions at agitation speeds over 1000 rpm with a high-speed stirrer and four wave breakers inside of the autoclave. Results for different agitation speeds are shown in Fig. 3. The conversion was found to be independent of the agitation speed above 600 rpm. Presumably, dispersion of the two phases reaches a maximum at this point.

To study the influence of coordinated polyethylene glycol on the rhodium center in $\text{HRh}(\text{CO})_3$ (TPPTS)₃ we investigated this complex with and without polyethylene glycol in comparison to the

Table 2
Hydroformylation of dodec-1-ene with the help of polyethylene glycol

Exp.	Catalyst ^a	Equiv TPPTS added	Rhodium concentration (ppm)	PEG-400 added (wt.%) ^b	Conversion ^c (%)	Rh _{org.} ^d phase ^d
1	$\text{HRhCO}(\text{TPPTS})_3^e$	4	120	0	< 1	< 0.1
2	$\text{HRhCO}(\text{TPPTS})_3^e$	4	120	30	11	< 0.1
3	$\text{Rh}(\text{PEG})_x^f$	0	85	0	98	1.9
4	$\text{Rh}(\text{PEG})_x^f$	0	80	30	45	1.8
5	$\text{Rh}(\text{PEG})_x^f$	1	80	30	97	1.4
6	$\text{Rh}(\text{PEG})_x^f$	4	85	0	99	< 0.1

^a Conditions: reaction temperature 100°C; 8 MPa CO/H_2 1:1; reaction time 2 h; dodec-1-ene 20 ml; water (polar phase) 20 ml; internal standard 2 ml *n*-nonane.

^b Weight percent of polyethylene glycol in the water phase.

^c Percent conversion — mmol aldehyde/mmol olefin.

^d Rhodium content (ppm) in the organic phase after 5 catalytic cycles.

^e Classical Ruhrchemie/Rhône-Poulenc catalyst prepared from watersoluble rhodium acetate in a *preforming* reaction.

^f Rhodium polyethylene glycolate.

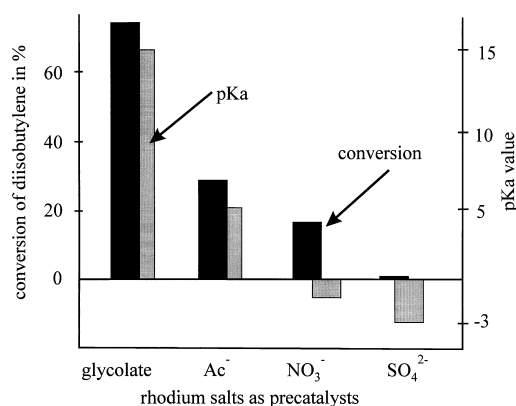


Fig. 4. Conversion in the hydroformylation reaction of diisobutylene with various rhodium salts and pK_a values of the corresponding acids. Reaction conditions: rhodium: (91.7 ppm, 86 ppm for rhodium polyethylene glycolate); diisobutylene: (128 mmol); water: (18.75 ml); polyethylene glycol: (1.25 ml); TPPTS: (4 equiv); $P_{CO} = P_{H_2} = 5$ MPa; $T: 100^\circ\text{C}$.

described $\text{Rh}(\text{PEG})_x$ under similar conditions as precatalysts for the hydroformylation of olefins. The results with dodec-1-ene are shown in Table 2.

The conversion rate in Table 2 shows a significant difference between the two catalysts. Addition of polyethylene glycol to $\text{HRh}(\text{CO})(\text{TPPTS})_3$ can increase the aldehyde formation only slightly (exp. Nos. 1 and 2), whereas the use of Rhodium polyethylene glycolate as a precatalyst leads to a nearly quantitative conversion of the olefin to aldehydes with negligible loss of rhodium (exp. No 6).

For different rhodium complexes [$\text{Rh}(\text{PEG})_x$, $\text{Rh}_2(\text{CH}_3\text{COO})_4$, $\text{Rh}(\text{NO}_3)_3$, $\text{Rh}_2(\text{SO}_4)_3$] as catalyst the conversion of diisobutylene together with the pK_a value of the corresponding acid of the complex are summarized (Fig. 4).

Obviously, there is a relation of the ligand used at Rh and the conversion to 3.5.5-trimethylhexylaldehyde which is correlated with the pK_a values of the free acids. A plot of conversion vs. time of rhodium polyethylene glycolate and rhodium acetate is shown in Fig. 5.

Fig. 5 clearly demonstrates that $\text{Rh}(\text{PEG})_x$ as a precatalyst is significantly more reactive. The turnover number for the hydroformylation of diisobutylene could be increased (550) and the

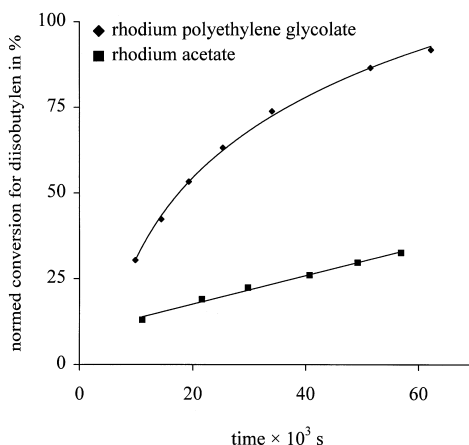


Fig. 5. Comparison of rhodium polyethylene glycolate and rhodium acetate as precatalysts for the hydroformylation of diisobutylene. Reaction conditions: rhodium: (86.0 ppm); diisobutylene: (128 mmol); water: (18.75 ml); polyethylene glycol: (1.25 ml); TPPTS: (4 equiv); $P_{CO} = P_{H_2} = 4$ MPa; $T: 100^\circ\text{C}$.

Table 3
Hydroformylation of diisobutylene with various rhodium concentrations

Rhodium concentration (ppm) ^a	Conversion, mmol (%) ^b	Turnover no (5 h) ^c	TOF (5 h) ^d
343.8	84.5 (67)	675	135
171.9	105.2 (84)	1680	336
86.0	84.4 (67)	2195	439
34.4	82.5 (66)	6580	1316
17.2	78.2 (62)	9360	1872
6.9	60.4 (48)	24090	4818

^aConditions: reaction temperature 100°C; initial pressure 10 MPa; diisobutylene 20 ml; water (polar phase) 20 ml; internal standard 2 ml *n*-nonane.

^bPercent conversion — mmol 3.5.5-trimethylhexylaldehyde/mmol diisobutylene charged, 8.5 h.

^cTurnover no — mol 3.5.5-trimethylhexylaldehyde/mol rhodium.

^dTurnover frequency — mol 3.5.5-trimethylhexylaldehyde/(mol rhodium × h).

selectivity for 3.5.5-trimethylhexylaldehyde was improved (by a factor of 1.2). Consequently, the pK_a values of the corresponding acids shows a strong correlation with the olefin conversion. The high pK_a value for polyethylene glycol indicates a weak interaction of the polyethylene glycolate with the water. Compared to anions of stronger acids, such as acetate or sulfate, the interaction with water decreases in the polyethylene glycol system. Chelate-like coordination of the ether oxygen atoms of polyethylene glycol to the rhodium atoms have to be considered too. We assume that these two effects, the weak interaction of the polyethylene glycolate with the water and the coordination of the oxygen atoms towards the rhodium, is responsible for the high activity of the catalyst.

The effect of the concentration of rhodium polyethylene glycolate precatalyst on the rate of hydroformylation of diisobutylene was studied at a temperature of 100°C and constant H₂/CO pressure (10 MPa) (Table 3).

The studies were performed using a rhodium concentration range (360 ppm to 7 ppm). After 5 h of reaction the highest conversion rate was observed for a rhodium concentration of 180 ppm. Reducing the rhodium amount resulted in a small drop of the conversion rate with increasing TOF up to nearly 5000. Despite the fact that the rhodium concentration is very low the behavior of increasing TOF with decreasing catalyst concentration is similar to results which were found recently by Deshpande et al. for the biphasic hydroformylation of dodec-1-ene at low pH-values [49].

The effect of the pressure on the rate of hydroformylation was studied first with a mixture of H₂ and CO (1:1) in a pressure range (6–12 MPa) (Table 4).

Table 4
The effect of the total pressure (CO/H₂) on the hydroformylation of diisobutylene

Total pressure (MPa) ^a	Conversion, mmol (%) ^b	Turnover no (5 h) ^c	TOF (5 h) ^d
12	87.2 (68)	2720	544
10	79.9 (62)	2495	499
8	71.5 (56)	2235	447
7	44.0 (34)	1375	275
6	2.2 (2)	70	14

^aConditions: reaction temperature 100°C; $P_{CO} = P_{H_2}$; precatalyst solution 0.25 ml (86.0 ppm rhodium); diisobutylene 20 ml; water (polar phase) 20 ml; internal standard 2 ml *n*-nonane; 4 equiv TPPTS.

^bSee Table 3.

^cSee Table 3.

^dSee Table 3.

The conversion was found to be strongly dependent on the total pressure and shows a significant drop of the rate at total pressures below 7 MPa and is in accordance to the results obtained by Zin et al. [50]. Due to the relative high pressure used the effect of mass transfer of the gases into the aqueous phase is minimized. By reducing the partial pressure of CO at constant total pressure the rate decreased. The dependence of the reaction rate on CO partial pressure is unexpected and shows an inverse behavior to the results mentioned earlier [49] is similar to results obtained from homogeneous hydroformylation experiments with dodec-1-ene [51]. On the other hand the selectivity for aldehydes decreased due to side reactions of the olefin with hydrogen. Fig. 6 shows a plot of conversion vs. time for the hydroformylation of styrene at different total pressures.

Hydroformylation of diisobutylene was also performed in a system without H_2 and using a CO pressure of 10 MPa. The reaction is somewhat slower but showed after 35 h a conversion of 35%. The source of hydrogen is water. Hydrogen is formed in a water gas shift reaction. Precedents for this type of reaction are known in literature [52–55]. In the case of catalytic systems under acidic conditions the metal center tends to be stabilized in higher oxidation states, but the coordination of CO by a metal center becomes more difficult if the metal is in a high oxidation state. The measured pH value for rhodium polyethylene glycolate in water is in the range of 3 to 4, and decreases during the catalytic reaction.

The strong influence of the pH value in various aqueous catalytic systems using TPPTS as ligand could be shown earlier in an impressive way by Joó et al. [56,57]. So we performed studies on the influence of the pH values by using solutions which were buffered at different pH values. Results between pH 2 and 7 together with the unbuffered solution are shown in Table 5.

As expected the rate of the hydroformylation depends on the pH value. Additional experiments were performed with addition of potassium dihydrogen phosphate (exp. no. 1), dipotassium hydrogen phosphate, and phosphoric acid which shows only small effects. This ensures that the changes in the TOF by buffering the solution ($H_2PO_4^-/HPO_4^{2-}$) is not a salt effect. Changing the composition of the polar phase from water to polyethylene glycol resulted in higher pH values and decreasing TOF. The conversion of the olefin and the composition of the solution are shown together with pH values of the solution at the beginning and at the end of the catalytic run in Table 6.

The reaction rate is strongly influenced by the reaction medium. The hydroformylation reaction in water/polyethylene glycol under the conditions described in Table 6 was terminated after 5 h. Water

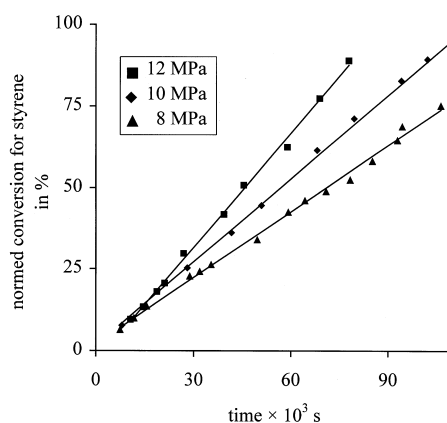


Fig. 6. The effect of the total pressure (CO/H_2) on the conversion for the hydroformylation of styrene. Reaction conditions: rhodium: (77.3 ppm); styrene: (167 mmol); water: (19.75 ml); TPPTS: (4 equiv); $P_{CO} = P_{H_2}$; T : 40°C; reaction time (8.5 h).

Table 5
Hydroformylation of diisobutylene with rhodium polyethylene glycolate at different pH values

Exp. No ^a	Salt/buffer	Init pH	End pH	Conversion, mmol (%) ^b	TOF (3 h) ^c
1	KH ₂ PO ₄	3.6	2.6	69 (55)	439
2	buffer ^d	2.0	2.0 ^e	5 (3.6)	48
3	buffer ^d	2.5	2.5 ^e	19 (14.6)	198
4	buffer ^d	3.4	3.4 ^e	29 (23.1)	308
5	buffer ^d	5.7	5.7 ^e	24 (18.7)	249
6	buffer ^d	6.3	6.3 ^e	17 (13.6)	182

^a Conditions: reaction temperature 100°C; initial pressure 10 MPa; precatalyst solution 0.25 ml (86.0 ppm rhodium); diisobutylene 20 ml; water (polar phase) 20 ml; internal standard 2 ml *n*-nonane; reaction time 3 h.

^b See Table 2.

^c See Table 2.

^d buffer made from H₃PO₄, KH₂PO₄, and K₂HPO₄ in various concentrations.

^e End pH = Init pH (error ± 0.2 units).

is essential for a high activity of the catalyst. Reducing the amount of water presumably shifted the equilibrium between polyethylene glycol and polyethylene glycolate, which leads to stronger interaction of polyethylene glycolate with the rhodium center. The result is a drop in the activity of the catalyst.

In order to elucidate the mechanism, kinetic parameters and activation energies were obtained. Conversion vs. time graphs for the hydroformylation of hex-1-ene, oct-1-ene, diisobutylene, dodec-1-ene and styrene, respectively, under the conditions described are shown in Fig. 7.

The order of the reaction is dependent on the olefin used. Conversion vs. time for styrene shows a linear behavior, whereas the diisobutylene and dodec-1-ene plots are not linear, product rates decreased with time. Under the reaction conditions described (Fig. 7) pseudo first order rate constants for hex-1-ene, oct-1-ene, dodec-1-ene, and diisobutylene hydroformylation can be seen, whereas styrene shows a pseudo zero order. To obtain activation energies in water and in polyethylene glycol the experiments were carried out in a temperature range of 80 to 120°C for hex-1-ene, oct-1-ene, dodec-1-ene, and diisobutylene.

The kinetic data for hex-1-ene, oct-1-ene, dodec-1-ene, and diisobutylene obtained in water or in polyethylene glycol show in principal a similar behavior, foreseen of the lower conversion rate in

Table 6
Hydroformylation of diisobutylene with rhodium polyethylene glycolate in water/polyethylene glycol mixtures and corresponding pH values

Rhodium concentration (ppm) ^a	Volume water (ml)	Volume P400 (ml)	Init pH	End pH	Conversion, mmol (%) ^b	Turnover no (5 h) ^c	TOF (5 h) ^d
85.95	19.75	0.25	3	2	68.9 (55)	2195	439
81.46	10.00	10.00	4	3	38.8 (31)	744	248
79.08	5.00	15.00	5	4	18.8 (15)	354	118
77.28	1.00	19.00	7	4	6.3 (5)	126	42
76.95	0.25	19.75	7	5	3.8 (3)	63	21
76.87	0.05	19.95	7	4	0	3	1
76.84	0.00	20.00	7	7	0	0	0

^a Conditions: reaction temperature 100°C; initial pressure 10 MPa; diisobutylene 20 ml; water (polar phase) 20 ml; internal standard 2 ml *n*-nonane.

^b See Table 2.

^c See Table 2.

^d See Table 2.

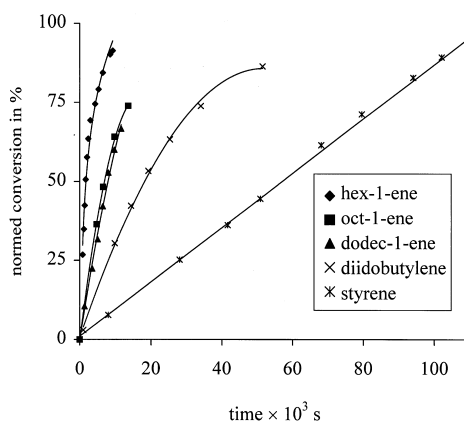


Fig. 7. Conversion vs. time for the hydroformylation of diisobutylene, dodec-1-ene and styrene. Reaction conditions: rhodium: (86.0 ppm, diisobutylene), (83.7 ppm, dodec-1-ene), (77.3 ppm, styrene); olefin: (128 mmol, diisobutylene), (91 mmol, dodec-1-ene), (167 mmol, styrene); water: (19.75 ml); TPPTS: 4 eq.; $P_{CO} = P_{H_2} = 4$ MPa (diisobutylene and dodec-1-ene), 5 MPa (styrene); T : 100°C (diisobutylene and dodec-1-ene), 40°C (styrene).

polyethylene glycol. The order of the reaction does not depend on the composition of the polar phase, whereas the conversion rate does. For styrene the conversion of the olefins as a function of time was studied in water in a temperature range (30 to 50°C) at constant partial pressures of H_2 and CO (5 MPa).

The plots of conversion vs. time show no deviations from the linearity under all the temperature conditions studied. Higher temperatures than 60°C lead to the formation of polymeric materials and could not be evaluated. The rate constants ($\ln k/T$) for the hydroformylation of hex-1-ene, oct-1-ene, dodec-1-ene, and diisobutylene are plotted vs. $1/T$ (Figs. 8, 9), in which the used rate constants are first order for the olefins.

All plots show no significant curvature, indicating that the rate models are correct. The calculated activation energies for the hydroformylation reactions of the aliphatic olefins are summarized in Table 7.

All calculations are based on a model with rate constants which are first order for the olefins. In all cases, the activity of Rh (PEG)_x as a precatalyst in water as a solvent is higher than in polyethylene glycol. This effect is less drastic by using olefins which are more complex (higher carbon number). Polyethylene glycol itself as a solvent is more ordered and showed therefore a smaller drop in the entropy. The negative entropy is due to the formation of the aldehyde from carbon monoxide,

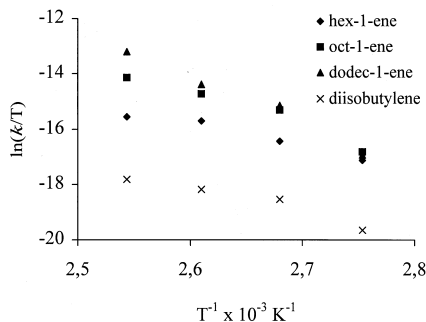


Fig. 8. Arrhenius plot for the hydroformylation of hex-1-ene, oct-1-ene, dodec-1-ene, and diisobutylene in water.

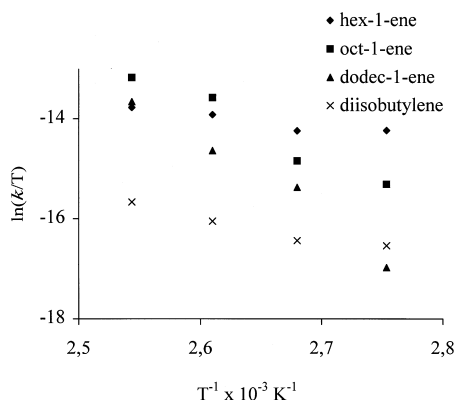


Fig. 9. Arrhenius plot for the hydroformylation of hex-1-ene, oct-1-ene, dodec-1-ene, and diisobutylene in polyethylene glycol.

hydrogen and olefin. The influence of the number of isomers which could be formed from a specific olefin is clearly reflected in the entropy. However, the activation parameters are experimental values and only valid for the described reaction conditions. Comparable results were obtained by Chaudhari et al. for the hydroformylation of dodec-1-ene using $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ as catalyst in a single phase system (57 kJ mol^{-1} for the activation energy) [51].

The kinetic data from rate constants for styrene are shown in the plot of $\ln k/T$ vs. $1/T$ (Fig. 10).

From the Arrhenius plot (Fig. 10) the activation energy can be calculated for styrene (E_a 34.1 kJ/mol).

A complete description of the kinetic in two phase systems is very complicated. Parameters, like mass transport between the phases or phase equilibrium, could not be measured in a two phase system under catalytic conditions. Other parameters, which have to be constant during the reaction, like diffusion coefficients, vary due to the product distribution in the system. The question where the reaction takes place moves into the focus in order to get a simple picture of the kinetic. Keeping in mind that the solubility of long-chained olefins, such as dodec-1-ene, in water is very low and the conversion rate for hydroformylation with rhodium polyethylene glycolate is very high, there are two mechanisms possible. The possibilities of a one-phase reaction and a reaction in the polar phase can

Table 7

Calculated activation energies for the hydroformylation reactions

Olefin	Solvent	ΔH^\ddagger (kJ mol^{-1}) ^a	ΔS^\ddagger ($\text{J K}^{-1} \text{ mol}^{-1}$) ^b	E_a (kJ mol^{-1}) ^c
Hex-1-ene	Water	20	-261	23
Oct-1-ene	Water	91	-75	94
Dode-1-cene	Water	92	-76	95
Diisobutylene	Water	27	-260	30
Hex-1-ene	PEG ^d	65	-160	71
Oct-1-ene	PEG ^d	102	-53	106
Dode-1-cene	PEG ^d	102	-50	105
Diisobutylene	PEG ^d	48	-223	51

^a $\Delta H^\ddagger/R$ is determined from the slope of the plot k/T against $1/T$.

^b ΔS^\ddagger is calculated on the basis of ΔH^\ddagger ($\Delta S^\ddagger = 4.576[\log(k/T) - 10.319] + \Delta H^\ddagger/T$); calculated error for ΔS^\ddagger is in the range of $\pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$.

^c E_a is calculated by: $E_a = \Delta H^\ddagger + RT$.

^dPEG: polyethylene glycol 400 with 1.25 wt.% water.

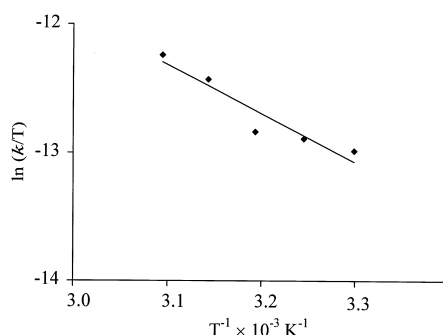


Fig. 10. Arrhenius plots for the hydroformylation of styrene.

be excluded. Since the solubility of low molecular weight polyethylene glycols (like the used polyethylene glycol 400) in water in the temperature range studied is not temperature-dependent⁶ [58], a thermoregulated phase transfer catalysis, like the recently described methods with polyether substituted phosphines [50,59] or smart ligands [60], could be excluded also. It can be assumed that either the catalyst is transported under the reaction conditions into the organic layer, or the hydroformylation takes place at the interphase. As long as the addition of ethanol results in an even more reactive one-phase system and a rhodium loss in our systems is not detectable, we favor the model that the hydroformylation takes place with the help of the polyethylene glycol at the interphase (water/organic phase). In order to develop a suitable rate equation for hydroformylation reactions with $\text{Rh}(\text{PEG})_x$, it was first essential to ensure that the data obtained are in the kinetic controlled regime. Since the agitation speed does not influence the conversion a mass transfer over the interphase is probably not involved, whereas diffusions of the olefins and the formed aldehydes to and from the catalytic center are involved. From the plots of conversion vs. time it can be seen, that hydroformylation of hex-1-ene, oct-1-ene, dodec-1-ene, and diisobutylene with $\text{Rh}(\text{PEG})_x$ are pseudo first order (first approximation), tending to a zero order for dodec-1-ene in the beginning with high olefin concentrations, while for styrene, the reaction is pseudo zero order. The different behavior of the olefins can be explained by using a model which distinguishes two cases: at high temperatures, the diffusion speed inside the organic layer is high, this leads to a very fast hydroformylation reaction which is not diffusion controlled. For diisobutylene and dodec-1-ene, the resulting reaction order is therefore pseudo first-order. The second case for low temperatures includes a low diffusion speed due to the lower Brownian movement. This case results in a pseudo zero order reaction which is applicable for styrene. Hydroformylation in polyethylene glycol proceeds in the same manner, although the activation energies in polyethylene glycol are higher (35–40 kJ/mol) than in water, resulting in a lower conversion rate. The observed relative reactivity for the olefins is in accordance with results for unmodified rhodium catalysts [47]. Due to the different reaction conditions, direct comparison of the activation energies found with data for other catalytic systems has only a limited meaning.

The most interesting aspect of hydroformylation reactions using $\text{Rh}(\text{PEG})_x$ as a precatalyst is the observed high activity of the catalyst compared to the hydroformylation of dodec-1-ene with the recently introduced water soluble polymer bound rhodium catalyst that shows low turnover frequen-

⁶ With decreasing molecular weight of a polyethylene glycol, the precipitation temperature from water increased.

cies at a moderate conversion [31] or with a catalyst using $\text{HRh}(\text{CO}) (\text{TPPTS})_3$ and additional polyethylene glycol (Table 2). In the case of diisobutylene, the situation is even more drastic. Using a high nuclearity rhodium carbonyl cluster as precatalyst in a homogeneous catalytic system at 100°C TOF reaches only $170 \text{ mol/mol Rh} \times \text{h}$ [61]. Activity with rhodium polyethylene glycolate as a precatalyst in water is 4 times higher with an excellent selectivity for the desired product. $\text{Rh}(\text{PEG})_x$ has been demonstrated as a useful catalyst with very high activity involving long-chained and branched olefins. We found an important role of polyethylene glycolate as a ligand, although the exact structure of the rhodium complex could still not be revealed. However, our mechanistic and kinetic studies gave some insights into the mechanism. Remarkably, water is essential for high activity of the catalytic system. From the experiments involving buffered solutions we know that only in an acidic medium hydroformylation takes place. The pH value during the catalysis decreases with time. As it can be seen from the hydroformylation reaction without H_2 , water gas shift reaction takes place, even in a strong acidic solution. Formation of $\text{Rh}(\text{OH})$ -species during the catalysis can be assumed, but we were not able to detect some of these intermediates.

1.4. Conclusion

The kinetic data of the hydroformylation of long-chained and branched olefins with $\text{Rh}(\text{PEG})_x$ has been investigated. In conclusion rhodium polyethylene glycolate is a novel highly active catalyst for two-phase hydroformylation reactions. For the first time, the TOF for the hydroformylation of long-chained and branched olefins in two phase systems are in a range of interest for industrial applications. Excellent selectivity was found for the hydroformylation of the diisobutylene mixture to the only desired product. In view of this encouraging results, one is inclined to believe that this route can prove to be very useful for further generations of new hydroformylation catalysts by appropriate modifications.

2. Experimental

2.1. General data

Reactions and measurements were carried out using standard Schlenk techniques under an atmosphere of nitrogen. All chemicals were purchased from Aldrich, Degussa and Merck. Synthesis gas, 99.90% $\text{H}_2:\text{CO}$, 1:1, was obtained from Gerling. The solvents used were degassed prior to use. Polyethylene glycol 400 was dried using molecular sieves under vacuum (0.13 Pa). NMR spectra were measured on Bruker WP 80 SY, Bruker AM 250, Bruker AM 200 and Bruker AS 400 spectrometers at room temperature. TMS was used as a standard for ^1H NMR and 85% H_3PO_4 for ^{31}P NMR. The key to the NMR data is: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer. UV/VIS-spectra were measured on a Perkin-Elmer 230 spectrometer. The quantitative analysis of the reactant and hydroformylation products was carried out by an internal standard method using a gas chromatographic technique on a HP 6890 Series GC System equipped with a HP-5 column $30 \text{ m} \times (0.32 \text{ mm} \times 0.25 \mu\text{m})$ and FID detector. Helium was the carrier gas.

2.2. Synthesis of rhodium polyethylene glycolate

Rhodium trichloride hydrate (500 mg, 1.90 mmol) was dissolved in polyethylene glycol 400 (15.0 ml, 1.125 g/cm^3 , 42.2 mmol) and water (50.0 mg, 2.78 mmol) was added. The reaction mixture was

stirred at 50°C for 2 h and then kept at reduced pressure (1.3 Pa) for an additional hour to remove formed hydrogen chloride. The resulting red, viscous liquid was used as a precatalyst in hydroformylation reactions. Anal no chlorine was found. ^1H NMR (acetonitrile- d_3): δ 3.4–3.6 ppm (m, br). IR (film, KBr): $\nu = 3449, 2098, 1956, 1740, 1649\text{ cm}^{-1}$. UV/VIS: 445 nm.

2.3. The synthesis of rhodium acetate, nitrate, sulfate

Rhodium acetate, nitrate and sulfate were prepared from rhodium trichloride hydrate. Rhodium acetate (56.0 mg, 0.13 mmol) was dissolved in water (1.00 g, 55.5 mmol). This procedure was repeated for rhodium nitrate and sulfate, and 0.25 ml of the resulting solutions were used as precatalysts in hydroformylation reactions.

2.4. Catalysis test

Two phase hydroformylation reactions were carried out in a Parr Minireactor 4560 (300 ml) equipped with temperature, stirring and pressure control device. The consumption of CO and H_2 at a constant pressure was monitored by the pressure drop from a gas reservoir. The pressure in the reservoir was recorded using a pressure transducer and recorder system.

2.5. Preparation of the catalyst

For a typical experiment the formation of the catalyst was carried out by charging the reaction vessel with a precatalyst solution (0.25 ml, containing 3.17×10^{-5} mol rhodium), an aqueous TPPTS solution (280 mg, containing 1.27×10^{-4} mmol TPPTS) and reaction gas (H_2/CO , 10 MPa). After 30 min, the autoclave was depressurized after cooling in a water bath. The resulting orange liquid was used as a catalyst in hydroformylation reactions. ^{31}P NMR: ($\text{Rh}(\text{PEG})_x/\text{TPPTS}$ 1/4): $\delta = -5.3$ (s), TPPTS; 34.5 (s) OTPPTS; 35.2 (dt), $J_{\text{Rh-P}} = 136$ Hz, 58.1 ppm (dd), $J_{\text{Rh-P}} = 203$ Hz, $J_{\text{P-P}} = 121$ Hz, $\text{Rh}(\text{OR})_3$ (TPPTS) $_3$ ($\text{Rh}(\text{PEG})_x/\text{TPPTS}$ 1/3, addition of TPPTS after 3 h, 8 MPa CO/H_2): $\delta -5.3$ (s), TPPTS; 35.2 (d), $J_{\text{Rh-P}} = 122$ Hz. IR of a catalyst made from $\text{Rh}(\text{PEG})_x$ (film, KBr): $\nu = 3354, 2056, 2040, 1989, 1734\text{ cm}^{-1}$. UV/VIS: 270 nm.

2.6. Hydroformylation reactions

For a typical hydroformylation experiment the reaction vessel was charged with olefin (20.0 ml), polar phase (water, polyethylene glycol in various proportions) (20 ml), precatalyst solution (0.25 ml, containing 3.17×10^{-5} mol rhodium), aqueous TPPTS solution (280 mg, containing 1.27×10^{-4} mmol TPPTS), and *n*-nonane (1.00 ml, 0.718 g/cm^3 5.60 mmol) was added as internal standard. The catalyst was formed in situ. After the adjustment of pressure and temperature the reaction mixture was stirred (1000 rpm) and the consumption of the reaction gas was recorded. Catalytic reactions were terminated by depressurizing after cooling in a water bath. The readily separated organic layer was analyzed.

2.7. Supporting information available

Plots (9) of conversion vs. time for the hydroformylation of hex-1-ene, oct-1-ene, diisobutylene, dodec-1-ene and styrene in water and polyethylene glycol at different temperatures are available (no. of pages 09).

Acknowledgements

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