Two-Phase Hydroformylation of Higher Olefins Using Randomly Methylated α-Cyclodextrin as Mass Transfer Promoter: A Smart Solution for Preserving the Intrinsic Properties of the Rhodium/Trisulfonated Triphenylphosphine Catalytic System

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Abstract: The two-phase hydroformylation of higher olefins with the rhodium/trisulfonated triphenylphosphine catalytic system in the presence of various chemically modified α-cyclodextrins has been investigated. These cyclodextrins allowed us to increase greatly the reaction rate and the chemoselectivity of the reaction but, contrary to what has been observed previously with the chemically modified β-cyclodextrins, the linear to branched aldehydes ratio was not affected by the presence of α-cyclodextrin derivatives. Indeed, the latter was found to be similar to that obtained without any mass transfer promoter, suggesting that the catalytic species are stable in the presence of α-cyclodextrin derivatives.

Keywords: cyclodextrins; hydroformylation; long-chain olefins; phosphanes; rhodium

Although olefins with variable chain lengths have been successfully hydroformylated in aqueous two-phase medium with rhodium complexes modified by the sodium salt of the trisulfonated triphenylphosphine (TPPTS), a distinction is generally made between lower and higher olefins.[1] Indeed, lower olefins such as ethylene, propene and butene have a solubility in the aqueous catalytic phase high enough to assure chemical reaction without mass transfer limitations.[2] In contrast, the solubility of higher olefins (five or more carbon atoms) is too low for industrially important rates to be achieved and the presence of cosolvent,[3] surfactant,[3a,4] amphiphilic ligands[5] or cyclodextrins[6–8] is required.

Among the different approaches proposed to increase the solubility of higher olefins, the use of chemically modified β-cyclodextrins preserves some economical viability. Indeed, the randomly methylated-β-cyclodextrin (RAME-β-CD) that is a cheap, non-toxic and bulk commercially available compound allowed one to achieve the hydroformylation of 1-decene with an initial turnover frequency and aldehyde selectivity of 300 h^{-1} and 95%, respectively, while avoiding the formation of an emulsion and the partition of the rhodium catalyst between the organic and aqueous phases.[7] This outstanding result was attributed to the complexing and surface active properties of the RAME-β-CD. Indeed, this compound forms host/guest complexes with the water-insoluble olefin at the liquid/liquid interface and transfers the olefin into the aqueous phase where it reacts with the water-soluble rhodium catalyst. After reaction, the product is released in the organic phase and the transfer cycle can go on (Figure 1).[8]

Unfortunately, it was found that the normal to branched aldehydes ratio (l/b) is always lower than that observed without the mass transfer promoter (1.8 *vs.* 2.8 without cyclodextrin).[8] This unexpected decrease in the l/b aldehydes ratio was until now the major drawback of the cyclodextrin-based hydroformylation process as the linear aldehyde is the most desired product. The origin of this decrease was recently attributed to the formation of inclusion complexes between RAME-β-CD and the TPPTS ligand. In fact, by trapping TPPTS, RAME-β-CD induces a displacement of the equilibria between the different catalytic species towards phosphane low-coordinated rhodium species poorly selective toward the formation of the linear aldehyde.[9]

As we have recently proved that chemically modified α-cyclodextrin cannot interact with the TPPTS ligand[10] or with the $[RhH(CO)(TPPTS)_3]$[9] complex (due to their smaller cavity than β-CD), it was of great interest to evaluate the behaviour of α-cyclodextrin derivatives in biphasic rhodium-catalyzed hydroformylation. Herein, we report the influence of the addition of these compounds on the hydroformylation rate and the linear to branched aldehydes ratio. These experiments were con-

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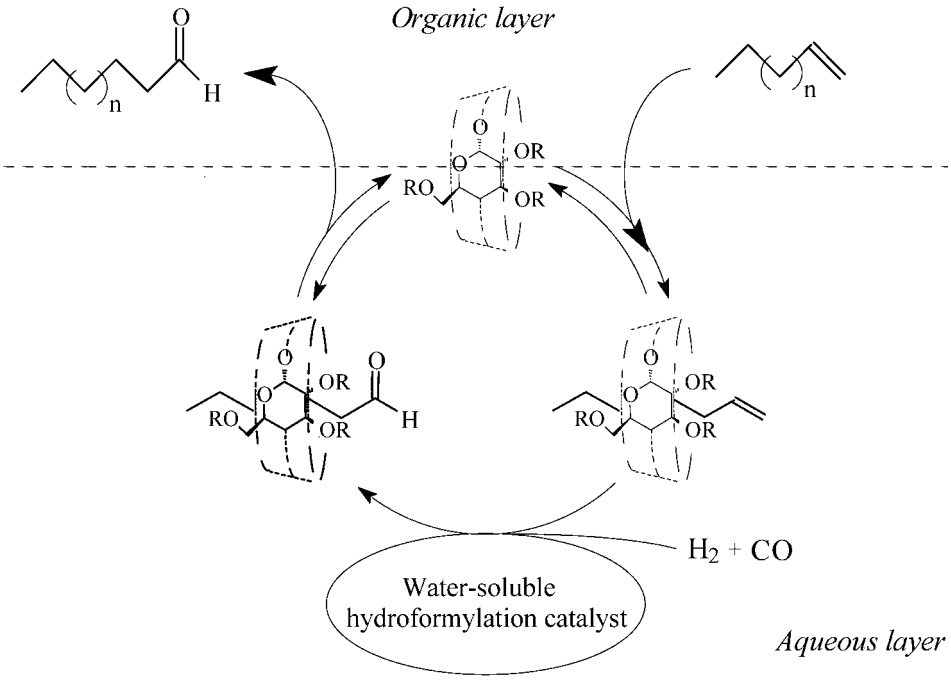
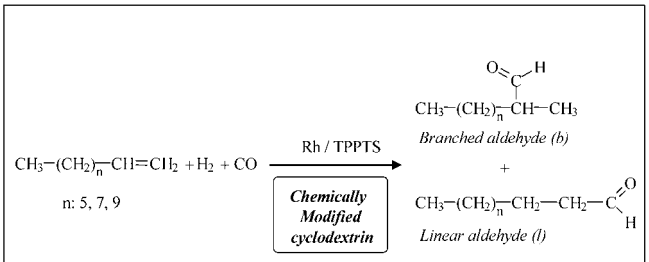


Figure 1. Principle of the cyclodextrin-based hydroformylation process.

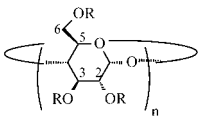
ducted using a $Rh(acac)(CO)_2$/TPPTS combination as catalyst precursor and 1-octene, 1-decene or 1-dodecene as higher olefins (Figure 2).

The more significant results are summarised in Table 1. At first, control experiments were performed in the absence of any phase-transfer promoter under standard reaction conditions in order to determine precisely the influence of each cyclodextrin (entries 1–3). As expected, the conversion was very low without cyclodextrin and did not exceed 2 or 3% after 6 h. Moreover, an important part of the starting olefin was isomerized and the aldehyde selectivity varied between 33 to 67%. As already reported,[7] addition of RAME-β-CD to the reaction medium greatly increased the reaction rate since the conversion of 1-octene and 1-decene reached 90 and 95%, respectively, after 6 hours with an aldehyde selectivity up to 97%. Concomitantly, the l/b aldehyde ratio dropped from 2.8 to 1.7 or 1.8.

Before discussing the effect of chemically modified α-cyclodextrins on the hydroformylation rate and aldehyde selectivity, it is worth mentioning that some preliminary experiments were performed with the native α-cyclodextrin. As already reported by Anderson et al.,[6c] the results were totally disappointing. Indeed, large amounts of solid were recovered in the bottom of the reactor at the end of the reaction and no increase in the reaction rate was observed with this cyclodextrin. NMR analyses indicated that the recovered solid was composed of water-insoluble inclusion complexes formed between the higher olefins and the unmodified cyclodextrin. This experiment demonstrates clearly that native α-cyclodextrin cannot be used as a mass



Structure of the chemically modified cyclodextrin



Abbreviations	n	R	Carbon bearing the OR group	OH group substituted per glucopyranose unit
RAME-β-CD	7	$-CH_3$	2, 3, 6	1.8
HP-α-CD	6	$-CH_2-CH(OH)-CH_3$	2	0.6
RAME-α-CD	6	$-CH_3$	2, 3, 6	1.8

Figure 2. Rhodium-catalyzed hydroformylation of long-chain olefins in the presence of chemically modified cyclodextrins.

Table 1. Hydroformylation of long-chain olefins in the presence of different chemically modified cyclodextrins.[a]

Entry	Olefin	CD	CD/Rh ratio	Time [h]	Conversion [%][b]	Selectivity [%][c]	l/b ratio[d]
1	C_8H_{16}	(-)	(-)	6	3	33	2.8
2	$C_{10}H_{20}$	(-)	(-)	6	3	59	2.8
3	$C_{12}H_{24}$	(-)	(-)	6	2	67	2.8
4	C_8H_{16}	RAME-β-CD	12	6	90	97	1.7
5	$C_{10}H_{20}$	RAME-β-CD	12	6	97	98	1.8
6	C_8H_{16}	HP-α-CD	12	6	28	97	2.9
7	C_8H_{16}	HP-α-CD	12	24	67	98	2.9
8	$C_{10}H_{20}$	HP-α-CD	12	6	24	88	3.0
9	$C_{10}H_{20}$	HP-α-CD	12	24	26	88	3.0
10	$C_{10}H_{20}$	HP-α-CD	6	6	15	74	3.0
11	$C_{10}H_{20}$	HP-α-CD	24	6	40	88	3.0
12	$C_{10}H_{20}$	HP-α-CD	48	6	57	89	3.0
13	$C_{12}H_{24}$	HP-α-CD	12	6	6	84	2.9
14	**C_8H_{16}**	**RAME-α-CD**	**12**	**6**	**96**	**99**	**3.0**
15	$C_{10}H_{20}$	RAME-α-CD	12	6	43	91	2.8
16	$C_{10}H_{20}$	RAME-α-CD	12	24	65	92	2.8
17	$C_{12}H_{24}$	RAME-α-CD	12	6	9	92	2.8
18	$C_{12}H_{24}$	RAME-α-CD	12	24	28	93	2.8

[a] Experimental conditions: Rh(acac)$(CO)_2$ (4.07×10^{-2} mmol), TPPTS (0.21 mmol), H_2O (11.5 mL), olefin (20.35 mmol), 80 °C, CO/H_2 (1/1): 50 atm.
[b] Calculated with respect to the starting olefin.
[c] (Mol. of aldehydes)/(mol. of converted olefins) × 100. The side products were mainly isomeric olefins.
[d] Ratio of linear to branched aldehyde product.

transfer promoter due to the water insolubility of the olefin/α-cyclodextrin inclusion complexes.

As indicated in Table 1, hydroxypropylated-α-cyclodextrin (HP-α-CD) was not such an efficient mass transfer promoter as RAME-β-CD under comparable reaction conditions (Table 1, entries 6, 8, 13). Nevertheless, no solid product was formed during the reaction and the conversion can be notably increased. For instance, in the case of 1-octene, the conversion after 6 hours was almost ten-fold higher than in the corresponding control experiment (compare entries 1 and 6). On the other hand the effect was less marked with 1-dodecene (6% conversion after 6 h instead of 2% without cyclodextrin – entries 3 and 13). In the same way, the aldehyde selectivity was higher in the presence of HP-α-CD. The best aldehyde selectivity was observed with 1-octene (97%) and regularly decreased from C_8 to C_{12} olefins (97%, 88% and 84% for the C_8, C_{10} and C_{12} olefins, respectively). Interestingly, the aldehyde selectivity was always higher than that obtained without cyclodextrin. These promising results prompted further investigation to delineate the behaviour of this α-cyclodextrin in the biphasic hydroformylation reaction. The effect of cyclodextrin concentration was investigated with 1-decene as substrate (entries 8 and 10–12). The activity and selectivity increased with the HP-α-CD concentration whereas the l/b ratio remained unchanged. It is also noteworthy that the conversion regularly increased during the reaction in the case of 1-octene whereas with 1-decene the reaction practically stopped after 6 hours that corresponds to 25% conversion (compare entries 6 and 7 and entries 8 and 9). This decay of the global activity of the system is not ascribable to the decomposition of the rhodium catalytic species since the $[RhH(CO)(TPPTS)_3]$ complex was stable under similar reaction conditions[9] and that the phenomenon seems not to occur with the 1-octene. A poisoning of the HP-α-CD by the reaction products is probably the origin of this phenomenon. In fact, the C_{11} aldehydes produced during the reaction likely form more stable inclusion complexes with HP-α-CD than the C_9 aldehydes. Thus, the HP-α-CD cannot play its role of phase transfer agent for the substrate when the aldehyde concentration is too high.

This problem can be easily overcome by using another chemically modified α-cyclodextrin: the randomly methylated α-cyclodextrin (RAME-α-CD). Indeed, Table 1 shows that the RAME-α-CD was much more efficient than HP-α-CD especially in the case of 1-octene. Actually, the conversion with 1-octene was *even higher than the one observed with RAME-β-CD* and reached 96% after 6 hours with an excellent aldehyde selectivity of 99%. On the other hand, RAME-α-CD was less suitable with 1-decene since the conversion after 6 hours was only the half of that observed with RAME-β-CD under the same conditions. Nevertheless, it must be pointed out that the conversion regularly increased and there was no inhibition of the reaction (entries 15 and 16). In the same way, no inhibition of the reaction was found with 1-dodecene although the efficiency of the system based on RAME-α-CD markedly decreased again (entries 17 and 18). Interestingly, whatever the

olefin, the aldehyde selectivities obtained with the RAME-α-CD were higher than those obtained with the HP-α-CD, confirming the beneficial effect of α-cyclodextrins on the aldehyde selectivity. Much more interesting is the value of the l/b ratio obtained with this cyclodextrin. Indeed, whatever the olefin, the l/b ratio remained identical to the one observed in control experiments, suggesting again that the behaviour of the Rh/TPPTS catalytic system was not modified by the presence of methylated α-cyclodextrins.

Two factors can likely account for the high reaction rates observed with RAME-α-CD. The first is the surface-active behaviour of this cyclodextrin[11] and, the second, the lower stability of the RAME-α-CD/aldehydes inclusion complexes.[12] Indeed, the possibility to form a stabilizing hydrogen bond between the aldehyde group of the product and the OH group of the cyclodextrin is greatly reduced in such a host compound. The high aldehydes selectivities (up 99%) observed with the α-cyclodextrins result probably from the formation of inclusion complexes. Indeed, when the olefin is inside the hydrophobic host cavity of the α-cyclodextrins, the formation of isomerizing species leading to internal olefins by β-hydride elimination is prohibited by the steric hindrance. The very high selectivities ($>91\%$) observed with RAME-α-CD could be due to presence of a deep hydrophobic host cavity. Indeed, attachment of 11–14 methyl groups to the α-CD greatly extends the cavity of the α-CD. Thus, the RAME-α-CD has a much more important lipophilic domain and cavity volume than HP-α-CD or native α-CD due to the increase in the height of the CD torus. This gives rise to CDs that wrap more efficiently the hydrophobic olefins.[12] Finally, it is noteworthy that we have also observed this remarkable protective effect of complexation with chemically modified β-cyclodextrin during hydrocarboxylation[13] and Wacker oxidation[14] of water-insoluble olefins.

In conclusion, contrary to modified β-cyclodextrins, the use of modified α-cyclodextrins as mass transfer promoter in the aqueous two-phase hydroformylation of higher olefins allows us to preserve the intrinsic properties of the classical Rh/TPPTS catalytic system as no decrease in the l/b aldehyde ratio was observed. From a point of view of reaction rate, the stability of the inclusion complexes between the α-cyclodextrin derivatives and the substrate or the product appears as a crucial point. Work is underway to investigate quantitatively this important aspect of the two-phase hydroformylation assisted by chemically modified α-cyclodextrins.

Experimental Section

General Remarks

Dicarbonylacetylacetonatorhodium(I) and organic compounds (undecane, 1-octene, 1-decene, 1-dodecene) were purchased from Strem Chemicals and Aldrich Chemicals in their highest purity and used without further purification. Randomly methylated β-cyclodextrin (RAME-β-CD) was purchased from Aldrich Chemicals. Randomly methylated α-cyclodextrin (RAME-α-CD) was prepared by adapting a procedure reported by Kenichi et al.[15] These two cyclodextrins were partially methylated. Methylation occurred at positions 2, 3, or 6 and 1.8 OH groups per glucopyranose unit were statistically modified. Hydroxypropylated α-cyclodextrin (HP-α-CD) was obtained from Aldrich Chemicals. This cyclodextrin was partially *O*-2-hydroxypropylated; statistically 0.6 OH groups were modified per glucopyranose unit. Tris(3-sodium sulfonatophenyl)phosphine [TPPTS – $P(m\text{-}C_6H_4SO_3Na)_3$] was synthesized as reported by Gärtner et al.[16] The purity of the TPPTS was carefully controlled. In particular, ^{31}P solution NMR indicated that the product was a mixture of phosphine (*ca.* 98%) and its oxide (*ca.* 2%). Carbon monoxide/hydrogen mixtures (1:1) were used directly from cylinders ($>99.9\%$ pure; Air Liquide). Distilled deionized water was used in all experiments. All catalytic reactions were performed under nitrogen using standard Schlenk techniques. All solvents and liquid reagents were degassed by bubbling nitrogen for 15 min before each use or by two freeze-pump-thaw cycles before use.

Catalytic Experiments

$Rh(acac)(CO)_2$ (4.07×10^{-2} mmol), TPPTS (0.21 mmol) and the required amount of chemically modified cyclodextrin were dissolved in 11.5 mL of water. The resulting aqueous phase and an organic phase composed of olefin (20.35 mmol) and undecane (4 mmol – GC internal standard) were charged under an atmosphere of N_2 into the 50-mL reactor which was heated at 80 °C. Mechanical stirring by means of a multipaddle unit was then started (1500 rpm) and the autoclave was pressurized with 50 atm of CO/H_2 (1/1) from a gas reservoir connected to the reactor through a high pressure regulator valve allowing us to keep constant the pressure in the reactor throughout the whole reaction. The reaction medium was sampled during the reaction for GC analyses of the organic phase after decantation. For kinetic measurements the time corresponding to the addition of CO/H_2 was considered as the beginning of the reaction.

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