ELSEVIER

Journal of Molecular Catalysis A: Chemical 176 (2001) 105–116

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Rhodium catalyzed hydroformylation of water insoluble olefins in the presence of chemically modified β-cyclodextrins: evidence for ligand-cyclodextrin interactions and effect of various parameters on the activity and the aldehydes selectivity

Thomas Mathivet [a], Catherine Méliet [a], Yves Castanet [a], André Mortreux [a], Laurent Caron [b], Sébastien Tilloy [b], Eric Monflier [b,*]

[a] *Laboratoire de Catalyse de Lille, UPRESA 8010, ENSC Lille, B.P. 108, 59652 Villeneuve d'Ascq, France*
[b] *Laboratoire de Physico-Chimie des Interfaces et Applications, Faculté des Sciences J. Perrin, Université d'Artois, Rue Jean Souvraz, S.P. 18, 62307 Lens, France*

Received 3 August 2000; accepted 17 April 2001

Abstract

The biphasic rhodium catalyzed hydroformylation of water insoluble olefins in the presence of chemically modified β-cyclodextrins has been investigated. The influence of various parameters, such as the nature of the β-cyclodextrin, the concentrations of phosphine or cyclodextrin and the temperature is illustrated using 1-decene as a model substrate. The formation of inclusion complexes between the different components of the system is also discussed on the basis of NMR experiments. The results indicate that the chemically modified cyclodextrins (CyDs) must not be considered only as inverse phase transfer catalysts but also as compounds which, by trapping the water soluble ligand, can modify the equilibria between the different catalytic species.

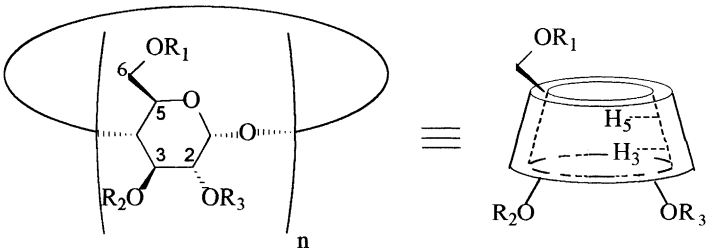
Keywords: Biphasic catalysis; Cyclodextrins; Hydroformylations; Phase-transfer catalysis; Rhodium

1. Introduction

Hydroformylation of olefins is one of the most important commercial processes for the production of aldehydes and alcohols [1,2]. Although the rhodium based process widely dominates in the hydroformylation of C_2–C_4 olefins, the hydroformylation of higher olefins is exclusively carried out with cobalt catalysts [3]. As a matter of fact, separation of products from rhodium solution by distilling off the aldehydes becomes troublesome with increasing molecular weight of olefin. Among the different approaches that have been described to solve this crucial problem, the two-phase catalysis where the catalyst is dissolved in a phase which contains neither the substrate nor the products is of great interest [4–12]. Indeed, the catalyst can be recovered at the end of the reaction by simple decantation of the two layers and reused several times without impairment of the catalyst properties. The rhodium catalyst can be dissolved in an aqueous [13–18] or fluorous [19–21] phase or an ionic salt [22,23]. The aqueous-organic two-phase system is one of the most attractive systems from an

* Corresponding author. Fax: +33-3-21-79-17-55.
E-mail address: monflier@univ_artois.fr (E. Monflier).

1381-1169/01/$ – see front matter
PII: S1381-1169(01)00229-1



n = 6, 7, 8: α-,β-,γ-cyclodextrin

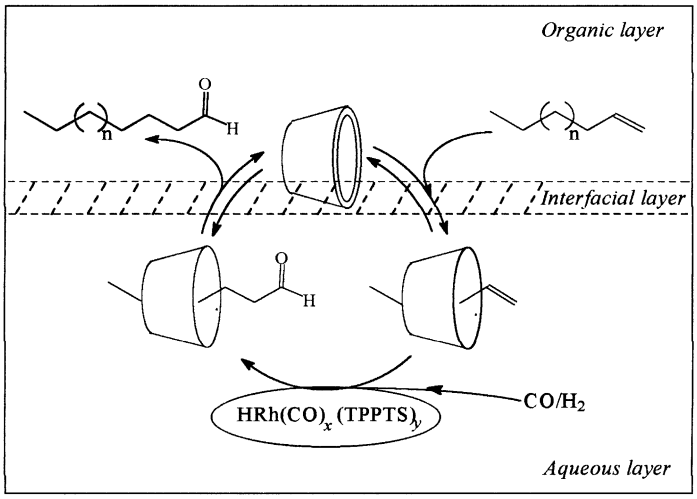
R_n: alkyl, acyl, hydroxypropyl, hydrogen

Scheme 1. Schematic representation of the shape of α-, β- and γ-CyD. The protons H-3 and H-5 are situated inside the host cavity, whereas protons H-1, H-2 and H-4 point outwards. The cyclodextrin is called DMCyD when R_1, R_2, R_3 are equal to $–CH_3$, $–CH_3$ and H, respectively.

economical and environmental point of view [24–27]. However, owing to the low water solubility of higher olefins, commercially viable hydroformylation rate can only be obtained by using surface active [28–36] or thermoregulated phase transfer ligands [37–40] or mass transfer promoter, such as surfactants [41–44] and cosolvents [45,46].

In this context, we have proposed the use of chemically modified β-cyclodextrins to improve the mass transfer between the organic and aqueous phases [47,48]. Cyclodextrins (CyDs) are cyclic oligosaccharides composed of 6, 7 or 8 glucose units linked by a α-(1–4) glucosidic bond and have traditionally been designated as α-, β- and γ-CyD, respectively [49,50]. Their molecular geometries are characterized by the shape of a truncated cone with the 3-OH and 6-OH hydroxyl groups of the respective glucose units occupy the wider and the narrower rim of the cone, respectively [51,52]. The CyD cavity is essentially hydrophobic and can host a wide range of organic molecules [53]. Substitution of the alcohol functions of CyD by other groups leads to the chemically modified CyDs. (Scheme 1) [54].

The nature of the substituent and the degree of substitution of chemically modified CyDs affect greatly their ability to form inclusion complexes and their



Scheme 2. Rhodium catalyzed hydroformylation of water-insoluble olefins in the presence of cyclodextrin. The cyclodextrin is schematically represented by a truncated cone.

relative solubility in water and organic solvents [55–59].

The role played by modified CyDs in biphasic catalysis is ascribed to their complexing properties and we have proposed that CyDs operate as inverse phase transfer catalysts according to the mechanism depicted in Scheme 2.

CyDs form an inclusion complex with the substrate in the organic phase and/or at the liquid–liquid interface. Owing to its significant solubility in water, the inclusion complex can migrate into the aqueous phase, allowing the substrate to react with the catalyst. After reaction, the reaction product is released in the organic phase and the transfer cycle can go on [60–63]. In each case, mass transfer is only efficient if the following conditions are satisfied: (i) CyD forms easily an inclusion complex with the substrate; (ii) the inclusion complex is soluble in the aqueous phase; (iii) the reactive function of the substrate is accessible to the catalyst; (iv) the reaction product can dissociate easily from the inclusion complex.

As numerous factors can affect the above conditions, we have studied the effect of different parameters (functionalization of the β-CyD; concentrations of phosphine and CyD; temperature) on the reaction rate and aldehydes selectivity. The formation of inclusion complexes between the different components of the system (CyD/olefin; CyD/aldehydes; CyD/phosphine) will be discussed from NMR experiments. The two-dimensional rotating-frame overhauser enhancement spectroscopy (ROESY) method has been also used for this purpose since it was known that this tool provides the most sensitive approach to the structural analysis of CyDs inclusion complexes [64].

2. Results and discussion

2.1. Catalytic behavior of different modified CyDs

1-Decene was chosen as a model substrate. In the absence of CyD, the conversion after 8 h is very low and isomerization of the substrate is important (Table 1, entry 1). In the presence of native β-CyD, the conversion is only increased by a factor of about 2 (entry 2). Interestingly, functionalization of the β-CyD enables to enhance greatly the conversion and aldehyde selectivity. The best results are obtained with dimethyl-β-cyclodextrin (DMCyD), a cyclodextrin mainly methylated in position 2 and 6 (Scheme 1

Table 1
Hydroformylation of 1-decene in the presence of chemically modified β-cyclodextrins[a]

Entry	β-Cyclodextrin			*t* (h)	Conversion (mol%)	Aldehydes selectivity (mol%)[b]	Aldehydes yield (mol%)	*n*/*i* ratio[c]
	R[d]	Nb[e]	S[f]					
1	–	–	–	6	10	60	6	2.7
2	H	0	18.5	8	19	78	15	2.1
3	CH_3	12.6	570 (20)	8	76	91	69	1.8
4[g]	CH_3	12.6	570 (20)	6	100	95	95	1.9
5	CH_3	14	570 (20)	8	75	91	68	1.9
6	CH_3	21	570 (<10)	8	30	57	17	2.5
7	$COCH_3$	14	>100	8	46	57	26	2.6
8	$COCH_3$	21	<1	8	6	66	4	2.6
9	$CH_2CH(OH)CH_3$	6.3	>330	8	32	84	27	2.0
10	SO_3Na	9	>400	8	7	69	5	2.8

[a] Conditions, $Rh(acac)(CO)_2$: 0.16 mmol, TPPTS: 0.8 mmol, cyclodextrin: 1.12 mmol except entry 4 mmol, H_2O: 45 ml, olefin: 80 mmol, undecane: 4 mmol, $P(CO/H_2)$: 50 bar, T: 80°C.

[b] (Mol. of aldehydes)/(mol. of converted olefin) × 100. The side products were mainly isomeric olefins.

[c] Normal to branched aldehyde ratio.

[d] Cyclodextrin modification.

[e] Average number of substituted hydroxy group.

[f] Solubility of cyclodextrin in water at 25°C (g/l). The number in brackets corresponds to the solubility of cyclodextrin in water at 80°C (g/l).

[g] Cyclodextrin: 4 mmol.

and experimental part). Thus, a total conversion and a 95% yield in undecanal are reached after 6 h for a DMCyD/Rh ratio of 14 (Table 1 entry 4).

Further substitutions of OH groups have a rather detrimental effect. Actually, permethylated β-CyD exhibits a much lower activity and selectivity than DMCyD (compare entries 6 and 3). Other substituents, such as $COCH_3$ or $CH_2CH(OH)CH_3$ also induce an enhancement of the efficiency of the process but this effect is less marked than with OCH_3 and is still function of the degree of substitution of the CyD (entries 7–9).

The effectiveness of chemically modified β-CyD seems closely related to their solubility in both aqueous and organic phases. As β-CyD and sulfonated β-CyD are almost insoluble in the organic phase, they cannot form easily an inclusion complex with the substrate and the mass transfer is very low. In contrast, DMCyD and diacetylated β-CyD that are soluble in water and much more soluble in organic phase can efficiently transfer the substrate from the organic to the aqueous phase. Finally, permethylated and peracetylated β-CyD are highly soluble in the organic layer but weakly soluble in water at 80°C. Consequently, the transfer of 1-decene diminishes in comparison with the one observed with DMCyD.

DMCyD leads also to a significant increase for aldehyde selectivity (90% versus ca. 60% without CyD). In both cases, the main by-products are the internal olefins resulting from isomerization of the substrate via a β-H elimination process. The high selectivities observed with DMCyD can be probably attributed to the deeper cavity of the methylated cyclodextrin. Indeed, methylation of CyD extends to about 1.1 nm the depth of the cavity and enables a better recognition of the olefin [65,66]. Thus, the position of the β-CH_2 group, included in the cavity, is not favorable for the β-H elimination process.

As the 1-decene/DMCyD couple leads to the best results, the influence of the other reaction parameters was investigated with these compounds.

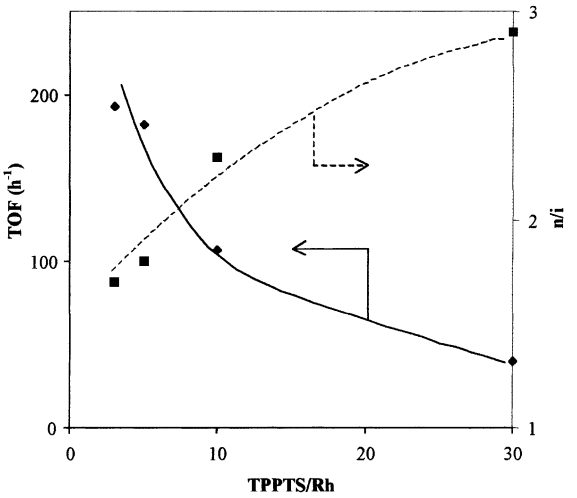


Fig. 1. Effect of TPPTS/Rh ratio on the initial TOF and the *n*/*i* ratio. Conditions: $Rh(acac)(CO)_2$: 4.07×10^{-2} mmol (10.5 mg), DMCyD: 0.48 mmol (640 mg), water: 11.5 ml, 1-decene: 20.5 mmol (2.87 g), undecane: 1.92 mmol (300 mg), *P* (CO/H_2): 50 bar, *T*: 80°C. TOF = mole number of 1-decene converted per mole of Rh and per hour calculated from the conversion after 30 min.

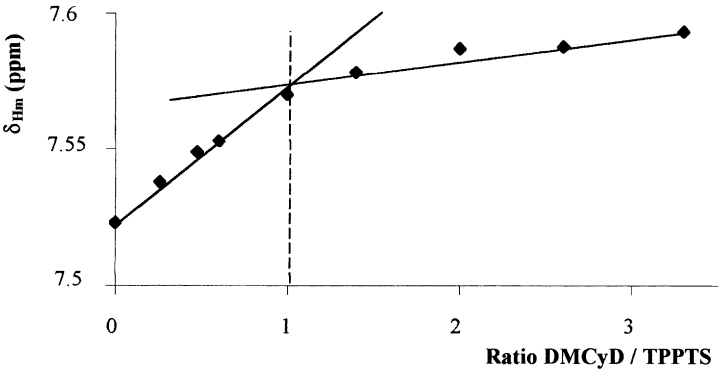


Fig. 2. Plot of the changes in chemical shift of the *meta* proton resonances of the TPPTS (δ_{H_m}) as a function of the DMCyD to TPPTS molar ratio. [TPPTS]: 3 mM (300 MHz; D_2O; 298 K).

2.2. Influence of the TPPTS concentration

The effect of the TPPTS concentration was investigated at constant Rh concentration (3.4 mmol/l) and constant DMCyD/Rh ratio (DMCyD/Rh = 12) (Fig. 1).

Fig. 1 shows that the initial activity markedly decreases with the amount of TPPTS and that the *n*/*i* ratio increases. The decrease in activity with the amount of ligand is well-known in biphasic medium and is attributed (i) to the increase in the solution ionic strength and (ii) to the fact that the equilibrium between $HRh(CO)(TPPTS)_3$ and $HRh(CO)(TPPTS)_2$ is shifted toward the inactive $HRh(CO)(TPPTS)_3$ species [67].

With our catalytic system, the formation of TPPTS/DMCyD complexes which mobilizes a part of the DMCyD also contributes to the rate decrease. Indeed, although the formation of such inclusion complexes is more difficult to characterize than in the case of β-CyD due to the use of a mixture of methylated CyDs [68], we have obtained some evidences

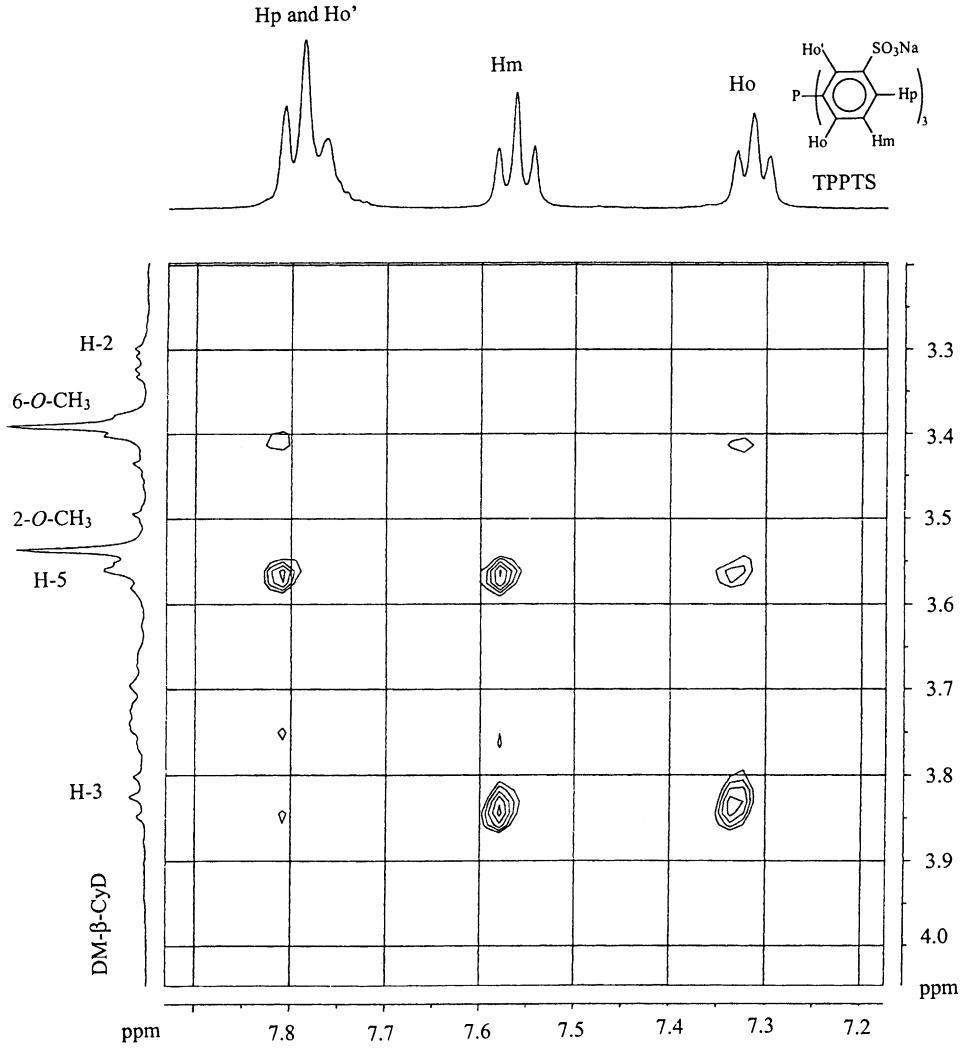


Fig. 3. Partial contour plots of ROESY experiment (D_2O, 298 K, 400 MHz) performed on a sample containing 10 mM of DMCyD and 10 mM of TPPTS.

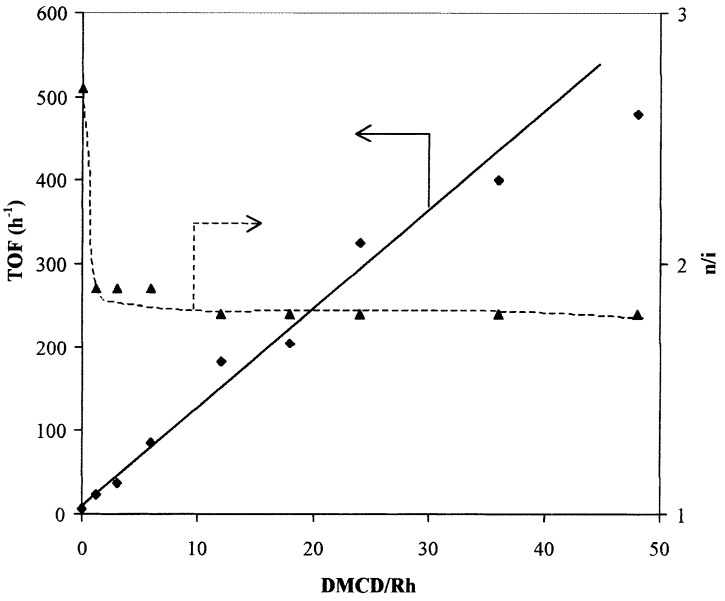


Fig. 4. Influence of the DMCyD/Rh ratio on the initial TOF and the *n*/*i* ratio. Conditions: $Rh(acac)(CO)_2$: 4.07×10^{-2} mmol (10.5 mg), TPPTS: 21×10^{-2} mmol (120 mg), water: 11.5 ml, 1-decene: 20.5 mmol (2.87 g), undecane: 1.92 mmol (300 mg) (GC internal standard), *P* (CO/H_2): 50 bar, *T*: 80°C. TOF = mole number of 1-decene converted per mole of Rh and per hour calculated from the conversion after 30 min.

for the formation of TPPTS/DMCyD inclusion complexes. Fig. 2 shows the experimental chemical shift of the *meta*-proton of the TPPTS as a function of the DMCyD to TPPTS molar ratio.

A continuous shielding of this proton until a 1:1 ratio was observed and an average 1:1 association constant of 2400 M^{-1} (±15%) could be determined by assuming a 1:1 equilibrium [68]. The 2D-ROESY spectrum of a mixture of TPPTS and DMCyD provided also information on the structure of the inclusion complexes (Fig. 3).

The intense cross-peaks between the protons of TPPTS and protons H-3 and H-5 of DMCyD indicate that one of phenyl groups of TPPTS is included into the hydrophobic cavity. Moreover, as no cross-peak between the protons of TPPTS and the H-6 proton of DMCyD is observed, the inclusion occurs by the upper rim of DMCyD.

2.3. Influence of the cyclodextrin concentration

Fig. 4 shows the variation of initial turnover frequency (TOF) as a function of the DMCyD/Rh ratio.

The TOF increases linearly until a ratio of about 30, suggesting strongly that the overall rate of the reaction is under mass transfer control. At higher DMCyD/Rh ratio (DMCyD/Rh = 48) the plot diverges from

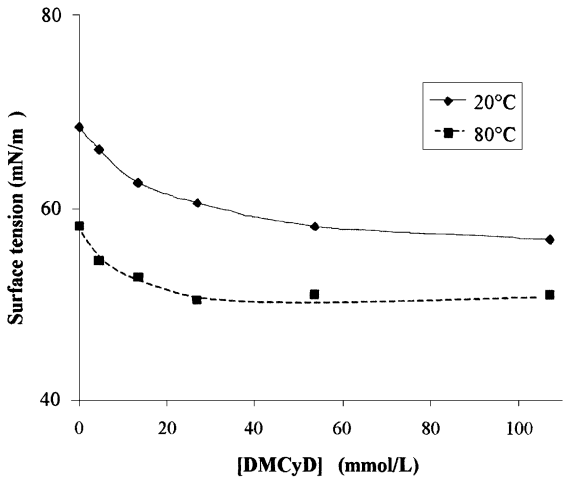


Fig. 5. Surface tension dependence on DMCyD concentration at 20 and 80°C. Conditions: water: 20 ml; TPPTS: 209 mg.

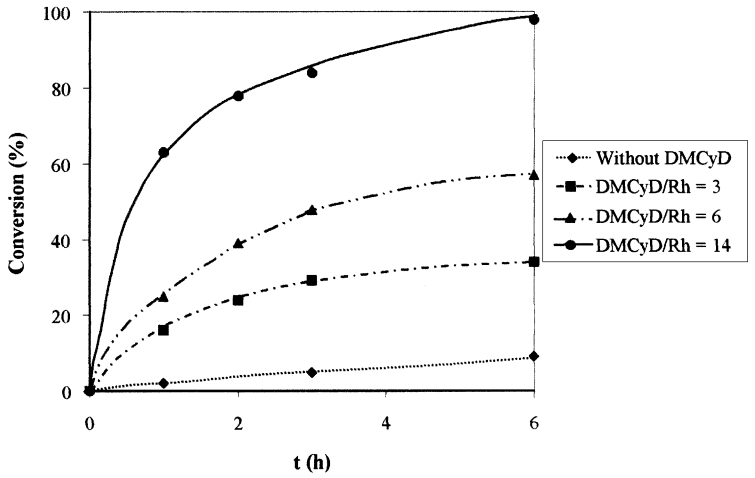


Fig. 6. Decene conversion as a function of reaction time for different DMCyD/Rh ratios. Conditions: $Rh(acac)(CO)_2$: 0.16 mmol, TPPTS: 0.8 mmol, H_2O: 45 ml, olefin: 80 mmol, undecane: 4 mmol, P (CO/H_2): 50 bar, T: 80°C

the straight-line, indicating a change of the limiting step.

As it is known that DMCyD is a surface active compound [59], some interfacial tension measurements have been performed to be sure that the increase in the activity with the DMCyD concentration cannot be attributed to the decrease in the interfacial tension between the organic phase and the aqueous phase. The evolution of the surface tension (γ) of an aqueous solution with the DMCyD concentration has been studied at 20 and 80°C (Fig. 5).

In each case, addition of DMCyD to pure water induced a rapid decrease of the surface tension until a DMCyD concentration of 20 mmol/l, corresponding to a DMCyD/Rh ratio of 3 in the catalytic runs. Above this concentration, γ remains almost constant. These results prove undoubtedly that the beneficial effect of the DMCyD cannot be attributed to its surface active properties. Indeed, whereas the surface tension varies only very slightly above a concentration of 20 mmol/l (DMCyD/Rh = 3), a significant increase in the catalytic activity is observed until a DMCyD/Rh ratio of about 30.

Careful examination of the curves depicting the conversion as a function of time for different DMCyD concentrations indicates that the activity decreases markedly at high conversion (Fig. 6).

The slowing down of the catalytic activity with the increase in aldehydes concentration could be due to poisoning of the DMCyD by the aldehydes. Actually, at high aldehyde concentration, much of the cyclodextrin forms rather inclusion complexes with aldehydes than with the olefin. The higher affinity of aldehydes for cyclodextrin was partially confirmed by ^{1}H NMR experiments. Whereas the ^{1}H NMR spectrum of the β-CyD or the DMCyD exhibited no change in the presence of 1-decene, the ^{1}H NMR spectrum of the DMCyD or β-CyD is strongly affected by the aldehydes. For instance, the addition of undecanal resulted in upfield shifts of the resonances of the proton H-3 and H-5 of β-CyD (Fig. 7).

As these protons are located in the β-CyD cavity, the reality of the inclusion process between the aldehyde and the cyclodextrin is undeniable. It is worth mentioning that similar results with nonanal have also been reported [69,70].

2.4. Temperature effect

From the curves depicting the overall aldehyde formation versus time at different temperatures over the 40–120°C range, the initial catalytic activity can be determined. The corresponding activation parameters were calculated from a classical Arrhenius plot (Fig. 8).

The graph obtained consists of two straight-line segments that intersect for a temperature of about 68°C. It appears that Ea is significantly higher at low

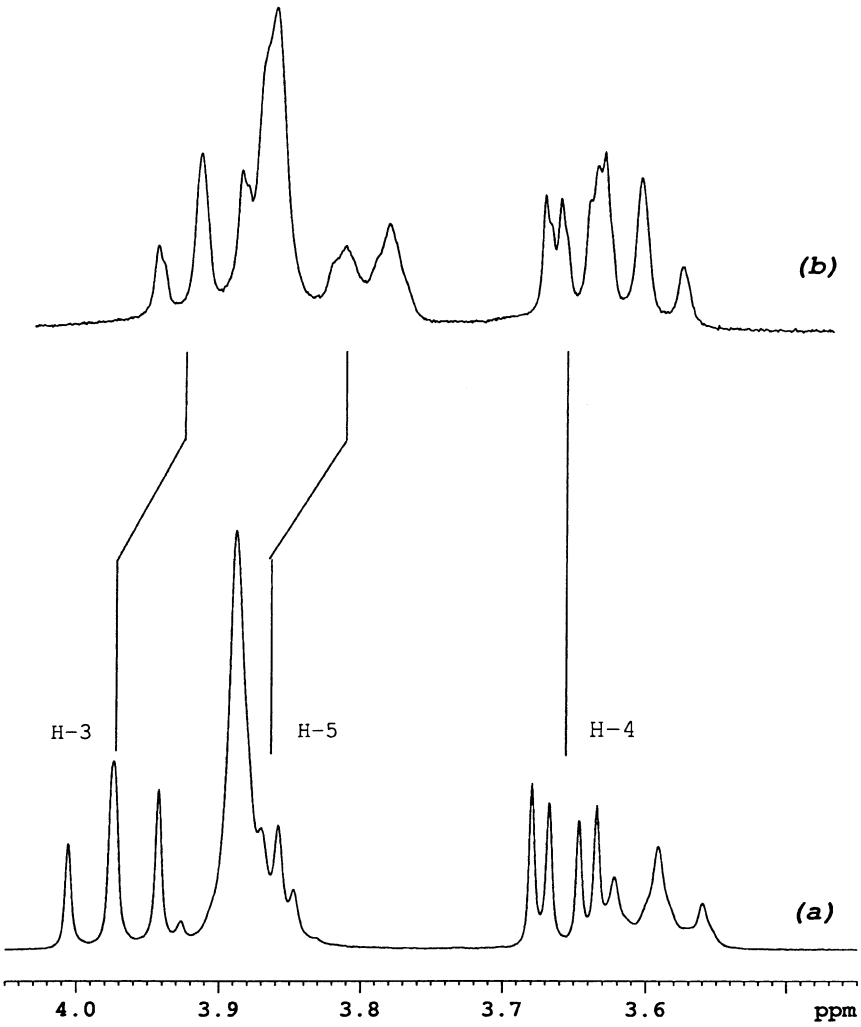


Fig. 7. Partial ^{1}H NMR spectra of 4 mM β-CyD in the absence (a) and in the presence (b) of 4 mM undecanal (D_2O, 298 K, 300 MHz).

temperature (63.5 kJ mol^{-1}) than at high temperature (5.8 kJ mol^{-1}). The latter value is typical of a process in which the mass transfer is the limiting step. This result is in good agreement with the one observed at 80°C with variable concentrations of DMCyD and for which we have found that the reaction was mass transfer controlled at low DMCyD/Rh ratios (<30). It is also significant to note that the representative point of the initial activity obtained at 80°C for a DMCyD/Rh ratio of 48 is situated on the Arrhenius plot on the prolongation of the straight-line corresponding to low temperatures results (dotted line on the graph). This indicates that the reaction kinetic controls the process at this high DMCyD/Rh ratio.

The activation energy found at low temperatures (below 68°C) is relatively close to that reported for hydroformylation of various alkenes in the presence of homogeneous catalytic systems (57.3 kJ mol^{-1} for 1-dodecene [71–73], 48.1 kJ mol^{-1} for 1-decene [71–73], 76.1 kJ mol^{-1} for ethylene [74]) and heterogeneous catalytic systems (biphasic conditions 65.6 kJ mol^{-1} for 1-octene [75]; supported aqueous phase catalysis 48.8–79.4 kJ mol^{-1} for 1-heptene [8,9]). This result suggests strongly that, in the

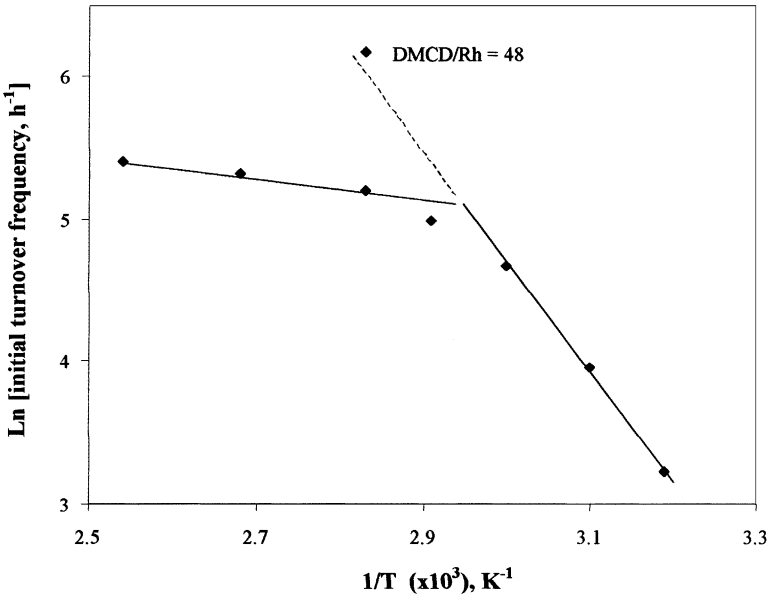


Fig. 8. Initial rate dependence on the reaction temperature. Conditions: $Rh(acac)(CO)_2$: 4.07×10^{-2} mmol (10.5 mg), TPPTS: 21×10^{-2} mmol (120 mg), DMCyD: 0.48 mmol (640 mg), water: 11.5 ml, undecane: 1.92 mmol (300 mg), P (CO/H_2): 50 bar.

presence of DMCyD, the elementary steps of the hydroformylation catalytic cycle and the catalytic species are similar to those without DMCyD. Nevertheless, the fact that the *n*/*i* ratio significantly decreases in the presence of DMCyD (1.8 with DMCyD versus 2.5–3 without (Table 1 and Fig. 4 where the decrease was observed even at low concentration)) could indicate that the equilibria between the different catalytic intermediates or/and the reactivity of the catalytic species toward the included olefin are modified.

3. Conclusion

This work indicates for the first time that CyDs must be considered not only as supramolecular carriers which transfer the olefin into the aqueous layer but also as compound that form inclusion complexes with some components of the catalytic system. In particular, CyDs can be poisoned by an excess of TPPTS and could also modify the equilibria between the different catalytic species by trapping the ligand. So, the cyclodextrin choice must be dictated not only by amphiphilic properties but also by its "passivity" towards the catalytic system components. Synthesis of chemically modified CyDs which will not form inclusion complexes with TPPTS is currently under way in our laboratory.

4. Experimental

4.1. Materials and apparatus

The chemically modified CyDs were supplied by Cyclolab (Budapest-Hungary) and Aldrich Chemical Co. and were used as received without further purification. In particular, commercially available DMCyD is a mixture of methylated β-cyclodextrins. Indeed, electrospray mass spectrum of this modified cyclodextrin exhibits signals at *m*/*z* 1311, 1325, 1339, 1353, 1367 and 1381 corresponding to different degrees of methylation. Dicarbonylacetylacetonato rhodium (I) and organic compounds were purchased from Strem Chemicals, Aldrich Chemical Co. and Acros Organics in their highest purity and used without further purification. Trisodium tris(*m*-sulfonatophenyl)phosphine (TPPTS) was synthesized as reported by Gärtner et al. [76]. The purity of the TPPTS was carefully controlled. In particular, ^{31}P solution NMR indicated

that the product was a mixture of TPPTS (ca. 98%) and its oxide (ca. 2%). Carbon monoxide and carbon monoxide/hydrogen mixture (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.

All the high pressure hydroformylation experiments were carried out in a 100 ml stainless steel autoclave supplied by Autoclave Engineers or in a 50 ml stainless steel microclave supplied by Parr. The reactors were fitted with arrangements for liquid sampling, automatic temperature control, variable stirring with precise speed measurement by tachometer display and pressure gauge. A safety rupture disk was also fitted to the reactor. Gas liquid chromatography analyses were carried out on a Chrompack 9001 apparatus equipped with a CP Sil 5-CB column (25 m × 0.32 mm).

Surface tension measurements were obtained by using a Lénard stirrup ($L = 20 \pm 0.2$ mm; $Ø = 0.5$ mm; weight = 0.68 g) with a LAUDA TD 1 tensiometer. The surface tensions of aqueous solutions were measured at 20 or 80°C until constant values.

The ^{1}H NMR spectra were recorded at 400.13 and 300.3 MHz on Bruker ASX 400 and DRX 300 apparatus, respectively. The 2D-ROESY experiments were run on the 400 MHz instrument using the software supplied by Bruker. Mixing times in ROESY experiments were 500 ms. The data matrix for the ROESY was made of 128 free induction decays, 1 K points each, resulting from the coaddition of 32 scans. The real resolution was 2.7, 4.9 Hz per points in F2 and F1, respectively. Chemical shifts are given in parts per million (ppm) relative to trimethyl-silyl-3-propionic acid D4 2,2,3,3 sodium salt (98% atom D) in D_2O using internal capillary. All NMR experiments were performed under nitrogen atmosphere with carefully deoxygenated D_2O.

4.2. Typical experiment for hydroformylation of olefins

In all experiments, the stirring speed and the CO/H_2 pressure were fixed to 1500 rpm and 50 bar, respectively. Indeed, a study on the effect of the stirring rates on the catalytic activity shows that the catalytic activity increases linearly up a rate equal to 600–800 rpm and levels off markedly beyond this rate. Above 800 rpm, stirring had practically no effect on the results. Experiments on effect of the CO/H_2 pressure show that the activity and to a lesser extent the aldehydes selectivity increase with pressure until about 10 bar. Above 10 bar, the increase in the pressure has a limited effect on both the activity, selectivity and *n*/*i* ratio. A pressure of 50 bar was chosen to avoid CO/H_2 diffusion problems.

In a typical experiment, $Rh(acac)(CO)_2$ (0.16 mmol), TPPTS (0.8 mmol) and chemically modified cyclodextrin (1.12 mmol) were dissolved in 100 ml of water. The resulting aqueous phase and a organic phase composed of olefin (80 mmol) and undecane (4 mmol, GC internal standard) were charged under an atmosphere of N_2 into the 100 ml reactor which was heated at 80°C. Mechanical stirring equipped with 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 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. The same procedure was used with the 50 ml autoclave except that the quantities used were those specified in the text.

Acknowledgements

We thank the Centre National de la Recherche Scientifique (CNRS) and Elf Atochem for their financial supports.

References

[1] C.D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes, Vol. 1, VCH, Weinheim, 1996, pp. 27–104.
[2] M. Beller, B. Cornils, C.-D. Frohning, C.-W. Kohlpaintner, J. Mol. Catal. 104 (1995) 17.
[3] B. Cornils, in: J. Falbe (Ed.), New Synthesis with Carbon Monoxide, Springer, Berlin, 1980 (Chapter 1).

[4] T. Jongsma, G. Challa, P.-W.-N.-M. Van Leeuwen, Macromol. Symp. 80 (1994) 241.
[5] A. Buhling, P.-C.-J. Kamer, P.-W.-N.-M. Van Leeuwen, J. Mol. Catal. 98 (1995) 69.
[6] S. Kanagasabathy, Z. Xia, G. Papadogianakis, B. Fell, J. Prakt. Chem. 337 (1995) 446.
[7] H. Bahrmann, M. Haubs, T. Muller, N. Schopper, B. Cornils, J. Organomet. Chem. 545 (1997) 139.
[8] J.-P. Arhancet, M.-E. Davies, J.-S. Merola, B.-E. Hanson, J. Catal. 121 (1990) 327.
[9] J.-P. Arhancet, M.-E. Davies, B.-E. Hanson, J. Catal. 129 (1991) 94.
[10] J.-P. Arhancet, M.-E. Davies, B.-E. Hanson, J. Catal. 129 (1991) 100.
[11] B. Driessen-Hölscher, Advances Catal. 42 (1998) 473.
[12] D. Koch, W. Leitner, J. Am. Chem. Soc. 120 (1998) 13398.
[13] B. Cornils, E.G. Kuntz, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis-Concepts and Applications, VCH, Weinheim, 1998, pp. 271–283.
[14] B. Cornils, Org. Process Res. Develop. 2 (1998) 121.
[15] B. Cornils, E. Wiebus, Chem. Tech. 25 (1995) 33.
[16] W.-A. Herrmann, C.-W. Kohlpaintner, Angew. Chem. Int. Ed. Engl. 32 (1993) 1524.
[17] B. Cornils, E.-G. Kuntz, J. Organomet. Chem. 502 (1995) 177.
[18] R.-A. Sheldon, J. Mol. Catal. 107 (1996) 75.
[19] I.-T. Horvath, Acc. Chem. Res. 31 (1998) 641.
[20] I.-T. Horvath, J. Rabai, Science 266 (1994) 72.
[21] I.-T. Horvath, G. Kiss, R.-A. Cook, J.-E. Bond, P.-A. Stevens, J. Rabai, E.-J. Mozeleski, J. Am. Chem. Soc. 120 (1998) 3133.
[22] N. Karodia, S. Guise, C. Newlands, J.-A. Andersen, J. Chem. Soc. Chem. Commun., (1998) 2341.
[23] Y. Chauvin, L. Mussmann, H. Olivier, Angew. Chem. Int. Ed. Engl. 34 (1995) 2698.
[24] G. Papadogianakis, R.-A. Sheldon, New J. Chem. 20 (1996) 175.
[25] B. Cornils, E. Wiebus, Recl. Trav. Chim. Pays-Bas 115 (1996) 211.
[26] E.-G. Kuntz, Chemtech 17 (1987) 570.
[27] E. Wiebus, B. Cornils, Chem. Ing. Tech. 66 (1994) 916.
[28] M.-S. Goedheijt, B.-E. Hanson, J.-N.-H. Reek, P.-C.-J. Kamar, P.-W.-N.-M. Van Leeuwen, J. Am. Chem. Soc. 122 (2000) 1650.
[29] B.-E. Hanson, H. Ding, C.-W. Kohlpaintner, Catal. Today 42 (1998) 421.
[30] H. Ding, J. Kang, B.-E. Hanson, C.-W. Kohlpaintner, J. Mol. Catal. 124 (1997) 21.
[31] T. Bartik, H. Ding, B. Bartik, B.-E. Hanson, J. Mol. Catal. 98 (1995) 117.
[32] R.-V. Chaudari, B.-M. Bhanage, R.-M. Deshpande, H. Delmas, Nature 373 (1995) 501.
[33] H. Ding, T.-E. Glass, B.-E. Hanson, Inorg. Chem. Acta 229 (1995) 329.
[34] H. Ding, B.-E. Hanson, T. Bartik, B. Bartik, Organometallics 13 (1994) 3761.
[35] H. Bahrmann, G. Deckers, W. Greb, P. Heymanns, P. Lappe, T. Mueller, J. Szameitat, E. Weibus, Eur. Pat. Appl. 602 (1994) 442.
[36] B. Fell, G. Papadogianakis, J. Mol. Catal. 66 (1991) 143.
[37] Y. Wang, J. Jiang, R. Zhang, X. Liu, Z. Jin, J. Mol. Catal. 157 (2000) 111.
[38] R. Cheng, X. Liu, Z. Jin, J. Organomet. Chem. 571 (1998) 201.
[39] X. Zheng, J. Jiang, X. Liu, Z. Jin, Catal. Today 44 (1998) 175.
[40] Z. Jin, X. Zheng, B. Fell, J. Mol. Catal. 116 (1997) 55.
[41] M.-J.-H. Russel, B.-A. Murrer, U.S. Patent No. 4,399,312 (1983).
[42] H. Bahrmann, P. Lappe, Eur. Pat. Appl. 602 (1994) 463.
[43] T. Bartik, B. Bartik, B.-E. Hanson, J. Mol. Catal. 88 (1994) 43.
[44] B. Fell, Tenside Surf. Det. 35 (1998) 326.
[45] P. Purwanto, H. Delmas, Cat. Today 24 (1995) 135.
[46] R.-M. Deshpande, P. Purwanto, H. Delmas, R.-V. Chaudhari, J. Mol. Catal. 126 (1997) 133.
[47] E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, Angew. Chem. Int. Ed. Engl. 34 (1995) 2269.
[48] E. Monflier, G. Fremy, S. Tilloy, Y. Castanet, A. Mortreux, Tetrahedron Lett. 36 (1995) 9481.
[49] J. Szejtli, Chem. Rev. 98 (1998) 1743.
[50] G. Wenz, Angew. Chem. Int. Ed. Engl. 33 (1994) 803.
[51] F.-W. Lichtenthaler, S. Immel, Liebigs Ann. (1996) 27.
[52] A.-W. Coleman, I. Nicolis, N. Keller, J.-P. Dalbiez, J. Incl. Phenom. 13 (1992) 139.
[53] E. Fenyvesi, L. Szente, N.R. Russell, M. McNamara, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, Vol. 3, Pergamon Press, Oxford, 1996, pp. 305–366.
[54] A.-R. Khan, P. Forgo, K.-J. Stine, V.-T. D'Souza, Chem. Rev. 98 (1998) 1977.
[55] H. Taguchi, N. Kunieda, M. Kinoshita, Makromol. Chem. Rapid Commun. 3 (1982) 495.
[56] H. Ikeda, R. Kojin, C.-J. Yoon, T. Ikeda, J. Inclusion Phenom. 7 (1989) 11.
[57] C.-M. Spencer, J.-F. Stoddart, R. Zarzycki, J. Chem. Soc. Perkin Trans 2 (1987) 1326.
[58] Y. Kubota, T. Tanimoto, S. Horiyama, K. Koizumi, Carbohyd. Res. 192 (1989) 159.
[59] Uekama, T. Irie, in: D. Duchêne (Ed.), Cyclodextrins and their industrial uses, Editions de Santé, Paris, 1987, pp. 395–439.
[60] E. Monflier, S. Tilloy, E. Blouet, Y. Barbaux, A. Mortreux, J. Mol. Catal. A: Chem. 109 (1996) 27.
[61] E. Monflier, E. Blouet, Y. Barbaux, A. Mortreux, Angew. Chem. Int. Ed. Engl. 33 (1994) 2100.
[62] E. Monflier, S. Tilloy, F. Bertoux, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 857.
[63] E. Monflier, S. Tilloy, Y. Castanet, A. Mortreux, Tetrahedron Lett. 39 (1998) 2959.
[64] H.-J. Schneider, F. Hacket, V. Rüdiger, H. Ikeda, Chem. Rev. 98 (1998) 1755.
[65] M. Czugler, E. Ecke, J.-J. Stezowski, J. Chem. Soc., Chem. Commun. (1981) 1291.

[66] N. Tanaka, A. Yamaguchi, Y. Araki, M. Araki, Chem. Lett. (1987) 715.
[67] H. Bahrmann, S. Bogdanovic, in: B. Cornils, W.-A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis-Concepts and Applications, VCH, Weinheim, 1998, pp. 306–321.
[68] E. Monflier, S. Tilloy, C. Méliet, A. Mortreux, S. Fourmentin, D. Landy, G. Serpateanu, New J. Chem. 23 (1999) 469.
[69] A. Botsi, K. Yannakopoulou, B. Perly, E. Hadjoudis, J. Org. Chem. 60 (1995) 4017.
[70] A. Bosti, K. Yannakopoulou, E. Hadjoudis, Carbohydr. Res. 241 (1993) 37.
[71] B.-M. Bhanage, S.-S. Divekar, R.-M. Deshpande, R.-V. Chaudhari, J. Mol. Catal. 115 (1997) 247.
[72] S.-S. Divekar, R.-M. Deshpande, R.-V. Chaudhari, Catal. Lett. 21 (1993) 191.
[73] R.V. Chaudhari, B. Bhanage, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis-Concepts and Applications, VCH, Weinheim, 1998, pp. 283–294.
[74] G. Kiss, E.-J. Mozeleski, K.-C. Nadler, E. VanDriessche, C. DeRoover, J. Mol. Catal. 138 (1999) 155.
[75] R.-M. Deshpande, P. Purwanto, H. Delmas, R.-V. Chaudhari, Ind. Eng. Chem. Res. 35 (1996) 3927.
[76] R. Gärtner, B. Cornils, H. Springer, P. Lappe, DE Patent No. 3235030 (1982).