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Cleavage of water-insoluble alkylallylcarbonates catalysed by a palladium/TPPTS/cyclodextrin system: effect of phosphine/cyclodextrin interactions on the reaction rate

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Abstract

An astonishing aspect of the aqueous organometallic catalysis assisted by randomly methylated β-cyclodextrin (RAME-β-CD) has been elucidated. Actually, it has been shown that the molecular recognition ability of RAME-β-CD towards the TPPTS ligand was responsible for a decrease in the rate of a palladium catalysed cleavage reaction of the water-insoluble allylundecylcarbonate. Indeed, when the TPPTS/RAME-β-CD ratio is too high, the cyclodextrin is poisoned by the ligand and the substrate transfer is diminished. Thus, the use of RAME-β-CD as an inverse phase transfer catalyst in palladium/TPPTS catalytic system has to be accurately controlled. On the contrary, randomly methylated α-cyclodextrin (RAME-α-CD) which is not able to associate to TPPTS led to better performances since no decrease in the activity was observed with this cyclodextrin. NMR experiments have been performed throughout this study to substantiate the catalytic results.

Keywords: Palladium; Water-soluble phosphines; Cyclodextrins; ^{1}H and $^{31}P\{^{1}H\}$ NMR; Molecular recognition; Carbonate cleavage

1. Introduction

During these last years, considerable advancements have been made in the field of aqueous organometallic catalysis involving water-soluble receptors such as calixarenes [1–4] and cyclodextrins [5–16] as inverse phase transfer catalysts. Indeed, by forming inclusion complexes with water-soluble substrates, these compounds increase notably the solubility of substrates in the aqueous phase containing the catalytic system and, consequently, the reaction rates. Moreover, while avoiding the formation of an emulsion, these compounds allow to use standard hydrosoluble ligands such as the sodium salt of trisulfonated triphenylphosphine obtained by sulfonation of triphenylphosphine [17–20]. Among the different supramolecular carriers evaluated in aqueous organometallic catalysis, the randomly methylated β-cyclodextrin (RAME-β-CD) holds a special place. Indeed, this methylated cyclodextrin is cheap, non-toxic, bulk commercially available [21] and allows the best activity enhancements in hydrocarboxylation [22], hydroformylation [23,24], hydrogenation [25], Wacker oxidation [26] and cleavage of allylic substrates [27].

Although the attractive effect of RAME-β-CD on the cleavage rate of numerous water-insoluble allylic substrates such as allylic carbonates, urethanes, thiocarbonates, ethers and esters has been clearly demonstrated [28], influence of concentration of palladium, phosphine and methylated cyclodextrin on the reaction rate has not been yet investigated. Nevertheless, it is of great interest to determine the effect of such parameters as the cleavage of allylic substrates in biphasic medium could be a useful reaction in the field of protection/deprotection chemistry [29–35]. To fill this gap, we report hereby a detailled study of the cleavage of allylundecylcarbonate in the presence of different amounts of palladium and methylated cyclodextrins (Scheme 1). NMR experiments have been performed throughout this study to substantiate the catalytic results.

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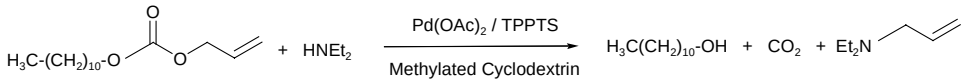

Scheme 1.

2. Experimental

2.1. General

The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 300 DPX instrument at 300.13 and 75.46 MHz, respectively. Gas chromatographic analyses were carried out on a Shimadzu GC-17A gas chromatograph equipped with a methyl silicone capillary column (25 m × 0.25 mm) and a flame ionisation detector (GC:FID). Palladium acetate and randomly methylated β-cyclodextrin were purchased from Aldrich. Randomly methylated α-cyclodextrin (RAME-α-CD) was prepared by adapting a procedure reported by Kenichi et al. [36]. These cyclodextrins were partially methylated; statistically two OH groups per glucopyranose unit were modified. Tris(3-sodium sulfonatophenyl)phosphine (TPPTS-P(*m*-$C_6H_4SO_3Na)_3$) was synthesised as reported by Gärtner et al. [37]. The purity of the TPPTS was carefully controlled. In particular, $^{31}P\{^{1}H\}$ NMR indicated that the product was a mixture of phosphine (ca. 98%) and its oxide (ca. 2%).

2.2. $^{31}P\{^{1}H\}$ NMR study on the Pd(TPPTS)$_3$ complex

$Pd(TPPTS)_3$ in a D_2O solution was synthesised according to a modified literature procedure [38]. $Pd(PPh_3)_4$ (412 mg, 0.36 mmol) was dissolved in 8 g of degazed toluene into a Schlenk tube under nitrogen. TPPTS (303.7 mg, 0.53 mmol) was dissolved in 8 g of D_2O and canulated on the palladium solution. The mixture was stirred for 30 min at room temperature. After decantation, the aqueous phase was recovered. The obtained $Pd(TPPTS)_3$ solution was then used for the $^{31}P\{^{1}H\}$ NMR study. This solution contained the expected palladium catalyst $Pd(TPPTS)_3$ and an excess of about 10% of free TPPTS (with regard to the initial amount of TPPTS). Study in the presence of RAME-β-CD was conducted as follow: to 1 ml of the above $Pd(TPPTS)_3$ solution was introduced under nitrogen the required amount of RAME-β-CD. After 15 min of stirring, the solution was transferred via canula into a nitrogen pressurised 5 mm NMR tube.

2.3. General procedure for the catalytic experiments

$Pd(OAc)_2$, TPPTS (9 eq.), methylated cyclodextrin and water (2 g) were introduced under nitrogen atmosphere into a Schlenk tube. After stirring with a magnetic bar for 1 h, the yellow solution was transferred into a mixture of allylundecylcarbonate (1.12 mmol), diethylamine (2.24 mmol) and heptane (2 g). The medium was stirred at 1000 rpm at room temperature and the reaction was monitored by quantitative gas chromatographic analysis of the organic layer.

3. Results and discussion

In the following study, the palladium and cyclodextrin contents are expressed in molar percentage with regard to the initial amount of substrate. They will be marked as %Pd and %RAME-β-CD or %RAME-α-CD.

First of all, we wanted to determine the effect of the palladium catalyst concentration with respect to the reaction rate. The %Pd has been varied from 0.1 to 8 whereas the %RAME-β-CD remained constant for each series of measurements. The palladium dependence of allylundecylcarbonate cleavage rate is presented in Fig. 1. The different curves are relative to the variation of the initial rate of the reaction at low conversion of substrate (20%) for various Pd and %CD.

As expected, the first series of experiments conducted without RAME-β-CD showed that the reaction occurred very slowly whatever the amount of palladium (2.0 μmol of substrate were converted per hour on average, Fig. 1 curve X). This result confirms that the limiting step of the reaction is the mass transfer in the absence of RAME-β-CD.

A second series of reactions has been carried out in which 4% of RAME-β-CD were added to the mixture. As shown in Fig. 1, at low %Pd (<0.5), the addition of RAME-β-CD accelerated the reaction rate compared to the reaction without cyclodextrin (for example, $34\,\mu mol\,h^{-1}$ versus $2.2\,\mu mol\,h^{-1}$ respectively, %Pd = 0.4). But astonishly, for higher %Pd and a %RAME-β-CD of 4%, the results were unexpected as an increase in the %Pd did not lead to a linear increase in the initial rate of the reaction. Actually, between 0.4 and 1% of palladium, the initial rate remained constant ($\approx 34\,\mu mol\,h^{-1}$). Moreover, above 1%, a slight but regular decrease in the rate was observed ($30\,\mu mol\,h^{-1}$ %Pd = 2.4 and $7.4\,\mu mol\,h^{-1}$ %Pd = 4). Consequently, the catalytic performances are lowered noticeably at high concentration of palladium.

We then tried to learn more about this atypical behaviour by increasing the amount of cyclodextrin in the medium. The %RAME-β-CD was then fixed at 16 and the %Pd was varied from 0.1 to 8. As expected, at low %Pd (<0.5%), the initial rate of the reaction was higher with 16% of RAME-β-CD ($210\,\mu mol\,h^{-1}$ at 0.4% Pd) than that of the reaction with only 4% of cyclodextrin ($34\,\mu mol\,h^{-1}$ at 0.4% Pd). As observed with 4% of RAME-β-CD, the rate levelled off ($230\,\mu mol\,h^{-1}$) when the palladium catalyst

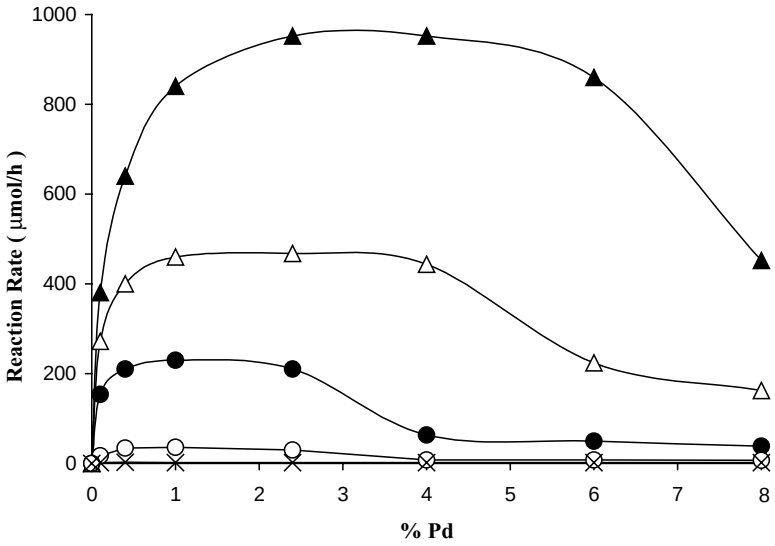

Fig. 1. Reaction rate (μmol/h) of allylundecylcarbonate vs. %Pd for different. %RAME-β-CD: (×); 0%, (○); 4%, (●); 16%, (△); 28%, (▲); 40%.

was between 0.5 and 2.5% and dramatically decreased when the %Pd was superior to 2.5% ($64\,\mu\,mol\,h^{-1}$ %Pd = 4 and $38\,\mu\,mol\,h^{-1}$ %Pd = 8). Two other series of measurements with 28 and 40% of RAME-β-CD led to the similar observations. Here again, a plateau appeared, the length of which depended on the %RAME-β-CD. Finally, the initial rate droped slightly as a function of the palladium concentration (above 4% Pd for RAME-β-CD = 28% and above 6% Pd for RAME-β-CD = 40%). It can be noticed through the analysis of these last two curves that the phenomenon was shifted to higher %Pd when the cyclodextrin percentage increased. For example, at 1% of palladium, the rate of the reaction levelled off when RAME-β-CD = 4% whereas it continued to grow when RAME-β-CD = 40%. In the same manner, at 4% of palladium, the rate of the reaction has already decreased when 16% of RAME-β-CD were added while that of the reaction with 28% of RAME-β-CD was still on the plateau. This unambiguously proves that the RAME-β-CD upsets the activity of the catalytic system.

Surprisingly, when the above results are translated in terms of TPPTS/RAME-β-CD ratio, the phenomenon reveals itself under a new light. In Fig. 2, the evolution of the reaction rate is represented as a function of the introduced TPPTS/RAME-β-CD ratio for each percentage of RAME-β-CD.

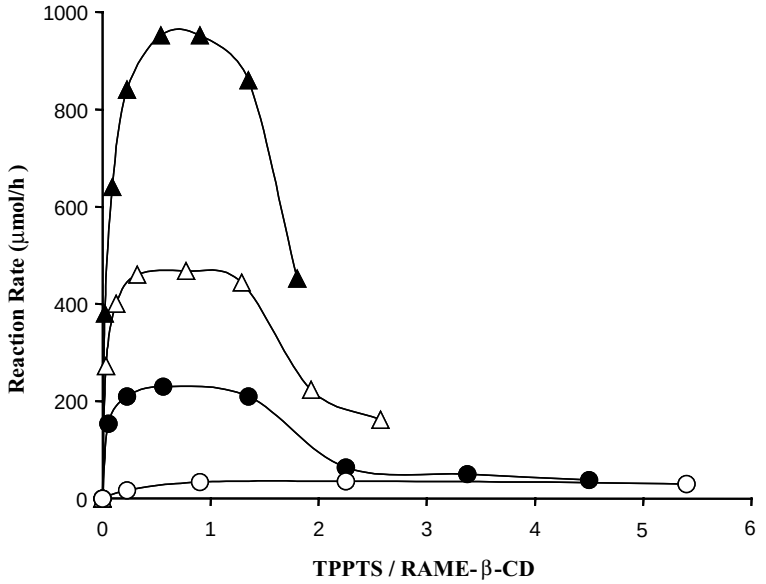

Fig. 2. Reaction rate (μmol/h) of allylundecylcarbonate vs. TPPTS/RAME-β-CD ratio for different %RAME-β-CD: (○); 4%, (●); 16%, (△); 28%, (▲); 40%.

As can be seen from Fig. 2, the TPPTS/RAME-β-CD ratio from which the decreases were observed was the same whatever the %RAME-β-CD. In each case, the rate decreased for an approximately stoichiometric TPPTS/RAME-β-CD ratio.

To explain such an unexpected result, a modification of the catalyst structure in the presence of RAME-β-CD has been envisaged. Indeed, we have recently demonstrated that rhodium complexes in the presence of β-cyclodextrin or RAME-β-CD can be partially converted to phosphane low coordinated rhodium species [39,40]. Thus, a $^{31}P\{^{1}H\}$ NMR study has been undertaken to evaluate the evolution of the $Pd(TPPTS)_3$ catalyst precursor when changing the amount of RAME-β-CD. Starting from the analysis of the catalytic results (Fig. 2), two different TPPTS/RAME-β-CD ratios have been chosen for this NMR study: TPPTS/RAME-β-CD = 1 which corresponds to a decreasing reaction rate as a function of %Pd and TPPTS/RAME-β-CD = 0.25 which corresponds to a increasing reaction rate as a function of %Pd. The $^{31}P\{^{1}H\}$ NMR spectra relative to this study are shown in Figs. 3–5.

In Figs. 3a–c are represented the spectra recorded at 27 °C with various amounts of RAME-β-CD in the palladium solution. As an excess of TPPTS was present in the medium (Section 2), the broad signal at 19.5 ppm was an average signal due to the fast equilibrium between free TPPTS and the $Pd(TPPTS)_3$ species according to Eq. (1) [41–44]

$$Pd(TPPTS)_3 + TPPTS^* \rightleftharpoons Pd(TPPTS)_2(TPPTS^*) + TPPTS \quad (1)$$

Similar phenomemon was reported by Kalck and co-workers [42,44]. Indeed, they have observed that in water the ^{31}P NMR signal of an authentic sample of $Pd(TPPTS)_3$ (δ = 24.0 ppm) is shifted toward high field in the presence of added TPPTS. The phosphane oxide impurity was also detected on this spectrum (35.7 ppm). We then reproduced this experiment in the presence of about three equivalents of RAME-β-CD with regard to $Pd(TPPTS)_3$, which means a stoichiometric TPPTS/RAME-β-CD ratio. In that case, as can be seen in Fig. 3b, addition of RAME-β-CD induced the appearance of two peaks, one at lower field (24.0 ppm) (compare to the initial resonance (Fig. 3a)) and the very broad other one at higher field (≈−4.5 ppm, visible by zooming). It can also be noticed that the peak width at half-height of the signal at 24.0 ppm was three times more important (280 Hz) than the preceding one (93 Hz) and an enlargement of the spectral width between 1 and −10 ppm showed a broad signal with a peak width at half-height >1500 Hz. Interestingly, a slight shift of the peak corresponding to the TPPTS oxide was also noticed (34.9 ppm versus 35.7 ppm) suggesting an interaction between the TPPTS oxide and the RAME-β-CD. With 4 eq. of RAME-β-CD with respect to TPPTS (Fig. 3c),

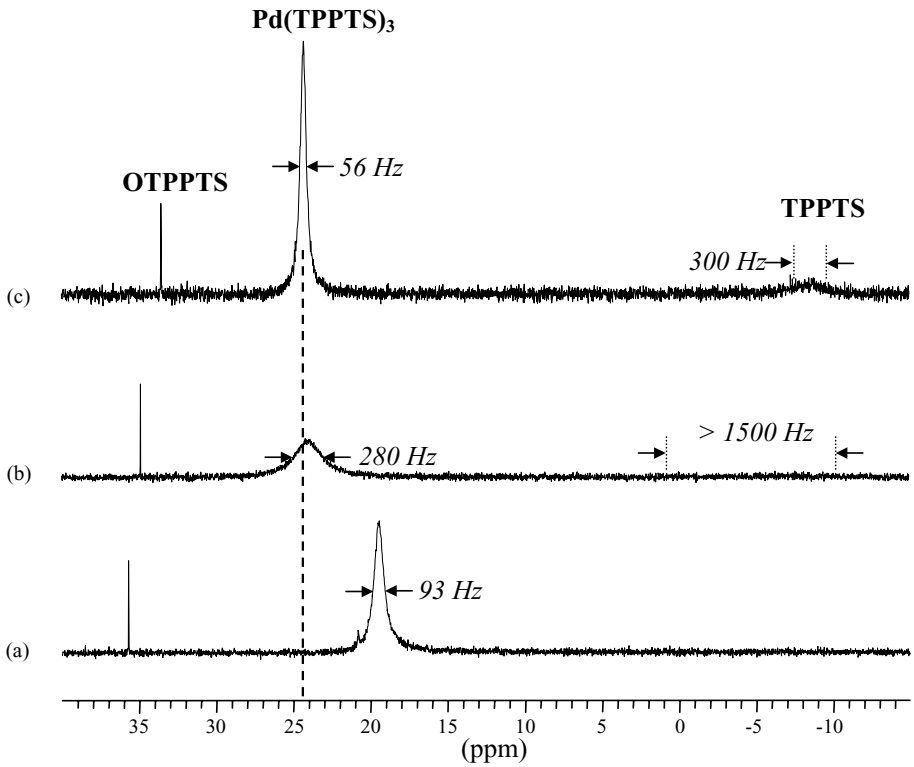

Fig. 3. Effect of RAME-β-CD on the $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of $Pd(TPPTS)_3$ and TPPTS (10%) in D_2O at 27 °C: (a) without cyclodextrin; (b) in the presence of RAME-β-CD (1 eq./TPPTS); (c) in the presence of RAME-β-CD (4 eq./TPPTS).

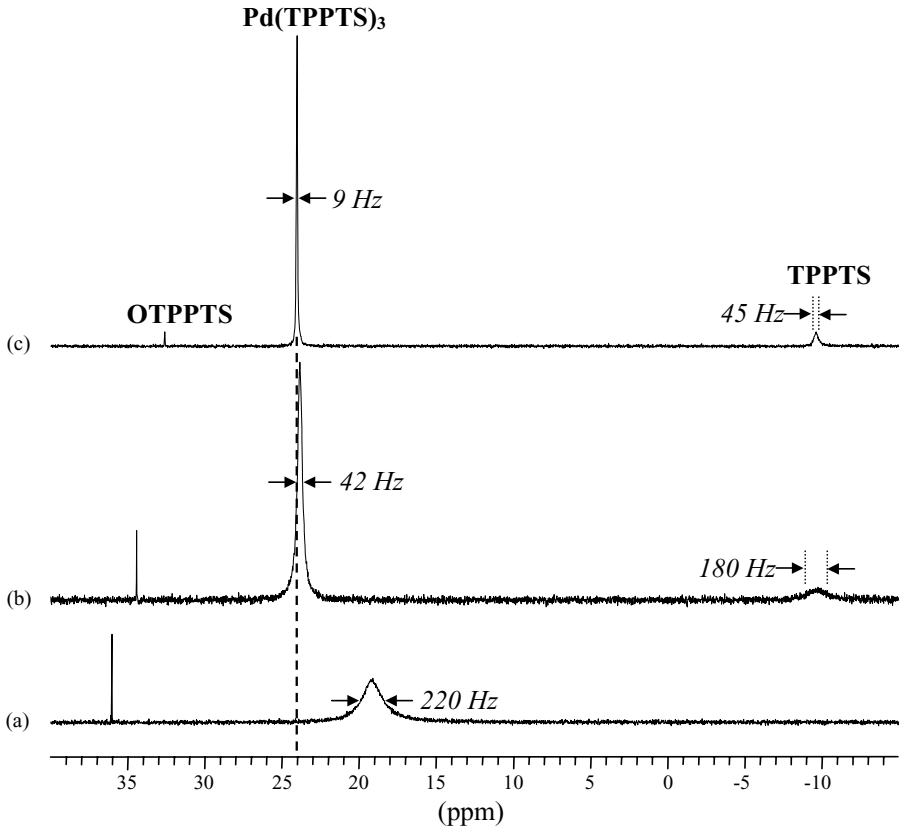

Fig. 4. Effect of RAME-β-CD on the $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of $Pd(TPPTS)_3$ and TPPTS (10%) in D_2O at 5 °C: (a) without cyclodextrin; (b) in the presence of RAME-β-CD (1 eq./TPPTS); (c) in the presence of RAME-β-CD (4 eq./TPPTS).

the spectrum was substantially similar to that obtained with 1 eq. of RAME-β-CD. A very small shift of the signal around 24 ppm was detected (0.5 ppm downfield) when compared to Fig. 3b. The shift was more important for the signal at higher field (−8.3 ppm versus −4.5 ppm). The narrowing of the two peaks (wh = 56 Hz versus 280 Hz for the signal at 24.5 ppm and wh = 300 Hz versus 1500 Hz for the signal at −8.3 ppm) is indicative of a slower equilibrium. Based

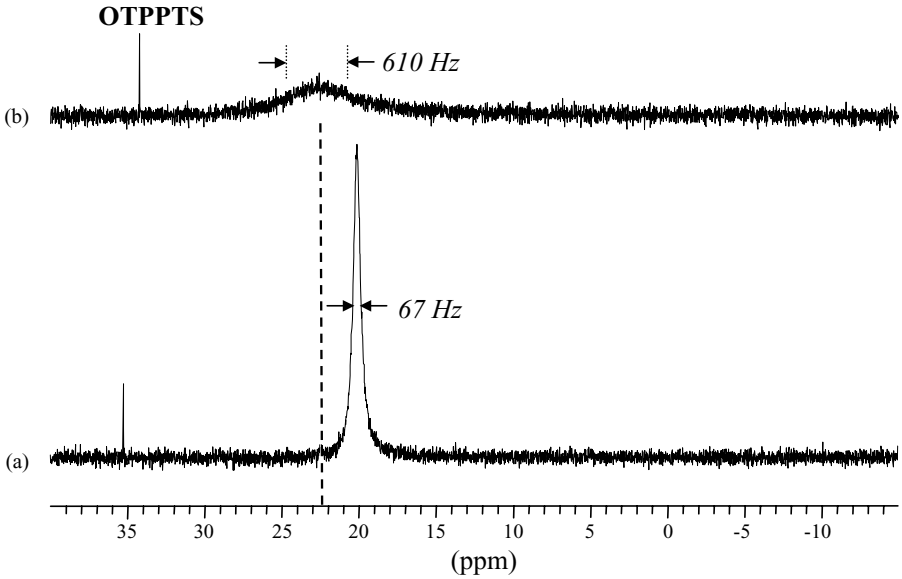

Fig. 5. Effect of RAME-β-CD on the $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of $Pd(TPPTS)_3$ and TPPTS (10%) in D_2O at 60 °C: (a) without cyclodextrin; (b) in the presence of RAME-β-CD (4 eq./TPPTS).

on previous studies, the signal around 24 ppm has been assigned to the $Pd(TPPTS)_3$ species [38,44,45] and the signal between −4.5 and −8.3 ppm has been assigned to the TPPTS in interaction with RAME-β-CD [46–48]. Indeed, we have previously demonstrated that an inclusion complex may form between TPPTS and RAME-β-CD with an association constant of 1000 M^{-1} [39,48] according to the Eq. (2).

$$\text{TPPTS} + \text{RAME-}\beta\text{-CD} \overset{K_{25^\circ C}=1000\,M^{-1}}{\rightleftarrows} [\text{TPPTS; RAME-}\beta\text{-CD}] \quad (2)$$

So, from this NMR study, it can be concluded that the RAME-β-CD decreases the exchange rate between TPPTS and $Pd(TPPTS)_3$ species by trapping the TPPTS ligand. Moreover, no new palladium species can be observed.

To confirm this result, NMR experiments at a lower temperature were conducted (Fig. 4).

When no cyclodextrin was added in a cooled palladium solution ($T = 5\,^\circ C$), only one average broad peak (wh = 220 Hz) was observed at 19.2 ppm (Fig. 4a). By addition of 1 eq. of RAME-β-CD in respect to TPPTS, two distinct signals were observed at 23.9 and −9.7 ppm (Fig. 4b). The peak width at half-height of these two peaks were 42 and 180 Hz, respectively. Here again, a slower exchange rate between TPPTS and $Pd(TPPTS)_3$ might be the explanation of such an evolution in the presence of cyclodextrin. The effect was much more visible with 4 eq. of RAME-β-CD. Although the spectrum of Fig. 4c seemed to be very similar to that of Fig. 4b, one relevant difference could be exploited to confirm our preceding assertion about the exchange rate in the equilibrium (1). Actually, an increase in the amount of RAME-β-CD has allowed a narrowing of the peaks (9 Hz versus 42 Hz at −24 ppm and 45 Hz versus 180 Hz at −9.6 ppm). Moreover, a comparison of Figs. 3 and 4 clearly demonstrated that the exchange rate also decreased when decreasing the temperature since a narrowing of the peaks was observed when the experiments were performed at 5 °C. For instance, the peak width at half-height of the signal around 24 ppm has gone up from 280 to 42 Hz (Figs. 3b and 4b). The same observation can be made on the other signals except that at around 19.5 ppm for which a broadening of the signal was detected (wh = 93 at 27 °C and wh = 220 Hz at 5 °C, Figs. 3a and 4a). This paradoxal behaviour can be easily understood. Actually, a decrease in the temperature reduced the exchange rate which led to a distinction of species in equilibrium. Thus the signal at 19.5 ppm was in fact an overlapping of two signals which tend to separate one from each other. Consequently, the behaviour of this signal was also in good agreement with the evolution of the exchange rate as a function of the temperature.

To complete this NMR study, a last experiment has been performed at 60 °C. With no cyclodextrin, a signal at 20.1 ppm was detected with a peak width at half-height of 67 Hz. When 4 eq. of RAME-β-CD in respect of the TPPTS were mixed in the palladium solution, a broadened signal (wh = 610 Hz) corresponding to the palladium coordinated TPPTS appeared downfield (22.5 ppm versus 20.1 ppm). But contrary to what was observed previously in Fig. 4, the signal of the TPPTS included in the cyclodextrin was not visible on the NMR time scale. Thus, an increase in the temperature led to a broadening of the signals due to a faster exchange rate.

In all cases, at low or high RAME-β-CD/TPPTS ratio, no new palladium species have been detected. Throughout the analysis of these results, it can then be concluded that the addition of RAME-β-CD only influences the rate of the chemical exchange but do not lead to the formation of new palladium species. Hence, a change of the palladium catalyst structure is not the explanation of the catalytic results.

On the other hand, as noticed above, the decreases in the catalytic activity coincides with a stoichiometric TPPTS/RAME-β-CD ratio whatever the %Pd. This characteristic value of ratio was suspected to be the key to understanding the unexpected catalytic results. We have then attempted to prove that the amount of TPPTS was responsible for the observed phenomenon. Actually, when increasing the palladium percentage, the TPPTS/Pd ratio was keeped constant and equal to 9. That means that for a given %RAME-β-CD, an increase in %Pd was accompanied by an increase in the amount of TPPTS in the medium. As TPPTS forms inclusion complexes with RAME-β-CD, we postulate that this increase in TPPTS amount induce a lower amount of RAME-β-CD available for the mass transfer and consequently a decrease in the reaction rate. The phenomenon which is not visible at low %Pd appeared clearly as soon as the TPPTS/RAME-β-CD ratio becomes superior to 1.

To confirm the inclusion complex formation and thus the poisoning effect of the TPPTS on the RAME-β-CD, we have carried out several series of NMR and catalytic experiments in which RAME-α-CD has been used as a host. First of all, we wanted to prove that RAME-α-CD was unable to associate with TPPTS due to its too small cavity. ^1H and $^{31}P\{^1H\}$ NMR experiments have been performed on a stoichiometric mixture of RAME-α-CD and TPPTS. The obtained spectra were compared to those recorded on a stoichiometric mixture of TPPTS and RAME-β-CD. In Fig. 6, the effect of both RAME-β-CD and RAME-α-CD on the ^1H NMR spectrum of TPPTS in D_2O is detailed.

When comparing Figs. 6a and b, significant changes appeared in the spectrum since the addition of RAME-β-CD to the TPPTS solution led to an overlapping of the signals of H_p ($^3J(H_p - H_m) = 7.6$ Hz) and $H_{o'}$ ($^3J(H_{o'} - P) = 8.1$ Hz) and a shift of the signals of H_m ($^3J(H_m - H_p) = {}^3J(H_m - H_o) = 5$ Hz) and H_o ($^3J(H_o - H_m) = {}^3J(H_o - P) = 6$ Hz) to lower and higher fields respectively. On the contrary, when RAME-α-CD was added in the TPPTS solution, the spectrum was exactly the same than that obtained without cyclodextrin. In Fig. 7 are presented the $^{31}P\{^1H\}$ NMR spectra of TPPTS with or without methylated cyclodextrins in D_2O. A comparison of Fig. 7a (without cyclodextrin) and

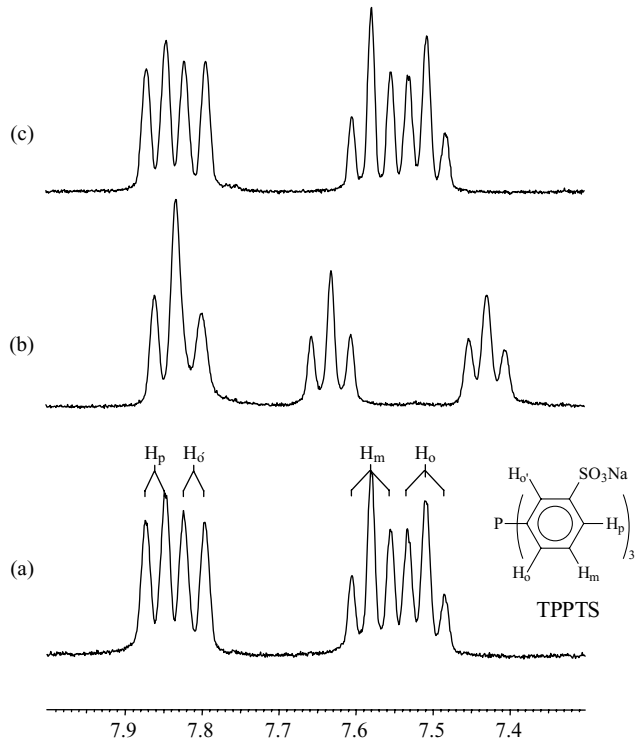

Fig. 6. Effect of methylated cyclodextrins on the ^{1}H NMR spectrum of TPPTS (3 mM) in D_2O: (a) without cyclodextrin; (b) in the presence of RAME-β-CD (3 mM); (c) in the presence of RAME-α-CD (3 mM).

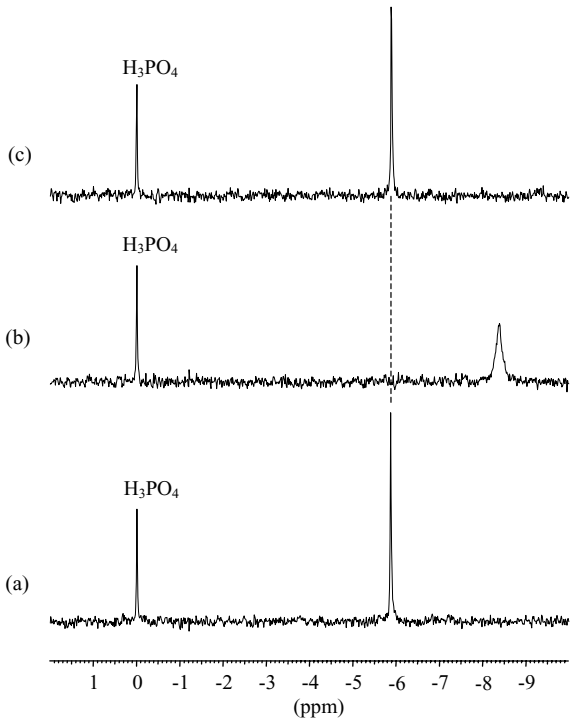

Fig. 7. Effect of methylated cyclodextrins on the $^{31}P\{^{1}H\}$ NMR spectrum of TPPTS (3 mM) in D_2O with H_3PO_4 as external reference: (a) without cyclodextrin; (b) in the presence of RAME-β-CD (3 mM); (c) in the presence of RAME-α-CD (3 mM).

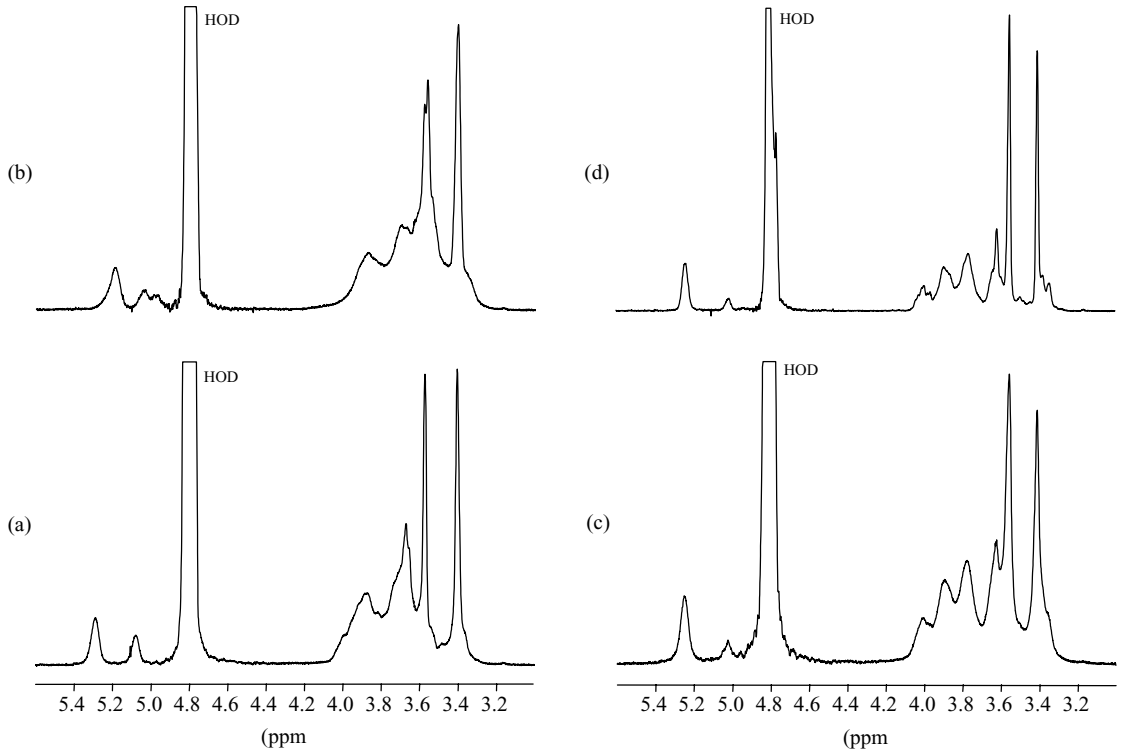

Fig. 8. Effect of TPPTS on the ^{1}H NMR spectra of methylated cyclodextrins (3 mM) in D_2O: (a) RAME-β-CD; (b) RAME-β-CD with TPPTS (3 mM); (c) RAME-α-CD; (d) RAME-α-CD with TPPTS (3 mM).

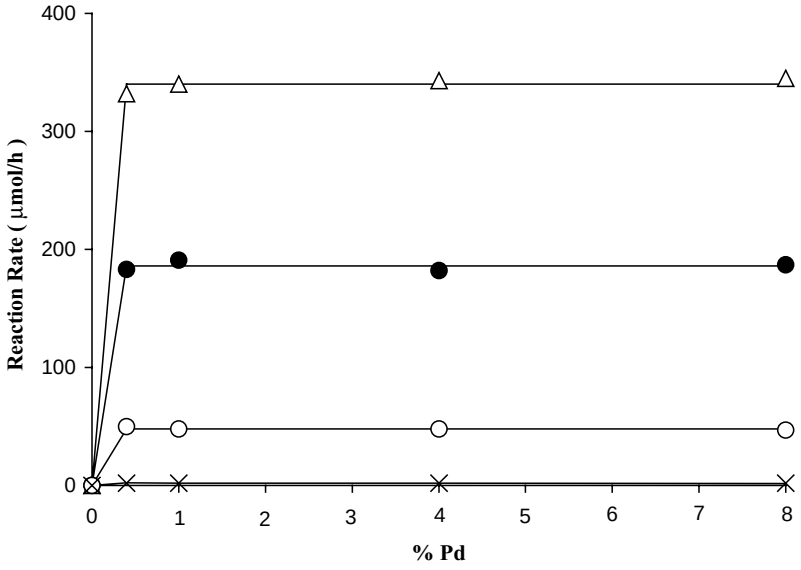

Fig. 9. Reaction rate (μmol/h) of allylundecylcarbonate versus %Pd for different. %RAME-α-CD: (×); 0%, (○); 4%, (●); 16%, (△); 28%.

Fig. 7b (addition of RAME-β-CD) illustrates the effect of the presence of RAME-β-CD on the chemical shift of phosphorus atom of TPPTS which was shifted to higher field (−8.3 ppm versus −5.9 ppm) because of the formation of an inclusion complex. Here again, no variation of the chemical shift of TPPTS was detected when RAME-α-CD was added to the TPPTS solution. A third NMR experiment confirmed the preceding ones since Figs. 8a and b revealed that the protons of RAME-β-CD were shifted in presence of TPPTS whereas the protons of RAME-α-CD did not move in the same conditions (Figs. 8c and d).

In conclusion of this NMR study, the ^{1}H or $^{31}P\{^{1}H\}$ NMR spectra clearly showed that no chemical shift was detected either for TPPTS or RAME-α-CD when they were mixed together, contrary to what was observed with TPPTS and RAME-β-CD. This unambiguously established the incapability of the RAME-α-CD to form an inclusion complex with TPPTS. On the other hand, RAME-α-CD can easily recognise the alkyl chain of the substrate [49] and can therefore suitably play the role of carrier to bring the substrate from the organic phase to the aqueous phase. Hence, RAME-α-CD has been used as an inverse phase transfer catalyst in the allylundecylcarbonate cleavage reaction. The catalytic results are given in Fig. 9.

As previously described for RAME-β-CD, the initial rate of the reaction significantly increased when the amount of RAME-α-CD increased (for example, $50\,\mu mol\,h^{-1}$ with %RAME-α-CD = 4 versus $332\,\mu mol\,h^{-1}$ with %RAME-α-CD = 28 %Pd = 0.4). These results are coherent with the fact that the higher the carrier percentage the higher the quantity of substrate solubilized in water. But contrary to what was established above, the rate of the reaction levelled off when the %Pd was up to 0.5% and did not decrease even at high percentages of palladium. This

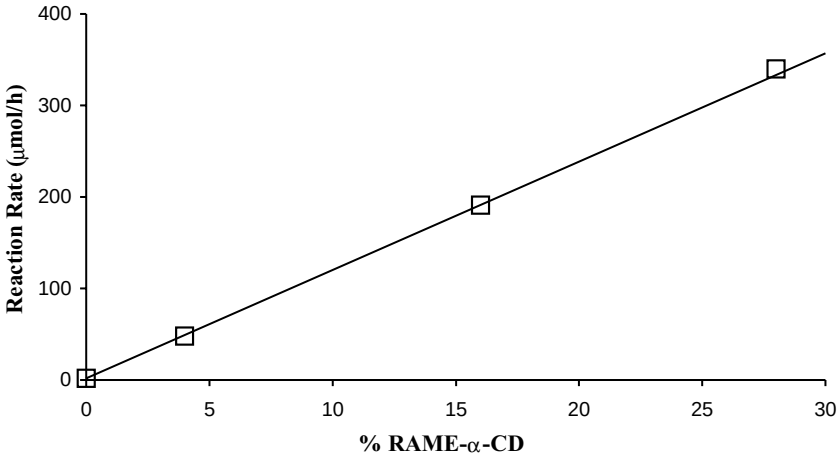

Fig. 10. Reaction rate (μmol/h) of allylundecylcarbonate vs. %RAME-α-CD for %Pd = 1.

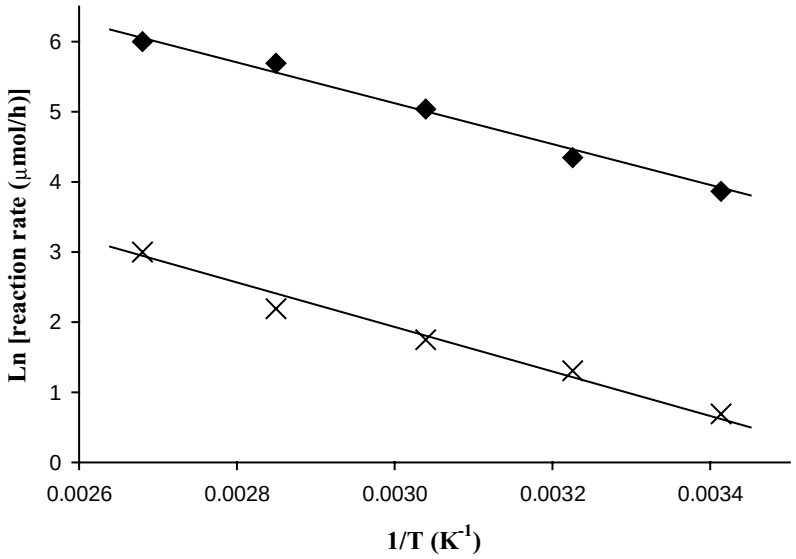

Fig. 11. Reaction rate dependence on the reaction temperature for %Pd = 1. %RAME-α-CD: (×); 0%, (◆); 4%.

clearly demonstrates three things. First, the fact that the rate does not decline is consistent with the suggestion that the RAME-α-CD was not trapped by TPPTS and consequently could fully assume its role of carrier even at high TPPTS concentration. Secondly, for a palladium concentration superior to 0.5%, the cleavage reaction of allylic substrate is first-order with regard to the inverse phase transfer catalyst (Fig. 10). Third, the plateaus which were observed for the three RAME-α-CD concentrations indicated a zero order with regard to palladium, suggesting that the mass transfer might constitute the limiting step of the system. To confirm this hypothesis, activation energy of reaction without and in the presence of 4% RAME-α-CD were calculated for a 1% palladium concentration from the plots of reaction rate versus 1/temperature (Fig. 11).

Two nearly parallel straight lines were obtained indicating that the activation energies are similar (26 kJ mol^{-1} without cyclodextrin and 24 kJ mol^{-1} in the presence of 4% RAME-α-CD). So, when %Pd is superior to 0.5%, the mass transfer between the aqueous and organic phases is always the limiting step of the reaction even in the presence of RAME-α-CD. Consequently, there is no interest to enhance inconsiderably the percentage of palladium catalyst insofar as the rate at which the substrate is carried from the organic phase to the aqueous phase has reached its limit.

4. Conclusion

This study allowed us to throw light on an astonishing aspect of the inverse phase transfer catalyst system using RAME-β-CD. It has been shown that molecular recognition ability of the latter for the TPPTS ligand is responsible for a decrease in the rate of the allylundecylcarbonate cleavage reaction. Indeed, when the TPPTS/RAME-β/CD ratio is too high, poisoning of the cyclodextrin by the ligand occurs. Therefore, the RAME-β-CD/TPPTS interaction has important consequences on the catalytic performances of the allylundecylcarbonate cleavage reaction. Of relevance to the biphasic catalysis approach with water-soluble phosphines is the observation that one has to be careful in the use of RAME-β-CD as an inverse phase transfer catalyst in metal/TPPTS catalytic system.

Experiments carried out on RAME-α-CD which is not able to associate to TPPTS gave a proof of these conclusions since no decrease in the activity was observed at high TPPTS/RAME-α-CD ratios. Thus, RAME-α-CD appears to be a better inverse phase transfer catalyst than RAME-β-CD. Starting from these conclusions, further investigations into the use of RAME-α-CD are under way to improve the performances of allylic carbonates cleavage reaction.

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