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Importance of counter-ion nature in aryl sulfonated ligands: An improvement in two-phase catalysis

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Abstract

Carbon–carbon coupling of myrcene with methyl acetylacetate in two-phase system using various water-soluble rhodium(I) complexes was studied. The influence of the sulfonate counter-ion nature in TPPTS and in 1,4-bis(diphenylphosphino)butane meta-tetra sulfonated was investigated.

Keywords: Water-soluble ligand; Rhodium; Two-phase catalysis; Quaternary ammonium ion; Carbon–carbon coupling

1. Introduction

Two-phase catalysis developments rely on the easy recovery of both products and organometallic species. Several industrial developments have been published among which hydroformylation of propene and diene conversions have been applied on industrial plants. These processes are based essentially on the exceptional water-solubility of triphenylphosphinetrisulfonate sodium salt (TPPTS–Na) [1].

Several factors not encountered in homogeneous systems become crucial in two-phase systems. At times, to achieve good rates in biphasic reaction, cosolvent addition is necessary to increase the solubility of the organic substrate in water. Such a process is applied by Rhône–Poulenc to synthesize a vitamin E precursor [2–5]. In this process, the use of TPPTS–Na, highly water-soluble, leads to very good yields in presence of a ligand excess and methanol as cosolvent. The challenge is now to prepare ligands with well fitted water-solubility so that they could promote the necessary contact between the lipophilic substrates and the hydrosoluble catalyst without any cosolvent addition, and the guarantee that all the catalyst is maintained in water. To ensure a better exchange at phase boundary, several methods are possible. One approach involves the use of amphiphilic additives or ligands, but further difficulties in catalyst recycling and products recovery occur [6–11]. Another approach consists in adding quaternary ammonium or phosphonium salts which act as solubilizing agents in water [11–17]. In this paper, we demonstrate how counter-ion modification in TPPTS can be an improvement

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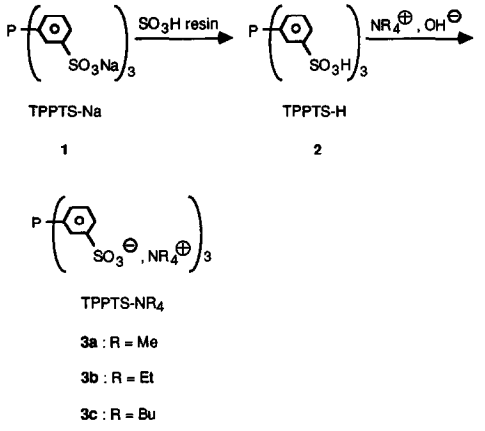
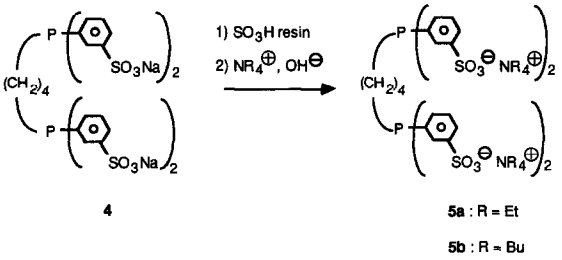


Scheme 1. Synthesis of TPPTS–NR_4.



Scheme 2. Synthesis of tetra sulfonated diphosphines.

for the carbon–carbon coupling of myrcene with methyl acetylacetate. Moreover, in order to avoid the addition of a large excess of ligands, we show that water-soluble chelating ligands can advantageously replace monophosphines [18].

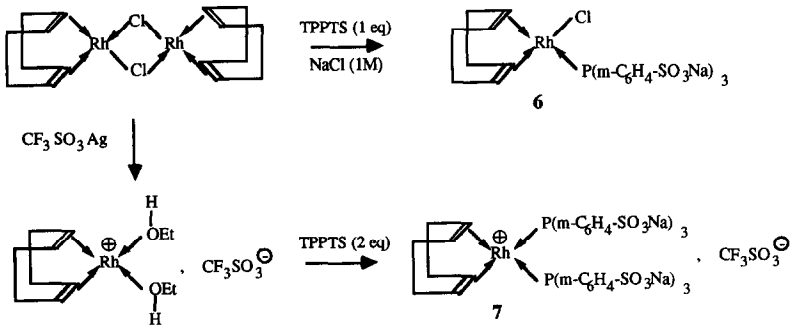
2. Results

2.1. Ligands preparation

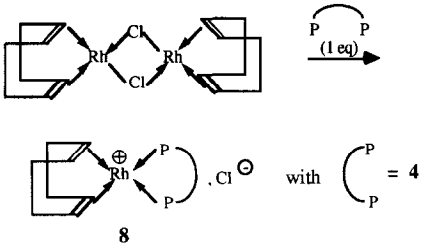
The exchange of Na^+ by NR_4^+ in TPPTS **1** was realized in two steps. In the first one triphenylphosphine meta trisulfonic acid **2** (TPPTS–H) was prepared by ion exchange over strong acidic resin (Amberlyst IR 120 plus). Then, to an aqueous solution of **2** bearing three sulfonic acid groups a quaternary ammonium hydroxide was added (1 equivalent/SO_3H) to afford modified TPPTS **3** (Scheme 1). A general method for the preparation of phosphine **3** was preliminary described by Kuntz [16]. The total transformation of TPPTS–Na was checked by ^1H NMR. The same procedure was used to prepare meta-tetra sulfonated diphosphine **5** with different counter-ions (Scheme 2).

2.2. Characterization of rhodium(I) complexes

Rhodium(I) complexes of TPPTS–Na (Scheme 3) and diphosphine **4** (Scheme 4) have been prepared from the dimer $[RhCl(COD)]_2$ and characterized in solution by ^{31}P NMR spectra (Table 1). All the complexes show a doublet and rhodium–phosphorus coupling constants in complete agreements with well known compounds [19–23]. As previously published [19], compound **6** can been stabilized in the presence of an excess of chlorine anions.



Scheme 3. Preparation of neutral and cationic rhodium complexes.



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Scheme 4. Preparation of [Rh(COD)(diphosphine 4)]$^+$ Cl$^-$.

2.3. Catalytic studies

The influence of ligand nature was tested in the carbon–carbon coupling reaction of methyl acetylacetate with myrcene leading to a vitamin E precursor. This catalytic addition is industrially performed in a two-phase system $[RhCl(COD)]_2/TPPTS/H_2O/MeOH/Na_2CO_3$ and is highly regioselective: attack of the carbanion occurring at the activated vinylic double bond (Scheme 5) [2,3,24].

2.3.1. Influence of counter-ion nature in TPPTS

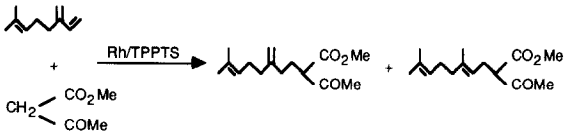
The importance of cosolvent addition has been described [2,3] and with TPPTS–Na methanol is necessary to allow a sufficient myrcene solubilization in water otherwise low conversion rates are obtained (Table 2). On the contrary, with ligand **3a** in which sulfonates counter-ions are NMe_4^+, cosolvent addition lead to lower yields than in pure aqueous medium.

When ligands **3b** and **3c**, with respectively NEt_4^+ and NBu_4^+ as sulfonates counter-ions, are used, comparable yields are observed in pure aqueous medium and in hydroalcoholic mixtures. Consequently, methanol addition is useless and even defavorable in most cases. Very

Table 1
^{31}P NMR spectra of rhodium complexes

Complex	δ (ppm)	$^1J_{Rh-P}$ (Hz)
6	32.8 [a]	154
7	28.4 [a]	147
8	26.6 [b]	144

[a] Solvent mixture of D_2O, H_2O and EtOH.
[b] Solvent mixture of D_2O and H_2O.



Scheme 5. Coupling reaction of myrcene with methyl acetylacetate.

good turn-over and rates are obtained with **3c** leading also to excellent recycling.

2.3.2. Use of a sulfonated diphosphine 4

No reaction was observed when a ligand excess of more than three equivalents was used and with three equivalents, poor yields are obtained. In fact, one or two equivalents of ligands allow an efficient catalysis in hydroalcoholic medium and there is no significant loss of catalytic activity in recycling. The high water-solubility of **4** necessitate the addition of cosolvent to obtain good yields of condensation for analogous reasons than with TPPTS–Na.

Table 2
Catalytic results [a]

Ligand	P/Rh ratio	Solvent	Conversion rate (%) [b]	
			τ_1	τ_2
1	21	$MeOH/H_2O$	100	68
1	21	H_2O	8	20
3a	21	$MeOH/H_2O$	38	33
3a	21	H_2O	62	69
3b	21	$MeOH/H_2O$	84	83
3b	21	H_2O	85	80
3c	21	$MeOH/H_2O$	95	86
3c	21	H_2O	98	95
4	10	$MeOH/H_2O$	0	—
4	5	$MeOH/H_2O$	0	—
4	4	$MeOH/H_2O$	0	—
4	3	$MeOH/H_2O$	15	2,5
4	2	$MeOH/H_2O$	69	59
4	1	$MeOH/H_2O$	63	55
4	1	H_2O	15	—
5a	1	H_2O	32	< 1
5b	1	H_2O	44	< 1

[a] Conditions: $[RhCl(COD)]_2$: 1.7×10^{-5} mol; myrcene: 10^{-2} mol; methylacetylacetate: 1.2×10^{-2} mol; Na_2CO_3: 7.22×10^{-5} mol; solvent: 3.4 mL; $T = 90°C$; $t = 3h20$; τ_1: first catalysis; τ_2: recycling.
[b] Determinated by GLC analysis.

2.3.3. Influence of counter-ion nature in diphosphine 4

Influence of counter-ion nature in diphosphine **4** has also been studied. In pure aqueous medium, with one equivalent of **5a** or **5b**, yields are lower than with **4** in hydroalcoholic medium. Furthermore, a total loss of catalytic activity is observed in recycling. Indeed, ligands **5a** and **5b**, bearing four ammonium counter-ions, are not able to ensure an efficient remaining of metal in aqueous phase during the catalytic reaction. These diphosphines are too much lipophilic when NR_4^+ replaces Na^+ the consequence being a partial solubilization of rhodium in the organic phase.

3. Experimental section

Catalytic studies and preparation of phosphines were carried out under anaerobic conditions. All solvents were degassed before use. NMR spectra were recorded on a Bruker ARX-400 FT-NMR spectrometer ($^{31}P\{^1H\}$ NMR, 20°C, 161.8 MHz referenced to external 85% H_3PO_4; $^{13}C\{^1H\}$ NMR, 20°C, 100.5 MHz; ^1H NMR, 20°C, 400 MHz; δ in ppm).

Surface tension measurements were obtained by the Du Nouy method with a Krüss K10T tensiometer. The surface tensions of aqueous solutions (ultrapure water) were measured at 25°C until constant values.

3.1. A typical procedure for catalytic studies

The C–C coupling system consisted of an aqueous layer and an organic one. The aqueous layer was made of 2.4 mL H_2O/1 mL MeOH or 3.4 mL H_2O with 1.7×10^{-5} mol of $[RhCl(COD)]_2$, 7.22×10^{-5} mol of Na_2CO_3 and various amount of ligand **1–5**. Methylacetylacetate (1.2×10^{-2} mol; 1.3 mL) and myrcene (10^{-2} mol; 1.8 mL) were successively added and catalytic reactions were stopped after 3 h and 20 min at 90°C. The reaction products and myrcene were analyzed by gas chromatography on a Carlo Erba GC 6000 chromatograph equipped with AT1 column (30 m × 0.25 mm × 0.25 μm) and FID detector and He was the carrier gas.

3.2. Ligands preparation

3.2.1. Preparation of 2

An aqueous solution of TPPTS **1** (10 g; 1.76×10^{-2} mol) was stirred with Amberlyst IR 120 plus resin (100 mL) under nitrogen during three hours. After resin filtration, the solvent was removed under vacuum and after several methanol additions in order to remove water. The product was obtained as a white solid and dried under vacuum in a desiccator.

Yield: 95%: $^{31}P\{^1H\}$ NMR (D_2O): −8.8. ^1H NMR (D_2O): 6.93 (t, $J_{H-P} \approx {}^3J_{H-H} = 67.6$ Hz, 1H); 7.03 (t, ${}^3J_{H-H} = 7.6$ Hz, 1H); 7.36 (d, $J_{H-P} = 87.7$ Hz, 1H); 7.43 (d, ${}^3J_{H-H} = 8.1$ Hz, 1H). $^{13}C\{^1H\}$ NMR (D_2O): 126.7 (s); 129.8 (d, $J_{P-C} = 6.8$ Hz); 130.3 (d, $J_{P-C} = 22$ Hz); 136.3 (d, $J_{P-C} = 18.6$ Hz); 136.5 (d, $J_{P-C} = 11.7$ Hz); 143.6 (s). Elemental anal. Found: C, 38.9; H, 4.0. $C_{18}H_{15}O_9S_3P \cdot 3H_2O$ calc.: C, 38.85; H, 3.8%.

3.2.2. Preparation of 3

An aqueous tetraalkylammonium hydroxide solution (6×10^{-3} mol) was added to ligand **2** (2×10^{-3} mol) in 25 mL aqueous solution. The solution was stirred 2 h at room temperature under nitrogen and after removal of solvent under vacuum and several methanol and ethylacetate addition in order to remove water, the product was obtained in quantitative yield.

3a: TPPTS–NMe_4^+: $^{31}P\{^1H\}$ NMR (D_2O): −8.71. ^1H NMR (D_2O): 2.89 (s, 12H); 7.21 (t, $J_{H-P} \approx {}^3J_{H-H} = 6.1$ Hz, 1H); 7.32 (t, ${}^3J_{H-H} = 7.6$ Hz, 1H); 7.54 (d, $J_{H-P} = 8.1$ Hz, 1H); 7.62 (d, ${}^3J_{H-H} = 7.6$ Hz, 1H). $^{13}C\{^1H\}$ NMR (D_2O): 55.50 (t, ${}^1J_{N-C} = 4.2$ Hz); 126.96 (s); 129.75 (d, $J_{P-C} = 6.5$ Hz); 130.0 (d, $J_{P-C} = 21.6$ Hz); 136.31 (d, $J_{P-C} = 18.6$ Hz); 136.53 (d, $J_{P-C} = 11.7$ Hz); 143.57 (s). Elemental anal. Found: C, 46.32; H, 7.13; N, 5.3. $C_{30}H_{48}O_9N_3S_3P \cdot 3H_2O$ calc.: C, 46.44; H, 7.01; N, 5.42%.

3b: TPPTS–NEt_4^+: $^{31}P\{^1H\}$ NMR (CD_3OD): −8.75. ^1H NMR (CD_3OD): 1.21 (t, $^3J_{H-H}$ = 7.6 Hz, 3H); 1.22 (t, $^3J_{H-H}$ = 7.1 Hz, 3H); 1.23 (t, $^3J_{H-H}$ = 7.6 Hz, 3H); 3.24 (q, $^3J_{H-H}$ = 7.6 Hz, 2H); 7.34 (t, $J_{H-P} \approx {}^3J_{H-H}$ = 7.1 Hz, 1H); 7.46 (t, $^3J_{H-H}$ = 7.4 Hz, 1H); 7.84 (d, J_{H-P} = 8.1 Hz, 1H); 7.91 (d, $^3J_{H-H}$ = 8.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (D_2O): 8.29 (s); 53.57 (t, J_{N-C} = 3.03 Hz); 128.60 (s); 131.62 (d, J_{P-C} = 6.1 Hz); 132.03 (d, J_{P-C} = 23.9 Hz); 137.94 (d, J_{P-C} = 16.3 Hz); 138.18 (d, J_{P-C} = 11.4 Hz); 145.59 (d, J_{P-C} = 6.8 Hz). Elemental anal. Found: C, 52.56; H, 8.25; N, 4.29. $C_{42}H_{72}O_9N_3S_3P \cdot 4H_2O$ calc.: C, 52.42; H, 8.38; N, 4.37%.

3c: TPPTS–NBu_4^+: $^{31}P\{^1H\}$ NMR (D_2O): −8.58. ^1H NMR (D_2O): 0.75 (t, $^3J_{H-H}$ = 7.1 Hz, 12H); 1.08 (m, $^3J_{H-H}$ = 7.1 Hz, 8H); 1.37 (m, 8H); 2.89 (t, J_{N-C} = 8.6 Hz, 8H); 7.39 (t, $J_{H-P} \approx {}^3J_{H-H}$ = 7.1 Hz, 1H); 7.52 (t, $^3J_{H-H}$ = 7.6 Hz, 1H); 7.73 (d, J_{H-P} = 7.1 Hz, 1H); 7.78 (d, $^3J_{H-H}$ = 7.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (D_2O): 13.06 (s); 19.23 (s); 23.16 (s); 57.49 (s); 126.85 (s); 129.79 (d, J_{P-C} = 6.1 Hz); 130.40 (d, J_{P-C} = 23.5 Hz); 136.18 (d, J_{P-C} = 15.2 Hz); 136.43 (d, J_{P-C} = 11.4 Hz); 143.69 (d, J_{P-C} = 6.5 Hz). Elemental anal. Found: C, 61.09; H, 9.6; N, 3.12. $C_{66}H_{120}O_9N_3S_3P \cdot 4H_2O$ calc.: C, 61.03; H, 9.93; N, 3.23%.

3.2.3. Preparation of 4

Diphosphine **4** was prepared according to a described method. The oleum concentration and the reaction time were slightly modified for complete sulfonation.

Oleum (40 mL; 30% SO_3) was added slowly to 1,4-bis(phenylphosphino)butane (6×10^{-3} mol) at 0°C under nitrogen and with vigorous stirring. The sulfonation was complete after 4 days at room temperature. The mixture was quenched by the slow addition of water (50 mL) and NaOH 10 N (200 mL) at 0°C. The solution was reduced under vacuum to 30 mL and after filtration, methanol (20 mL) was added. Crystallization occurred at 0°C. The solution was filtered and the solid dried under vacuum was washed by diethylether and acetone.

Yield = 65%: $^{31}P\{^1H\}$ NMR (D_2O): −15.69 (s) ^1H NMR (D_2O): 1.25 (s broad, 2H); 1.84 (s broad, 2H); 7.20 (m, 5H); 7.60 (m, 5H). $^{13}C\{^1H\}$ NMR (D_2O): 26.39 (d, $^1J_{P-C}$ = 8.1 Hz); 26.76 (dd, $^2J_{P-C}$ = 14.1 Hz and $^3J_{P-C}$ = 13.1 Hz); 126.49 (s); 129.68 (d, J_{P-C} = 11.3 Hz); 129.82 (d, J_{P-C} = 2.7 Hz); 135.59 (d, J_{P-C} = 16.8 Hz); 139.02 (d, J_{P-C} = 13 Hz); 143.20 (d, J_{P-C} = 7 Hz). Elemental anal. Found: C, 35.71; H, 3.9. $C_{28}H_{24}O_{12}Na_4S_4P_2 \cdot 6H_2O$ calc.: C, 35.67; H, 3.85%.

3.2.4. Preparation of 5

An aqueous solution of diphosphine **4** (10^{-2} mol) was stirred with Amberlyst IR 120 plus resin (100 mL) under nitrogen during 1 h. After filtration of the resin, the solvent was removed under vacuum and after several addition of methanol, in order to remove water, a white solid was obtained and dried under vacuum in a desiccator. Then an aqueous tetraalkylammonium hydroxide solution (5.4×10^{-3} mol) diluted in ethanol (10 mL) was slowly added to the white solid (1 g; 1.3×10^{-3} mol) in 20 mL ethanol. The solution was stirred 2 h at room temperature under nitrogen and after removal of the solvent, a viscous product was obtained in a quantitative yield.

5a: $^{31}P\{^1H\}$ NMR (CD_3OD): −18.77. ^1H NMR (CD_3OD): 1.15 (tt, $^3J_{H-H}$ = 7.1 Hz, J = 2 Hz, 24H); 1.50 (s, 2H); 1.90 (s, 2H); 3.16 (q, $^3J_{H-H}$ = 7.1 Hz, 16H); 7.40 (m, 4H); 7.72 (m, 2H); 7.85 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_3OD): 8.45 (s); 29.0 (d, J_{P-C} = 11.8 Hz); 29.27 (d, J_{P-C} = 15.2 Hz); 54.04 (t, J_{N-C} = 3 Hz); 128.33 (s); 130.70 (d, J_{P-C} = 5.3 Hz); 132.14 (d, J_{P-C} = 24.3 Hz); 136.03 (d, J_{P-C} = 15.2 Hz); 141.17 (d, J_{P-C} = 15.9 Hz); 147.77 (d, J_{P-C} = 6.1 Hz). Elemental anal. Found: C, 53.1; H, 8.61; N, 4.2. $C_{60}H_{104}O_{12}N_4S_4P_2 \cdot 5H_2O$ calc.: C, 53.23; H, 8.49; N, 4.14%.

5b: $^{31}P\{^1H\}$ NMR (CD_3OD): −18.93. ^1H NMR (CD_3OD): 0.91 (t, $^3J_{H-H}$ = 7.1 Hz, J = 2 Hz, 24H); 1.30 (q, $^3J_{H-H}$ = 7.5 Hz, 16H); 1.29 (m, 16H); 1.5 (m, 2H); 2.05 (m, 2H); 3.13 (t, $^3J_{H-H}$ = 8.6 Hz, 16H); 7.40 (m, 4H); 7.70 (m,

2H); 7.90 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_3OD): 13.99 (s); 20.66 (s); 24.74 (s); 28.73 (d, J_{P-C} = 6.8 Hz); 28.95 (d, J_{P-C} = 12.5 Hz); 59.42 (t, J_{N-C} = 2.7 Hz); 127.51 (s); 129.68 (d, J_{P-C} = 4.5 Hz); 131.56 (d, J_{P-C} = 26.5 Hz); 134.08 (d, J_{P-C} = 12.9 Hz); 141.1 (d, J_{P-C} = 15.9 Hz); 147.05 (d, J_{PC} = 8.3 Hz). Elemental anal. Found: C, 62.51; H, 7.7; N, 3.11. $C_{92}H_{128}O_{12}N_4S_4P_2 \cdot 5H_2O$ calc.: C, 62.7; H, 7.89; N, 3.18%.

3.3. Preparation of rhodium coordination compounds

3.3.1. Synthesis of (COD)RhCl(TPPTS) 6

An aqueous solution of NaCl (1 M) containing TPPTS–Na (3.6×10^{-4} mol) was added to $[RhCl(COD)]_2$ (1.8×10^{-4} mol) in THF. After stirring for 1 h, an orange solution was obtained and the complex characterized by ^{31}P NMR.

3.3.2. Synthesis of $[(COD)RhCl(TPPTS)_2]^+CF_3SO_3^-$ 7

$[RhCl(COD)]_2$ (1.8×10^{-4} mol) and silver triflate (3.6×10^{-4} mol) were dissolved in ethanol (3 mL). After stirring for 15 min, the precipitate of AgCl was filtered and the ethanolic solution was added to TPPTS–Na (7.2×10^{-4} mol) in water. The orange solution was stirred for 15 min and the complex characterized by ^{31}P NMR.

3.3.3. Synthesis of $[(COD)Rh(4)]^+Cl^-$ 8

An aqueous solution of diphosphine **4** (10^{-4} mol) and $[RhCl(COD)]_2$ (5×10^{-5} mol) was stirred one hour at room temperature. The structure of the complex was established by ^{31}P NMR analysis.

4. Discussion

In order to gain a better comprehension of the above results, the influence of counter-ion nature on interfacial tensions values of **1** and **3a–c** aqueous solutions has been studied (Fig. 1).

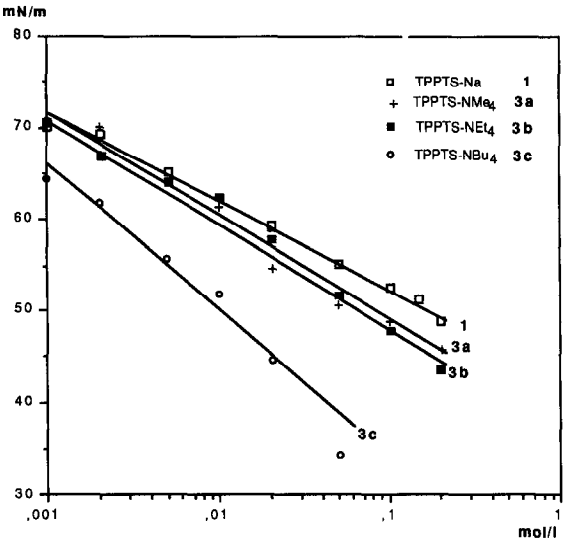


Fig. 1. Surface tension evolution. $\sigma = f(\log C)$, $T = 25°C$.

In the whole cases, the linear decrease of surface tension with $\log(c)$ indicates an hydrotropic behavior for the salts of TPPTS. When the ligand concentration is 0.21 mol/l, surface tension values with **1** and **3a,b** varies from 50 mN/m to 45 mN/m. This small variation has however an important influence on the catalytic system with **3a,b** showing an interesting behavior. These results suggest that the presence of tetraalkylammonium counter-ions in TPPTS confers to the catalytic species phase transfer agent properties in parallel with decreasing solvation of sulfonates and leads to a better molecular affinity between catalytic species becoming more lipophilic and myrcene.

In the case of **3c**, both a better solubility of myrcene in water ($\sigma = 29$ mN/m when $c =$ 0.21 mol/l) and an increase in molecular affinity explain the excellent results.

At the end of all the experiments, the organic layer was colourless while the aqueous layer had the typical orange colour of rhodium(I) complexes. Consequently there is no loss of metal in the organic layer in presence of **3a–c** ligands which was confirmed by rhodium con-

centration measurements in the aqueous phase by atomic absorption spectrometry [25].

Cosolvent addition is not necessary when TPPTS is modified because phase transfer agent properties are obtained without changing the solubility in water. These characteristics are brought by associating to sulfonate anion quaternary ammonium cation instead of sodium.

However we are conscious than when modified TPPTS **3** is the ligand, the solubility of the substrate in water is not yet the determining parameter because in this case, the reaction takes place at the phase boundary. These observations are in agreement with the recent conclusion drawn by Cornils [26] who pointed out the crucial importance of 'proper tailoring of the ligands' in order to 'carefully match hydrophilic and hydrophobic characteristics' of these ones.

5. Conclusion

We have demonstrated that the reaction of methylacetylacetate with myrcene can be achieved in high yields without cosolvent addition. Furthermore, from an economic and engineering stand point, the use of modified TPPTS **3** does not imply any change in the purification step in the existing process. These results should be of interest for developing other reactions in pure biphasic medium such as hydroformylation of non water-soluble olefins [27].

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