

Wacker oxidation of various olefins in the presence of per(2,6-di-*O*-methyl)- β -cyclodextrin: mechanistic investigations of a multistep catalysis in a solvent-free two-phase system

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Abstract

Oxidation of various olefins into methylketones by a catalytic system constituted of palladium, copper, phosphomolybdovanadic acid and per(2,6-di-*O*-methyl)- β -cyclodextrin is investigated. The role of each redox catalytic system component is discussed from experiments under argon atmosphere and from vanadium NMR spectroscopic studies. The influence of various parameters, such as the per(2,6-di-*O*-methyl)- β -cyclodextrin concentration and the nature of the phosphomolybdovanadic acid is also reported. Finally, a catalytic cycle is also proposed.

Keywords: Wacker oxidation; Olefins; Dextrin derivatives; Per(2,6-di-*O*-methyl)- β -cyclodextrin; Phosphomolybdovanadic acid; Copper sulfate; Palladium; Vanadium

1. Introduction

The palladium catalysed oxidation of ethylene to acetaldehyde has been extensively studied and successfully developed on an industrial scale (Wacker process) [1]. This well-known reaction combines the stoichiometric oxidation of ethylene by palladium(II) in aqueous solution with the in situ reoxidation of palladium(0) by molecular oxygen in the presence of copper salt [2] or heteropolyacids [3]. Owing to their poor solubilities in water, numerous olefins are oxi-

dized to methyl ketones very slowly and with poor selectivities under the standard Wacker conditions [4]. In order to solve these problems, the use of combinations of reoxidants [5], organic solvents [6], surfactants [7], cyclodextrins [8], supported aqueous phase Wacker catalysts [9] or polymer-supported palladium complexes [10] has been proposed. However, despite these numerous efforts, the formation of by-products arising from isomerisation of the double bond cannot be totally prevented and research in this field is still being pursued.

Recently, we were able to develop a new catalytic system for the quantitative and selective oxidation of higher α -olefins in an aqueous

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two-phase system. The success of this oxidation was mainly due to an efficient redox catalytic system and to the use of β -cyclodextrin – a cyclic oligosaccharide composed of seven glucopyranose units – functionalized with hydrophilic or lipophilic groups [11]. The best results have been obtained with a multicomponent catalytic system comprised of PdSO_4 , $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$, CuSO_4 and per(2,6-di-*O*-methyl)- β -cyclodextrin (Scheme 1).

In this reaction, the chemically modified β -cyclodextrins behaved mainly as inverse phase-transfer catalysts. Actually, owing to the formation of inclusion complexes, the chemically modified cyclodextrins transfer the higher olefins into the aqueous phase, and so improve the mass transfer between aqueous and organic layers. It has been found that the mass transfer efficiency was strongly dependent on the nature of the substituent group and on the degree of substitution of the cyclodextrin.

In this paper, we discuss the role of each redox catalytic system component, i.e. $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$, CuSO_4 , from experiments under argon atmosphere and from ^{51}V NMR spectroscopic studies. In order to confirm some mechanistic hypothesis, we also report results obtained with various phosphomolybdovanadic acids during the dec-1-ene oxidation.

2. Experimental

2.1. Materials

The olefins (dec-1-ene (97%), tetradec-1-ene (92%), styrene (98%), 4-vinylcyclohex-1-ene (99%), vinylcyclohexane (98%) and allylben-

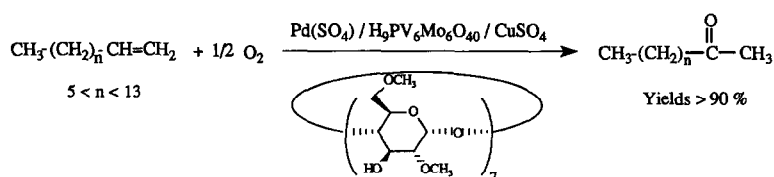
zene (98%)) and per(2,6-di-*O*-methyl)- β -cyclodextrin (M_w : 1310 g) were supplied by Aldrich and were used as received without further purification. Distilled, deionized water and palladium sulfate obtained from Aldrich (98% pure) were used in all experiments. Dioxygen (> 99.9% pure – Air Liquide) was used directly from the cylinder.

2.2. Apparatus

^{51}V NMR spectra were obtained at 25°C on a Bruker AM-400 NMR spectrometer at observation frequencies of 105.24 MHz. ^{51}V chemical shifts were referenced to external VOCl_3 . Gas liquid chromatography analysis were carried out on a Chrompack apparatus equipped with a CP Sil 5-CB column (25 m \times 0.32 mm).

2.3. Experimental procedure for the synthesis of heteropoly acids

In the solutions of this study, molybdenum, vanadium and phosphorus are always present in Keggin proportions ((Mo + V) = 12 P). The heteropoly acids $\text{H}_{3+n}[\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]\cdot\text{aq}$ ($n = 1, 2$ and 3) were prepared by standard methods [12]. The heteropoly acids $\text{H}_{11}\text{PMo}_4\text{V}_8\text{O}_{40}$, $\text{H}_7\text{PMo}_8\text{V}_4\text{O}_{40}$ were prepared as reported by Vasilevskis et al. [13]. A solution of the phosphomolybdovanadic acid $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ was made, as described below, by the method reported by Maitlis [14]. Vanadium pentoxide (21.6 g, 0.119 mol), molybdenum trioxide (34.2, 0.237 mol), sodium phosphate hydrate (15.1 g, 0.04 mol), and anhydrous sodium carbonate (6.4 g, 0.06 mol) were refluxed in distilled water (120 ml) for 1 h. The solution was cooled and



Scheme 1. Catalytic oxidation of olefins in the presence of per(2,6-di-*O*-methyl)- β -cyclodextrin.




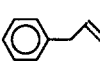
the pH adjusted to 1 by addition of concentrated sulphuric acid. The resulting solution was then refluxed with stirring (20 min), cooled and filtered. The filtered orange–brown stock solution was then used in the oxidation experiments. From ^{51}V NMR measurements, it was found that the heteropoly acids with $n = 2$ to 8 were not pure. For example, the $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ heteropoly acid was a mixture of isomers corresponding to the following formula: $[\text{H}_z\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]^{(3+n-z)-}$ ($n = 1, 2, \dots$) (see Fig. 2). So, the macroscopic elemental composition $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ corresponds, essentially, to the average heteropoly acid formula. If necessary, the counteranions in the catalytic aqueous solution (Cu^{2+} ; Pd^{2+}) can balance the anionic charge of the heteropoly acid (for example, see Eq. 1). No attempt to isolate such complexes has been carried out. Apart from $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$, we were unable to prepare a pure isomer. This

problem has already been highlighted in literature [14,15].

2.4. Experimental procedure for catalytic reactions

In a typical experiment, 0.206 g (0.86 mmol) of $\text{PdSO}_4 \cdot 2\text{H}_2\text{O}$, 1.64 g (10 mmol) of CuSO_4 and 1.3 g (1 mmol) of per(2,6-*O*-dimethyl)- β -cyclodextrin were introduced into an aqueous solution (30 ml) of phosphomolybdovanadic acid (10 mmol of phosphorus) adjusted to pH 1 with concentrated sulfuric acid. The resulting solution and the olefin (40 mmol) were then introduced in a 250 ml flask. Oxygen was bubbled through the solution which was vigorously stirred at 80°C. At the end of the reaction, the solution was then cooled and the organic layer was analysed by GLC using an internal standard. Products were identified by comparison of

Table 1
Wacker oxidation of various olefins in the presence of per(2,6-di-*O*-methyl)- β -cyclodextrin ^a

Entry	olefin	time (hours)	olefin conversion (mol %)	ketone selectivity ^[b] (mol %)	ketone yield ^[c] (mol %)	isomeric olefin yield (mol %)
1	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}_2$	6	100	98	98	2
2	$\text{CH}_3(\text{CH}_2)_{11}\text{CH}=\text{CH}_2$	90	100	94	94	6
3	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$	8	1	(-)	<1	<1
4	$\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{CH}=\text{CH}_2$	8	70	51	36 ^[d]	34
5		8	100	99	99	1
6 ^[e]		5	44	98	43	1
7		8	70	100	70	0
8		6	77	56	43	34

^a PdSO_4 : 0.86 mmol; CuSO_4 : 10 mmol; $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$: 10 mmol; per(2,6-di-*O*-methyl)- β -cyclodextrin: 1 mmol; H_2O : 1.66 mol (30 ml); olefin 40 mmol; T : 80°C.

^b Ketone/converted olefin.

^c Chromatographic yield.

^d 2,9-Decanedione: 24% and 9-oxodec-1-ene: 12%.

^e The single oxidation product was 4-acetylcyclohex-1-ene.

retention times and spectral properties with authentic samples.

3. Results and discussion

As described in Table 1, the multicomponent catalytic system constituted of PdSO_4 , $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$, CuSO_4 and per(2,6-di-*O*-methyl)- β -cyclodextrin allowed to oxidize efficiently a large variety of terminal olefins. It is noteworthy that the formation of a cyclodextrin–substrate inclusion complex is essential to the success of the oxidation process [11]. Indeed, we could not observe any catalytic effect with acyclic oligosaccharides composed of glucopyranose units like maltose, maltopentose and maltoheptose. These compounds have the same sub-units than the cyclodextrins but do not possess a lipophilic host cavity, and so cannot form inclusion complexes. It should also be noted that the internal olefins fail to react under our experimental conditions (Entries 3 and 6 in

Table 1). This disappointing result is probably due to the well-known poor reactivity of internal olefins but also to the lack of accessibility of the double bond. Indeed, when the double bond is inside the hydrophobic cavity of the methylated cyclodextrin, catalyst cannot reach it and the oxidation is suppressed.

These significant results are mainly due to the mass transfer improvement and to the efficiency of the $\text{CuSO}_4/\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ reoxidizing system [11]. Although the efficiency of this binary reoxidizing system has also been reported by J. Vasilevskis et al. in some patents [5](d), [13], little attention has been given to explain the role of each component. In order to fill up this lack, we have recently suggested two hypothesis: (i) the stabilization of heteropoly acid by copper or (ii) the substitution of a two step by a three step reversible electron transfer where each step requires a lower activation energy (Scheme 2) [11].

In order to confirm one of these hypothesis, the behavior the copper and heteropoly acid has

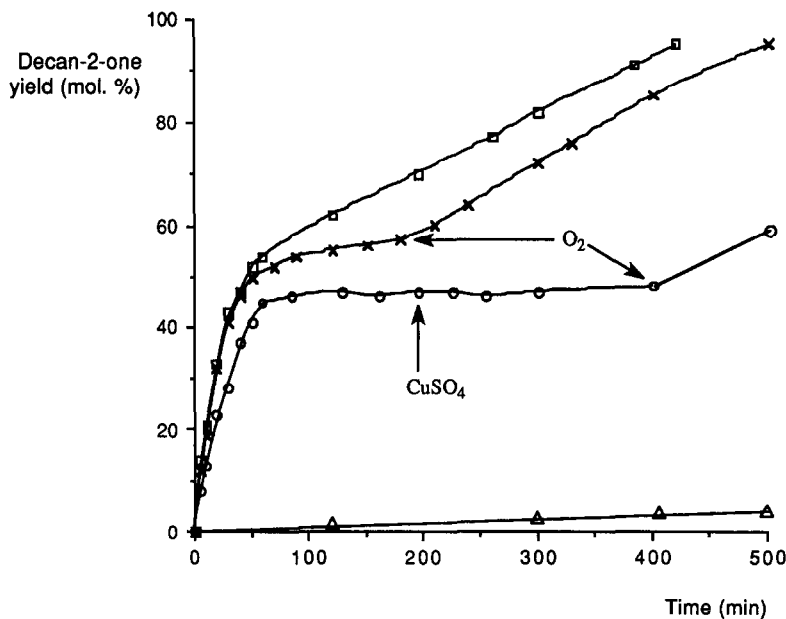
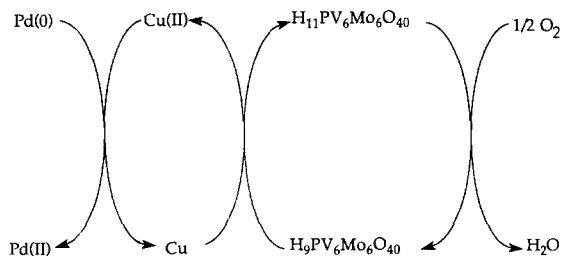


Fig. 1. Oxidation of dec-1-ene in the presence of various catalytic systems: Δ : $\text{PdSO}_4/\text{CuSO}_4$ (1/10) under oxygen, \circ : $\text{PdSO}_4/\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ (1/10) under argon, \times : $\text{PdSO}_4/\text{CuSO}_4/\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ (1/10/10) under argon, \square : $\text{PdSO}_4/\text{CuSO}_4/\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ (1/10/10) under oxygen. [olefin]/[palladium]: 40; Pd: 0.86 mmol; per(2,6-di-*O*-methyl)- β -cyclodextrin: 1 mmol; H_2O : 30 ml; T : 85°C.



Scheme 2. Palladium(0) reoxidation in the case of three-step reversible electron transfer.

been examined in different experimental conditions (Fig. 1).

From the experiments presented in Fig. 1, the following information can be obtained:

(i) In our experimental conditions, the copper sulfate alone is ineffective on the palladium reoxidation (the decan-2-one yield did not exceed 2% after 2 h of reaction).

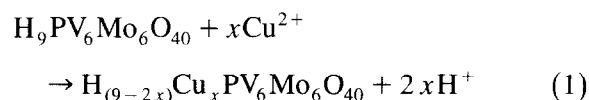
(ii) As described in literature [3], phosphomolybdovanadic acid $H_9PV_6Mo_6O_{40}$ alone is a suitable reoxidant. Under argon atmosphere, the reaction was essentially complete within ca. 60 min and gave 48% of decan-2-one yield and a turnover of about 19 on palladium. At the end of the reaction, the aqueous solution was dark blue. This colour is characteristic of reduced phosphomolybdovanadic acid [14]. We have also observed that addition of copper sulfate to this reduced phosphomolybdovanadic acid had no effect (the decan-2-one yield did not enhance and the solution remained blue). These results indicate that copper sulfate cannot oxidize the reduced phosphomolybdovanadic acid. However, reoxidation of this heteropoly acid can be achieved in the presence of oxygen. Indeed, under oxygen atmosphere, the solution became rapidly dark green and decan-2-one yield increased significantly.

(iii) The simultaneous use of $CuSO_4/H_9PV_6Mo_6O_{40}$ as reoxidizing system allowed to increase the reaction rate but also slightly decan-2-one yield. With this combination and under argon atmosphere, decan-2-one yields were about 10% higher than those obtained in the presence of $H_9PV_6Mo_6O_{40}$ without

copper sulfate. As decan-2-one yield did not exceed 2% after 2 h of reaction in the presence of copper sulfate alone, a synergy effect between copper and heteropoly acid seems to occur. It must also be noticed that the aqueous solution became rapidly dark blue under argon atmosphere and that the decan-2-one yields could be increased again when oxygen was bubbled through the solution.

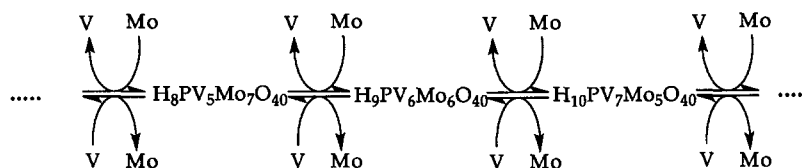
In light of these results, it clearly appears that the efficiency of the $CuSO_4/H_9PV_6Mo_6O_{40}$ couple is not due to the substitution of a two step by a three step reversible electron transfer where each step requires a lower activation energy. Indeed, in the case of a three step reversible electron transfer (Scheme 2), the decan-2-one yield would be equal to the sum of decan-2-one yields obtained in the presence of copper and heteropoly acid alone and no synergy effect between copper and heteropoly acid could be observed.

In fact, we think that efficiency of the copper–heteropoly acid couple can be attributed to in situ formation of copper/phosphomolybdovanadic acid complexes which would be very active species for palladium reoxidation. Although no conclusive evidence has been obtained, we believe that these complexes are obtained by cations exchange between phosphomolybdovanadic acids and copper sulfate, according to the equation (1):



It must be pointed out that synthesis of such complexes is well-known in the case of the heteropoly acid $H_4PVMo_{11}O_{40}$ [16] and some heteropoly acids modified by copper cation have already been tested successfully in numerous reactions [17].

Although ^{51}V NMR does not allow to determine if the phosphomolybdovanadic acids are modified by copper (chemical shifts of modified and unmodified heteropoly acids are identical [17]), this spectroscopic method gives some in-



Scheme 3. Schematic representation of the various equilibria between the phosphomolybdovanadic acids.

interesting results on the species involved in palladium reoxidation and on the rate-determining step. Fig. 2c shows changes in the ^{51}V NMR spectrum of an aqueous solution during the oxidation of dec-1-ene.

The ^{51}V NMR spectrum of the initial solution (spectrum (a), Fig. 2) displayed numerous signals. This indicates that the $\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$ heteropoly acid is a mixture of phosphomolybdovanadic acids corresponding to the following formula: $[\text{H}_z\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]^{(3+n-z)-}$ with $n = 1, 2$ to 11. The formation of these heteropoly acids is well documented and is due to exchange of molybdenum and vanadium atoms between the different phosphomolybdovanadic acids (Scheme 3) [15].

The spectrum (a) in Fig. 2 exhibits two sets of signals. The first one (-500 ppm to -540 ppm) was mainly assigned to isomers of heteropoly acids: $[\text{H}_z\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]^{(3+n-z)-}$ with $n = 1, 2$ and the second (-540 ppm to

-620 ppm) to isomers of heteropoly acids $[\text{H}_z\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]^{(3+n-z)-}$ with $n = 3$ to 11 and to $\text{V}^{(\text{V})}\text{O}_2^+$ [17,18].

Interestingly, at the beginning of the dec-1-ene oxidation, the signals between -540 ppm and -620 ppm disappeared (see spectra (b) and (c), Fig. 2). This suggests that, in our experimental conditions, the main species involved in the palladium reoxidation are probably $\text{V}^{(\text{V})}\text{O}_2^+$ and heteropoly acids containing a high number of vanadium atoms. In order to confirm this result, heteropoly acids containing 1, 2 and 3 vanadium atoms have also been tested in dec-1-ene oxidation. The results are presented in Table 2 and indicate undoubtedly that these heteropoly acids, even modified by copper, are ineffective on palladium reoxidation in our experimental conditions. For example, with the pure heteropoly acid $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$, the isomeric decenes yield reached 83% (Entry 1 in table 2). It is worth also mentioning that the decan-2-one

Table 2
Dec-1-ene oxidation in the presence of various phosphomolybdovanadic acids ^a

Entry	Phosphomolybdo vanadic acid	Dec-1-ene conversion (mol %)	Decan-2-one selectivity ^b (mol %)	Decan-2-one yield ^c (mol %)	Isomeric decenes yield ^d (mol %)
1	$\text{H}_4\text{PVMo}_{11}\text{O}_{40}$	100	27	27	83
2	$\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$	100	45	45	55
3	$\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$	100	60	60	40
4	$\text{H}_7\text{PV}_4\text{Mo}_8\text{O}_{40}$	80	96	77	3
5	$\text{H}_9\text{PV}_6\text{Mo}_6\text{O}_{40}$	100	98	98	2
6	$\text{H}_{11}\text{PV}_8\text{Mo}_4\text{O}_{40}$	70	92	65	5

^a PdSO_4 : 0.86 mmol; CuSO_4 : 10 mmol; phosphomolybdovanadic acid: 10 mmol (phosphorus atom); per(2,6-di-*O*-methyl)- β -cyclodextrin: 1 mmol; H_2O : 1.66 mol (30 ml); $\text{C}_{10}\text{H}_{20}$: 40 mmol (7.6 ml); T : 80°C; t : 6 h; $P(\text{O}_2)$: 1 bar.

^b Decan-2-one/converted dec-1-ene.

^c Chromatographic yield.

^d Dec-2-ene, dec-3-ene, dec-4-ene and dec-5-ene.

yields increased with the number of vanadium atoms in the phosphomolybdovanadic acids. Similar behavior has also been observed by Matveev during the ethylene oxidation [19].

Although the dec-1-ene conversion is not complete, spectra (d) and (e) in Fig. 2 show surprisingly that the signals between -540 ppm and -620 ppm are restored after 85 min of reaction. As these signals have been attributed to heteropoly acids which can oxidize palladium(0) to palladium(II), significant amounts of

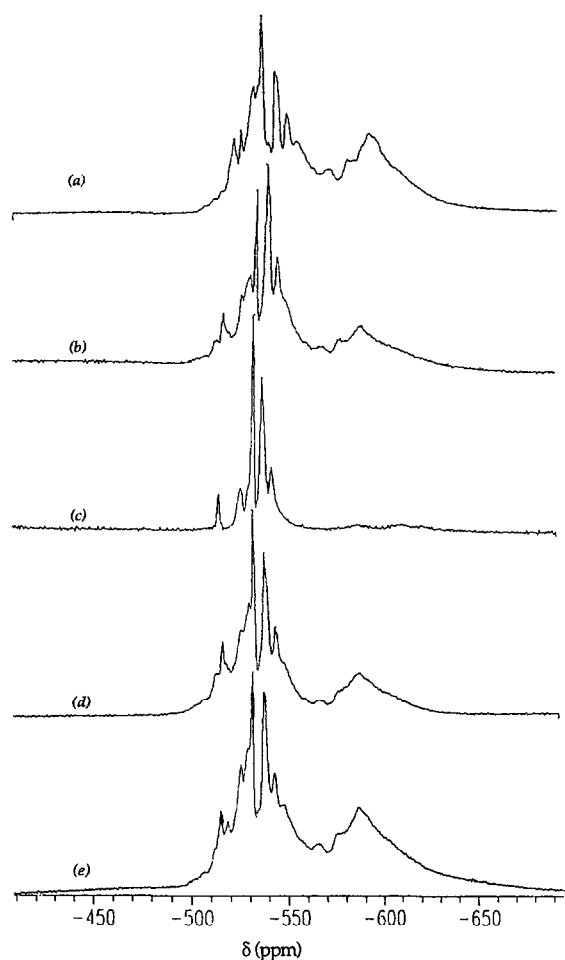
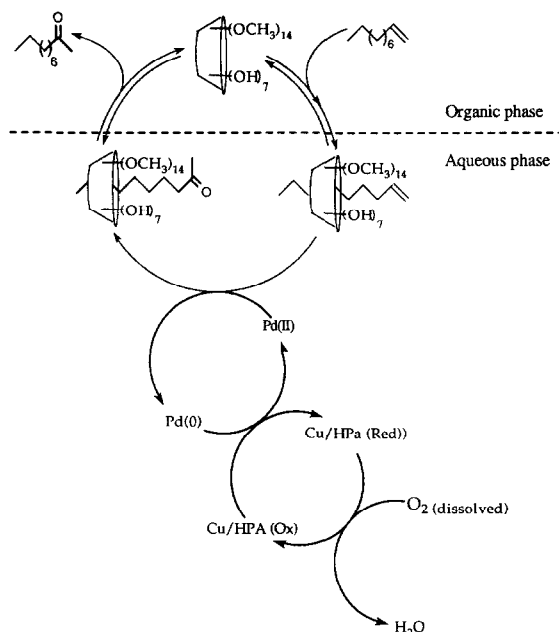


Fig. 2. ^{51}V NMR spectra of the aqueous phase during dec-1-ene oxidation: (a) $t = 0$ min, (b) $t = 5$ min, (c) $t = 30$ min, (d) $t = 85$ min, (e) $t = 400$ min. During the ^{51}V NMR spectroscopic study, the decan-2-one yield was monitored by gas liquid chromatography. The results obtained and the experimental conditions are presented in Fig. 1 (catalytic system: \square).



Scheme 4. Catalytic steps involved in the biphasic oxidation of dec-1-ene. The per(2,6-di-*O*-methyl)- β -cyclodextrin is schematically represented by a hollow truncated cone. Cu/HPa: phosphomolybdovanadic acid modified by copper.

palladium(II) must be present in the aqueous solution at this reaction stage. Furthermore, it is worth also mentioning that the catalytic activity is low when the signals between -540 ppm and -620 ppm are restored (see Fig. 1 – catalytic system \square). This catalytic activity can be improved partly by using increasing amounts of inverse phase transfer catalyst (see Fig. 3).

This increase in catalytic activity with the methylated cyclodextrin concentration and the presence of significant amounts of palladium(II) and oxidizing heteropoly acids suggest that, at low cyclodextrin concentration (1 mmol), the rate determining step is the mass transfer between aqueous and organic phases. The slowing down of the catalytic activity with the increase in ketone concentration could be due to poisoning of the per(2,6-di-*O*-methyl)- β -cyclodextrin by the decan-2-one. Actually, at high decan-2-one concentration, we think that much of the cyclodextrin preferentially forms an inclusion complex with decan-2-one and not with dec-1-

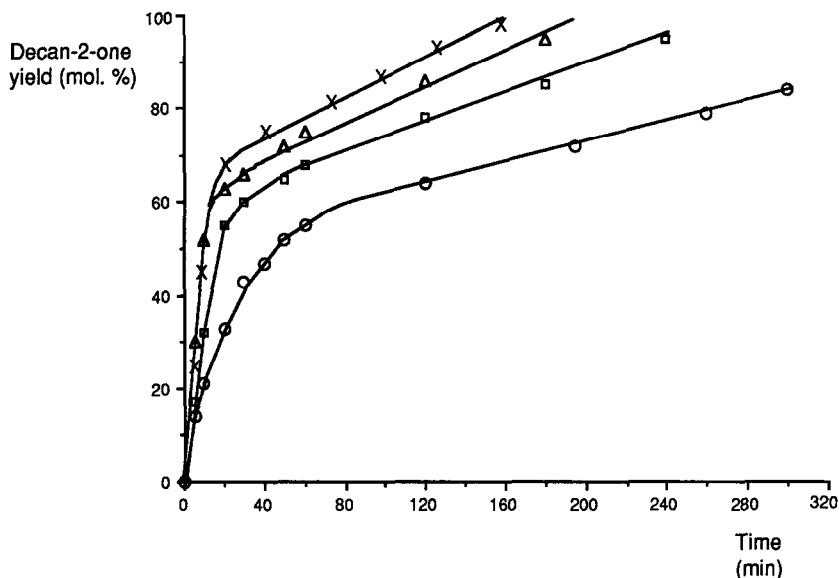


Fig. 3. Effect of per(2,6-di-*O*-methyl)- β -cyclodextrin concentration on dec-1-ene conversion. Per(2,6-di-*O*-methyl)- β -cyclodextrin: ○: 1 mmol; □: 2 mmol; △: 4 mmol; ×: 5 mmol [dec-1-ene]/[palladium]: 40; PdSO₄: 0.86 mmol; CuSO₄: 10 mmol; H₉PV₆Mo₆O₄₀: 10 mmol; H₂O: 30 ml; *T*: 85°C; *P*(O₂): 1 bar.

ene owing to the hydrogen bonding between hydroxy groups of the cyclodextrin and carbonyl group of the decan-2-one [11](b),[20].

Interestingly, when the per(2,6-di-*O*-methyl)- β -cyclodextrin concentration is high, the curves of the Fig. 3 show a breaking of slope (see curves: △ (4 mmol) and × (5 mmol)). Moreover, it should be noticed that these curves are identical for a decan-2-one yield lower than 60%. These results could be attributed to a change of the rate determining step. Indeed, when the decan-2-one concentration is low, the cyclodextrin is not poisoned and can transfer easily dec-1-ene into aqueous phase. In these conditions, we think that the rate determining step is not the mass transfer between aqueous and organic phases but probably the oxidation of dec-1-ene into decan-2-one by palladium(II). When the decan-2-one concentration increases, the cyclodextrin is poisoned sooner or later by the ketone and the catalytic activity drops significantly again. This problem could be solved theoretically by using stoichiometric amounts of inverse phase-transfer catalyts. Unfortunately, at

such a concentration, per(2,6-di-*O*-methyl)- β -cyclodextrin is not totally soluble in water.

4. Conclusion

We have demonstrated that the PdSO₄/CuSO₄/H₉PV₆Mo₆O₄₀/per(2,6-di-*O*-methyl)- β -cyclodextrin combination is an highly efficient catalytic system for oxidation of water-insoluble olefins in a solvent-free two-phase system. The efficiency of the above system has been attributed to the formation of copper/heteropoly acid complexes (reoxidizing system) and to the formation of inclusion complexes between per(2,6-di-*O*-methyl)- β -cyclodextrin and substrate (inverse phase-transfer catalysis). Finally, this system can also be considered as a new example of multistep catalysis in a two-phase system (Scheme 4) and further efforts to extend the scope of this process are currently underway in our laboratory.

Acknowledgements

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