

# Hydrogenation of mandelic acid derivatives to the corresponding phenyl acetic acid derivative catalysed by Pd/C. A kinetic study

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## Abstract

The hydrogenolysis of the  $\alpha$ -C–O bond of mandelic acid derivatives catalysed by 5% Pd/C, in the presence of hydrochloric or sulphuric acids as cocatalysts, was carried out in water or ethanol as solvent, under 35–150 kPa of hydrogen pressure, at 343 K. Typically, the substrate/catalyst/cocatalyst ratio was 200 : 1 : 10. The hydrogenation of the ethyl ester of mandelic acid in ethanol as solvent is much faster, ca. 20 times, than that of the acid in water. The influence of the concentration of the reagents, products and cocatalysts on the initial reaction rate was investigated. Upon increasing the concentration of the ester the rate increases to a plateau. The pressure of hydrogen has little influence. The products inhibit the reaction. The rate steeply increases and reaches a maximum upon increasing hydrochloric acid concentration. From equilibrium constant data, the concentration of protonated ester as a function of the hydrochloric cocatalyst concentration has been estimated. The trend of the concentration of the protonated species parallels the trend of the reaction rate, thus suggesting that the protonated species plays a key role in relation to the catalyst activity. It is suggested that from this species, adsorbed on the catalyst surface, a molecule of water is displaced by a hydride formed upon activation of molecular hydrogen by palladium. Though less effective than hydrochloric acid, sulphuric acid acts also as a cocatalyst. However, in the latter case, the initial hydrogenation rate increases to reach a plateau. In addition, when HCl is introduced in the reaction after the preactivation step of the catalyst, the hydrogenolysis rate is equal to the rate observed when sulphuric acid is used as cocatalyst. It is suggested that in the first case the possible formation of the superficial  $\text{PdO}_x\text{Cl}_y$  may be related to the higher activity of the chlorided catalyst. © 1997 Elsevier Science B.V.

**Keywords:** Mandelic acid derivative; Hydrogenation; Kinetics; Phenyl acetic acid

## 1. Introduction

The hydrogenation of mandelic acid derivatives,  $\text{ArCH}(\text{OR})\text{COOR}'$  (Ar=phenyl or substituted phenyl; R=H, Et, Ac, Bz; R'=H, Et) is known to occur with hydrogenolysis of the carbon–oxygen bond in  $\alpha$  position to yield the corresponding arylacetic acid deri-

vatives when carried out in the presence of a suitable catalyst such as nickel, palladium or platinum [1–3]. In an early study nickel was employed under relatively high temperature and pressure (553 K, 8 MPa, 14 h). Under these conditions the reaction was not highly selective as the hydrogenation at the aromatic ring to the corresponding cyclohexyl group occurred too (the desired product was obtained only in 40% yield starting from the sodium salt of mandelic acid and

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using nickel oxide as catalyst precursor, in water as solvent). Palladium is active under milder conditions. For example, the hydrogenation of ArCH(OAc)COOR' (R'=H, Me, Et) was carried out in the presence of metallic palladium and of an acid as cocatalyst (H<sub>2</sub>SO<sub>4</sub>, HCl, ZnCl<sub>2</sub>, HBr) at 373 K and 200–300 kPa of hydrogen in AcOH as solvent. The yield was 80–90% and partial hydrogenation at the aromatic ring occurred [2]. The hydrogenation of ArCH(OAr)COOR' (R'=H, Et, Ar) was carried out using also Pd/BaSO<sub>4</sub> as catalyst in the presence of NEt<sub>3</sub>, in EtOH, MeOH or AcOH as solvent, at 293 K and 100 kPa. Under these mild conditions the hydrogenation was 100% selective as no cyclohexyl derivative formed. A large excess of the base accelerated the reaction. The hydrogenolysis of optically active ethyl *O*-benzoylatrolactate and of  $\alpha$ -phenyltetraalkylammonium salts were accompanied by inversion [4].

Selective hydrogenolysis was obtained also via hydrogen transfer reactions from the couple H<sub>2</sub>O–CO, in the presence of HCl [5], and from formates in the presence of H<sub>2</sub>O [6].

Mandelic acid can be conveniently prepared by hydrolysis of the mandelonitrile obtainable by reacting benzaldehyde with hydrocyanic acid [7] or by reacting sodium or potassium cyanide with the sodium bisulfite addition product of benzaldehyde [8], which is largely available as by-product in the production of benzoic acid [9]. It can be easily obtained also by hydrolysis of dichloroacetophenone, which in turn can be prepared by chlorination of acetophenone [10], a by-product in the production of phenol via cumene [11].

Thus, since it appears that the selective hydrogenation of mandelic acid derivatives can be a viable and convenient way to arylacetic acid derivatives, we have undertaken a study on the highly selective hydrogenation of some mandelic acid derivatives to the corresponding phenylacetic acid derivatives catalysed by Pd/C catalysts. Here we present the results of a kinetic investigation.

## 2. Experimental

### 2.1. Materials

Mandelic acid (99.5%, RPE Carlo Erba), ethyl mandelate (97%, Acros), phenylacetate ethyl ester

(99%, Acros),  $\alpha$ -Cl-phenylacetate ethyl ester (99%, Acros), tetradecane (99%, Acros), acetonitrile (99%, Riedel de Hänn) were used without further purification. Hydrochloric acid (36%, BDH), sulphuric acid (98%, BDH), ethanol (>99%, Absolute Baker) were reagent grade. Hydrogen, nitrogen and carbon monoxide (purity>99.99%) were purchased from SIAD Co.

The catalysts used throughout this study were a 5% Pd/C (Engelhard ESCAT 11, ESCAT 10, ESCAT 111). Kinetic studies were carried out with ESCAT 11.

### 2.2. Equipment

Products were identified by GC on a Hewlett-Packard gaschromatograph model 5890 II, using a FFAP 530  $\mu$ , 25 m long, with nitrogen as carrier (SIAD, GC quality). Tetradecane was used as internal standard. Analysis conditions: injector 523 K; detector 543 K; oven 393 K, 20 K/min up to 483 K, 483 K for 10'; nitrogen 7.5 ml/min. Volumetric adsorption measurement were made in a Micromeritics ASAP 2010 chemisorption instrument.

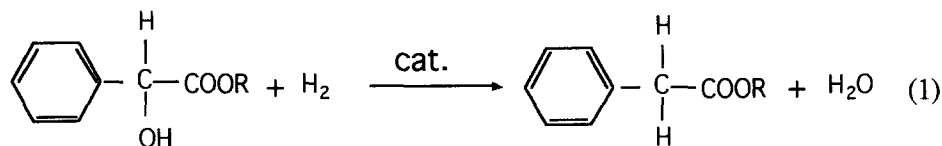
### 2.3. Catalytic hydrogenolysis reactions

The reaction was carried out in a glass reactor of ca. 200 ml of capacity, thermostated by a water bath, connected with a hydrogen reservoir of relatively small capacity (12.5 ml). The reaction was carried out at constant temperature and pressure. The course of the reaction was followed by monitoring the decrease of hydrogen pressure in the reservoir. The initial rate of the reaction was calculated by determining the pressure drop versus time at time=0.

In a typical experiment 106.4 mg of 5% Pd/C (corresponding to 0.05 mmol of palladium), and the exact amount of HCl were charged together with 25 ml of ethanol previously saturated with hydrogen into the reactor. This is heated to the reaction temperature, typically 343 K, under 50–200 kPa of hydrogen. The system is kept for ca. 1 h under efficient stirring to activate the catalyst. To this slurry a solution of ethyl mandelate (typically 10 mmol with 2 mmol of tetradecane) in 25 ml of EtOH, previously saturated with hydrogen, is added. The reaction is allowed to proceed for 1–2 h. The temperature and the pressure of hydrogen in the reactor are kept constant throughout

the experiment (typically 343 K,  $P_{H_2}=97$  kPa). The absence of hydrogen absorption control in the reaction was established by performing experiments at

catalyst, eventually in the presence of hydrochloric or sulphuric acid as cocatalysts. Typically, the substrate/catalyst/cocatalyst ratio was 200/1/10.



R = H, Et.

1500 rpm as well as 800 rpm: in both cases the rate of reaction were practically the same. More over the initial rate of reaction is proportional to the amount of catalyst in the range investigated (30–180 mg of catalyst). An apparent activation energy of  $43 \text{ kJ mol}^{-1}$  was determined by carrying out experiments at 303, 313, 328, 343 and 350 K. An inspection of the Carberry and Weeler–Weisz criterion shows that the reaction is out of diffusion control both at liquid/solid interface as well as into the pores of the catalyst [12].

#### 2.4. CO chemisorption

In a typical experiment 40–60 mg of catalyst were charged in a sample tube, heated at 373 K in nitrogen flow ( $40 \text{ ml min}^{-1}$ ) for 1 h and in hydrogen flow ( $30 \text{ ml min}^{-1}$ ) for 1 h, then the temperature was raised to 523 K (heat rate  $10 \text{ K min}^{-1}$ ) and held for 2 h. The pretreatment continues with a nitrogen flow ( $40 \text{ ml min}^{-1}$ ) at 523 K for 2 h and at the end with an evacuation for 2 h. CO chemisorption was performed at 303 K and uptake was evaluated with the dual isotherm technique [13,14]. Metal dispersion was calculated fixing up  $\text{CO}/\text{Pd}_{\text{sup}}=1$ .

### 3. Results and discussion

#### 3.1. Influence of the concentration of the reagents, of the reaction products, of the catalyst and cocatalyst on the rate of the hydrogenation

The hydrogenation of mandelic acid or of its ethyl ester, depicted by reaction (1), was carried out in water or ethanol as solvent, respectively, under 35–150 kPa of hydrogen pressure, at 343 K, using a 5% Pd/C

At high conversion the main reaction was accompanied by hydrogenation of the aromatic ring with formation of cyclohexylacetic acid derivative (3–4%).

The influence of the following variables on the hydrogenation rate of the ethyl ester was studied: concentration of substrate, of hydrogen, of the reaction products, of the catalyst, of the cocatalyst and of the temperature. The hydrogenation of  $\alpha$ -chloro-phenylacetate ethyl ester was also studied.

The influence of concentration of the hydrochloric acid cocatalyst on the initial hydrogenation rate of mandelic acid in water or of its ethyl ester in ethanol is shown in Figs. 1 and 2 respectively. It can be observed in the latter case the rate is much higher, ca. 20 times. Moreover, Fig. 1 shows that the initial reaction rate quickly increases upon increasing acid concentration up to  $0.05\text{--}0.1 \text{ mol l}^{-1}$ , then stays almost constant.

The hydrogenation of the ethyl ester of mandelic acid in ethanol as solvent is much faster, ca. 20 times, than that of the acid in water. Fig. 2 shows the influence of the hydrochloric acid concentration on the initial hydrogenation rate of the ester, at three different water concentrations, which is a reaction product. The rate steeply increases and reaches a maximum upon increasing acid concentration. This trend suggests that, at low concentration the acid has a promotional effect and, at higher concentration, also an inhibiting effect. Moreover, it can be observed that the maximum occurs at higher concentration of the acid as the concentration of water increases.

It is likely that the promoting effect of the acid is due to protonation of the hydroxyl group of the starting substrate, thus providing an easier way for

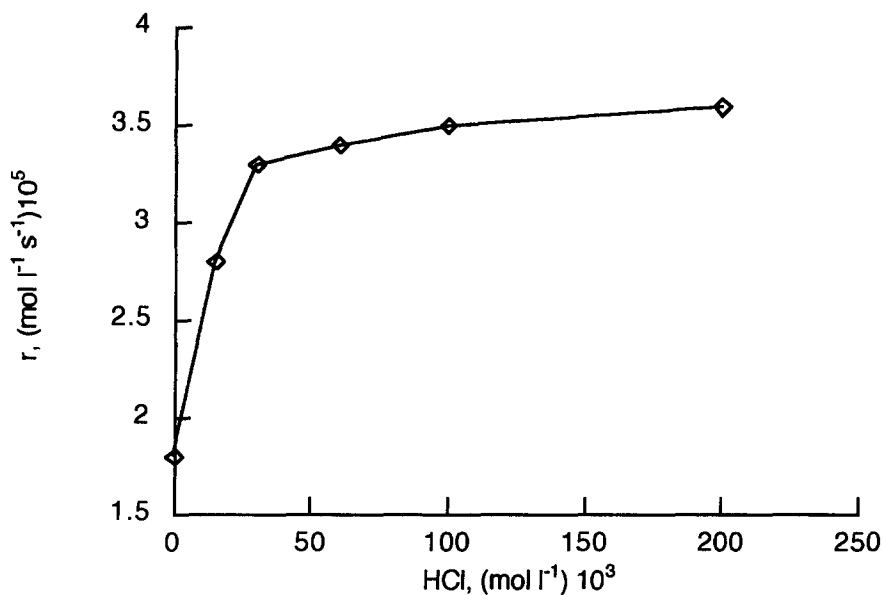


Fig. 1. Influence of the concentration of HCl on the initial reaction rate of hydrogenolysis of mandelic acid in water. Run conditions: concentration of mandelic acid  $0.19 \text{ mol l}^{-1}$ ;  $[\text{Pd}] = 1.9 \times 10^{-3} \text{ mol l}^{-1}$ ;  $T = 343 \text{ K}$ ;  $P_{\text{H}_2} = 100 \text{ kPa}$ ;  $P_{\text{tot}} = 130 \text{ kPa}$ .

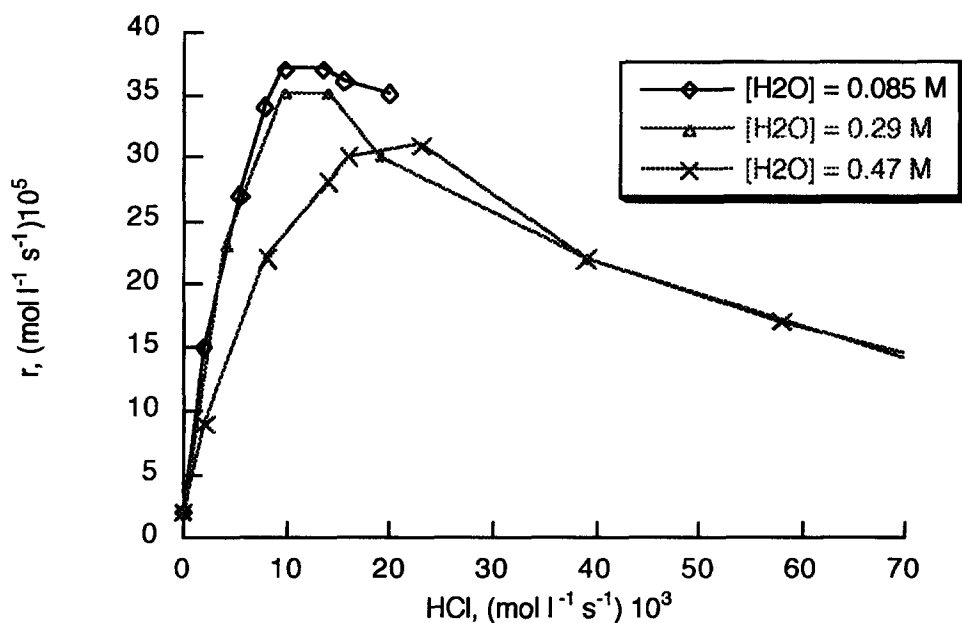
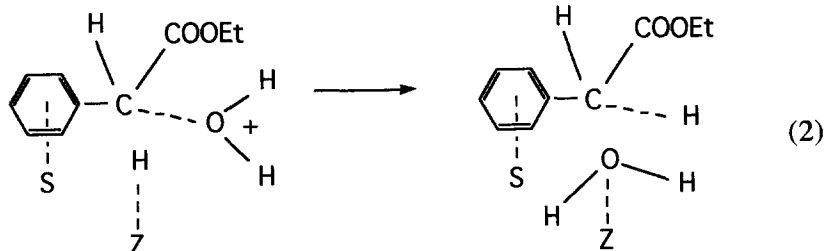


Fig. 2. Influence of the concentration of HCl on the initial reaction rate of hydrogenolysis of ethyl mandelate in ethanol. Run conditions: concentration of ester  $0.19 \text{ mol l}^{-1}$ ;  $[\text{H}_2\text{O}] = 0.085 \text{ mol l}^{-1}$  (A);  $0.29 \text{ mol l}^{-1}$  (B);  $0.47 \text{ mol l}^{-1}$  (C); concentration of  $[\text{Pd}] = 9.610^{-4} \text{ mol l}^{-1}$ ;  $T = 343 \text{ K}$ ;  $P_{\text{H}_2} = 97 \text{ kPa}$ ;  $P_{\text{tot}} = 170 \text{ kPa}$ .

the substitution of this group by a hydride activated on the metal



Such a suggestion has been proposed also for the closely related hydrogenolysis of benzyl alcohol derivatives to toluene derivatives catalysed by Pd/C [15].

Fig. 2 shows also that the maximum reaction rate decreases upon increasing water concentration. This observation suggests that water inhibits the reaction (see later).

Though less effective than hydrochloric acid, sulphuric acid acts also as a cocatalyst. However, in the

latter case, the initial hydrogenation rate increases to a plateau as shown in Fig. 3. The comparison of

Fig. 2 with Fig. 3 suggests that the chloride anion plays an important role on the hydrogenolysis reaction, at difference of the sulphate anion. Since it is known that the chloride anion is a better coordinating species than the sulphate anion, the promoting-inhibiting effect of hydrochloric acid, evidenced in Fig. 2, is likely associated with the competitive adsorption of the halogen anion on the surface of the catalyst.

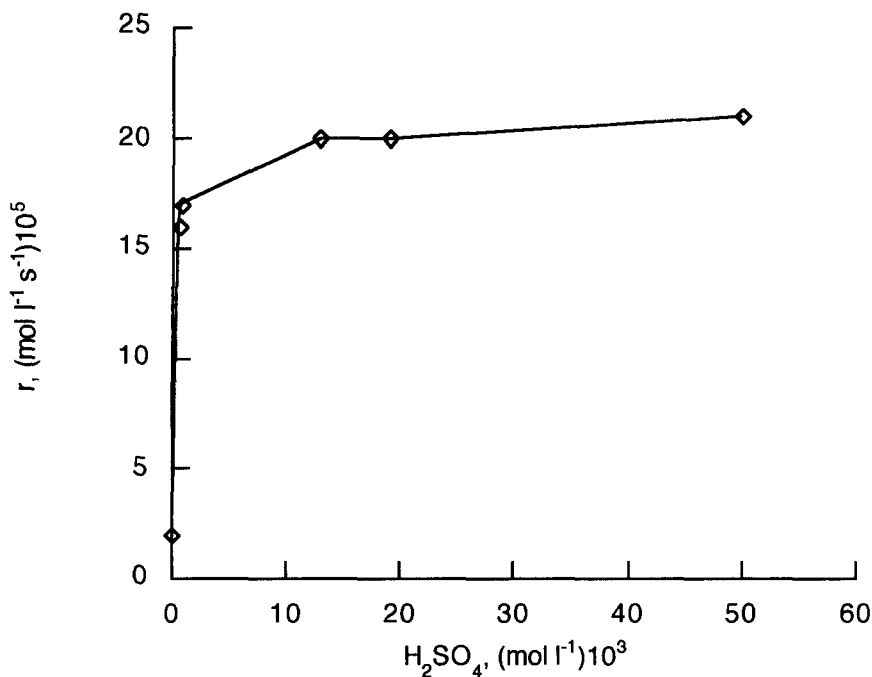


Fig. 3. Influence of the concentration of  $H_2SO_4$  on the initial reaction rate of hydrogenolysis of ethyl mandelate in ethanol. Run conditions: in Fig. 2 with  $[H_2O]=0.091\ mol\ l^{-1}$ .

Table 1

Hydrogenolysis of  $\alpha$ -Cl phenylacetic ethyl ester and ethylmandelate promoted with hydrochloric and sulphuric acid

	Ethylmandelate mol l <sup>-1</sup> × 10 <sup>3</sup>	$\alpha$ -Cl-phenylacetate mol l <sup>-1</sup> 10 <sup>3</sup>	<i>r</i> mol l <sup>-1</sup> s <sup>-1</sup> × 10 <sup>5</sup>	H <sub>2</sub> SO <sub>4</sub> mol l <sup>-1</sup> × 10 <sup>3</sup>	HCl mol l <sup>-1</sup> × 10 <sup>3</sup>
1	192	—	36	—	13
2	192	—	18	6.8	—
3	192	—	2	—	—
4	179	13	10	—	—
5	179	13	20	6.8	—
6	—	192	10	—	—
7	—	192	10	6.8	—

The comparison of the hydrogenation initial rates of ethylmandelate with  $\alpha$ -Cl-phenylacetate ethyl ester can explain the role of the chloride anion.

In Table 1 the initial rate of the  $\alpha$ -Cl phenylacetic ethyl ester hydrogenolysis is compared with that of ethylmandelate promoted with hydrochloric or sulphuric acid. Sulphuric acid does not affect the hydrogenation rate of  $\alpha$ -Cl-phenylacetate ethyl ester (entries 6 and 7). The hydrogenolysis rate of ethylmandelate in the presence of the  $\alpha$ -Cl derivative (0.0135 mol l<sup>-1</sup>) is equal to the rate of hydrogenation of  $\alpha$ -Cl-phenylacetate ethyl ester (entries 4 and 6). The same reaction in the presence of sulphuric acid gives an initial rate close to the sulphuric acid promoted hydrogenation of ethylmandelate (entries 2, 5 and 7). These results suggest that in the hydrogenolysis of ethylmandelate in the presence of hydrochloric acid the  $\alpha$ -chloride, eventually formed, does not play a major role.

Moreover, we found that, when the catalyst preactivation with hydrogen is carried out in the presence of HCl, the resulting catalyst is almost twice as active as when sulphuric acid is used as cocatalyst. On the contrary, when HCl is introduced in the reaction after the preactivation of the catalyst, the hydrogenolysis rate is practically equal to that obtained when sulphuric acid is employed as promoter.

It is well known that preactivation is necessary in order to eliminate the oxygen passivation layer. It is possible that when HCl is added before the preactivation step, the metal covered by oxygen partially dissolves and that the subsequent reprecipitation of the metal during the pretreatment with hydrogen may give rise to a metal dispersion different from that resulting when the acid is added after the pretreatment with

hydrogen. However no leaching of the metal has been detected by analysing the solvent in which Pd/C and HCl were added before preactivation. Moreover, X-ray measurements showed that the metal dispersion does not change upon this type of pretreatment (unpublished data).

It is also known [16] that chlorided Pt surface compounds are able to enhance the hydrogenation rate of carbonyl group. It is possible that in a similar way chloride anions act on Pd thus enhancing the hydrogenolysis reaction. As a matter of fact, several authors [17–19] found that both PtO<sub>2</sub> and PdO form MO<sub>x</sub>Cl<sub>y</sub> compounds in the presence of Cl<sup>-</sup> and that these oxychlorides lower the reducibility of the metal (PdO is easily reduced to metallic Pd at 270 K). When the preactivation is carried out in the presence of HCl, the possible formation of superficial PdO<sub>x</sub>Cl<sub>y</sub> may be related to the higher catalyst activity.

The influence of the ethylmandelate concentration on the initial reaction rate, at two different hydrochloric acid concentrations, was investigated. As shown in Fig. 4 the reaction at first steeply increases upon increasing ester concentration, reaches a plateau when the concentration is ca. 250 mmol l<sup>-1</sup>. This trend suggests that progressively saturates the sites that adsorb the ester.

The pressure of hydrogen has little effect on the hydrogenation rate as shown in Fig. 5. This is true at different acid and water concentrations. This suggests that hydrogen saturates the sites on the catalyst surface capable of activating this molecule.

The effects of the reaction products, phenylacetate ethyl ester and water, on the initial reaction rate are shown in Figs. 6 and 7. Both inhibit the reaction. The effect of water can have different origins: (i) compe-

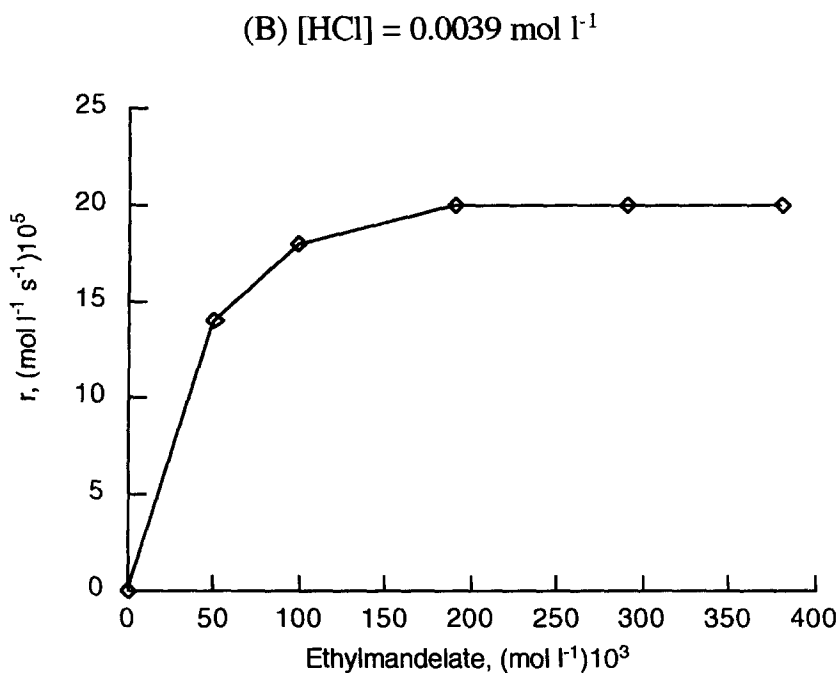
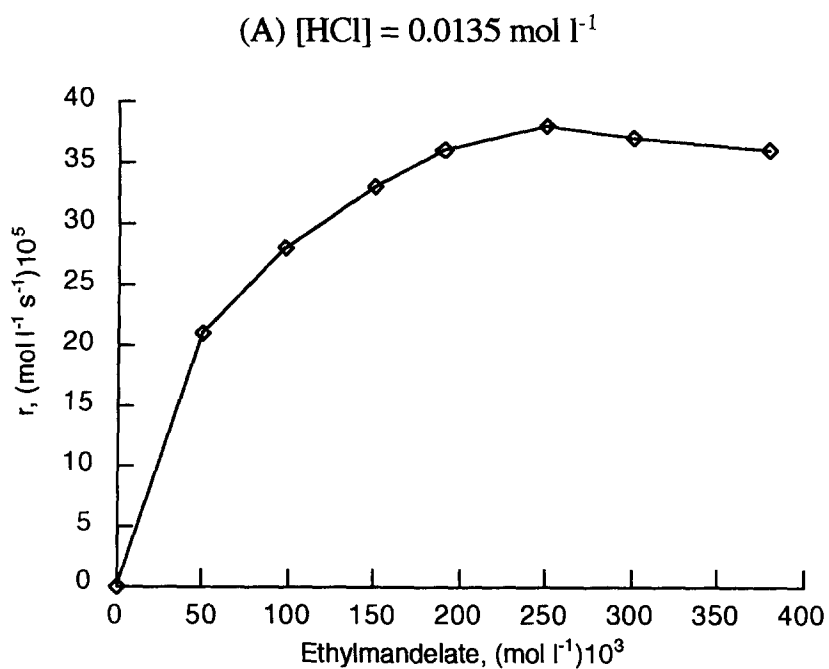


Fig. 4. Influence of the concentration of ethyl mandelate on the initial reaction rate of hydrogenolysis of ethylmandelate in ethanol at two different concentration of HCl:  $[\text{HCl}] = 0.0135 \text{ mol l}^{-1}$  (A) and  $[\text{HCl}] = 0.0039 \text{ mol l}^{-1}$  (B). The remaining run conditions as in Fig. 2, case (A), except for the concentration of the acid and of the ester.

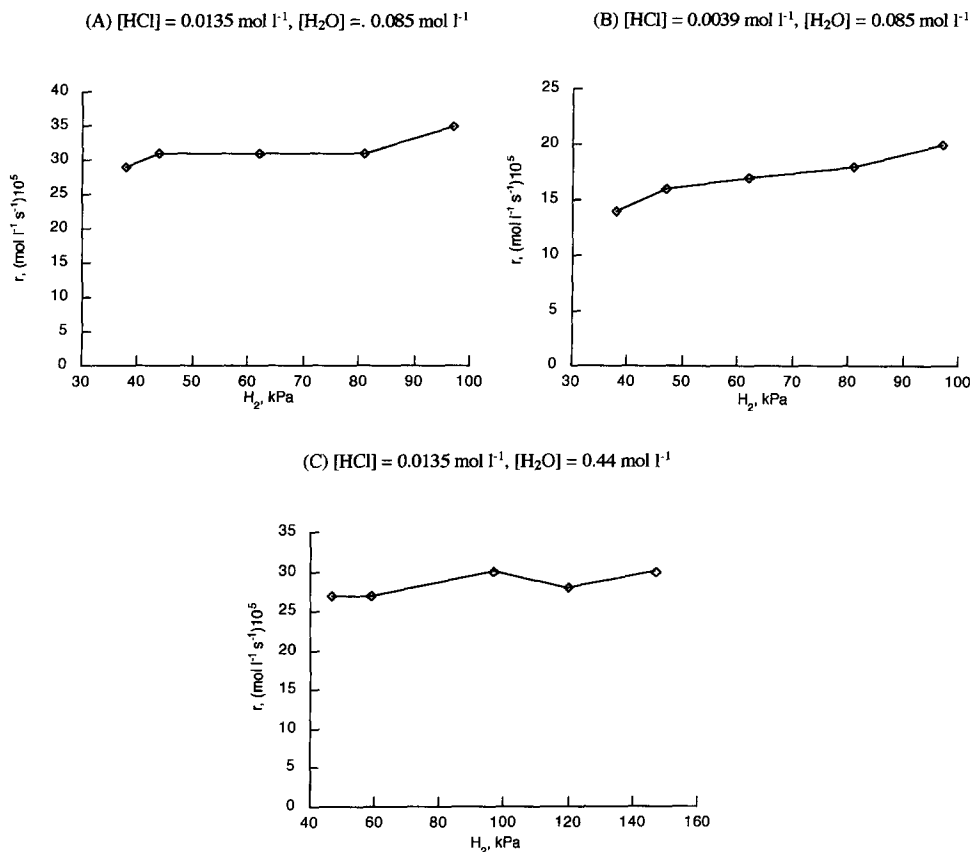
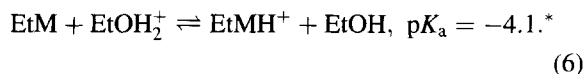
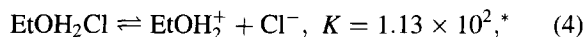
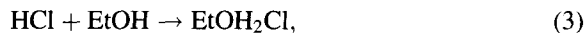


Fig. 5. Influence of the pressure of hydrogen on the initial reaction rate of hydrogenolysis of ethylmandelate in ethanol at two different concentration of HCl and of  $\text{H}_2\text{O}$ : (A)  $[\text{HCl}] = 0.0135 \text{ mol l}^{-1}$  and  $[\text{H}_2\text{O}] = 0.085 \text{ mol l}^{-1}$ , respectively; (B)  $[\text{HCl}] = 0.0039 \text{ mol l}^{-1}$  and  $[\text{H}_2\text{O}] = 0.085 \text{ mol l}^{-1}$ , respectively; (C)  $[\text{HCl}] = 0.0135 \text{ mol l}^{-1}$  and  $[\text{H}_2\text{O}] = 0.44 \text{ mol l}^{-1}$ , respectively. The remaining run conditions as in Fig. 2.

titive adsorption of water with the reacting molecules [20]; (ii) the acid protonates also the water molecule thus the concentration of the protonated ester, which plays an important role in the catalytic process, is lower; (iii) water gives rise to hydrolysis of the ester with formation of free mandelic acid.

In order to check point (i), the effect of water was studied in the absence of HCl. The result is shown in Fig. 8. The inhibition observed is quite similar to that measured in the reactions promoted with HCl. These results suggest that the competitive adsorption of water can be a cause of inhibition of the ethylmandelate hydrogenation.

Concerning point (ii), in an ethanol solution of aqueous HCl, the following protonation equilibria should be considered:



\* Measured at 298 K; EtM=ethylmandelate.

The concentration of the species involved in the equilibria were calculated solving the simultaneous equations obtained from the equilibrium relations, the mass balance and the electroneutrality balance. The equilibrium constants reported in literature [21–25] were used in the calculation, and the basicity of the ethylmandelate was estimated from the data available



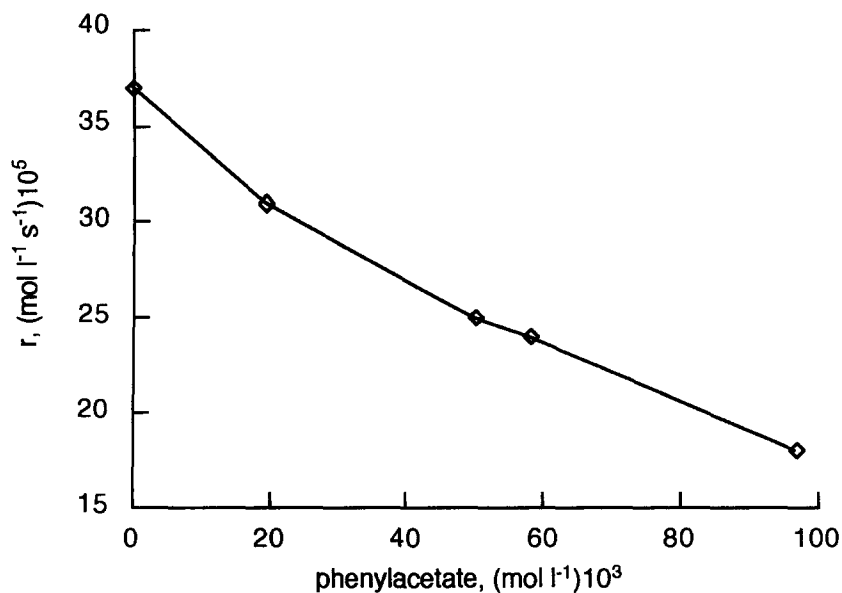


Fig. 6. Influence of the concentration of ethyl phenylacetate on the initial reaction rate of hydrogenolysis of ethylmandelate in ethanol. Run conditions as in Fig. 2, case (A), except for the concentration of  $[\text{HCl}] = 0.0135 \text{ mol l}^{-1}$ .

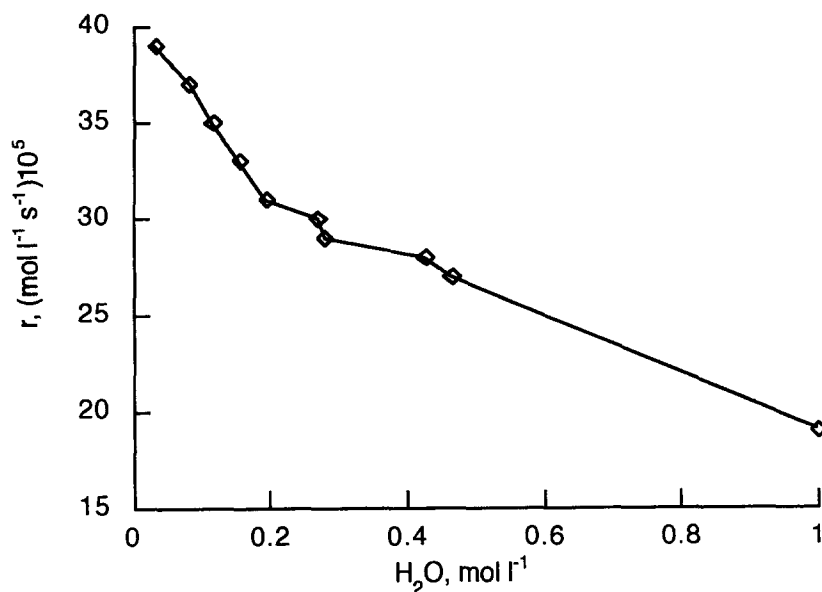


Fig. 7. Influence of the concentration of  $\text{H}_2\text{O}$  on the initial reaction rate of hydrogenolysis of ethyl mandelate in ethanol. Run conditions as in Fig. 2, except for the concentration of  $[\text{HCl}] = 0.0135 \text{ mol l}^{-1}$ .

for benzyl alcohol [24,25] (esters are 2–4 orders of magnitude less basic than an alcohol). On the basis of such calculations the concentration of the protonated ester was estimated.

In Fig. 9 the concentration of the protonated ester vs. the reaction rate, obtained from the data of Figs. 7 and 4(A) are plotted. The trends are quite similar. This fact suggests that the preequilibrium (6) influences the

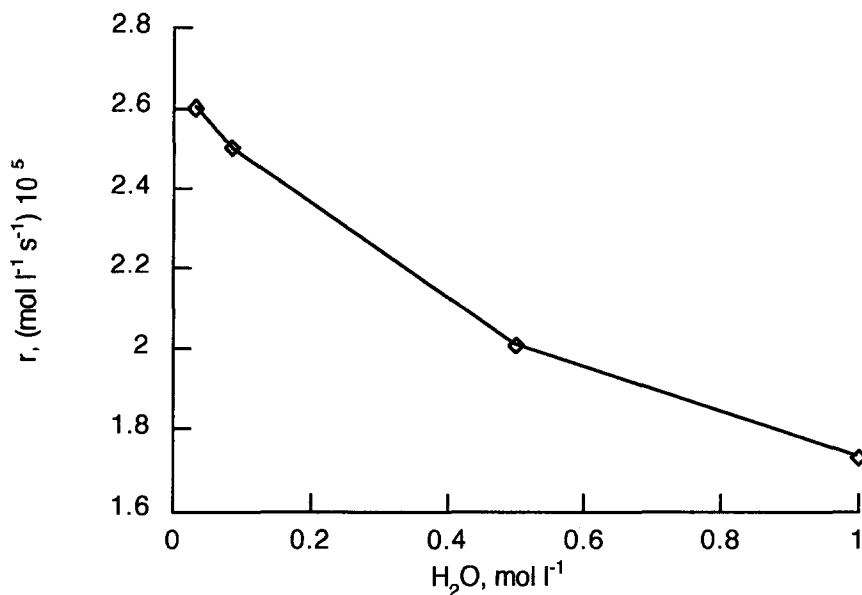


Fig. 8. Influence of the concentration of H<sub>2</sub>O on the initial reaction rate of hydrogenolysis of ethylmandelate in ethanol. Run conditions as in Fig. 2, but without adding HCl.

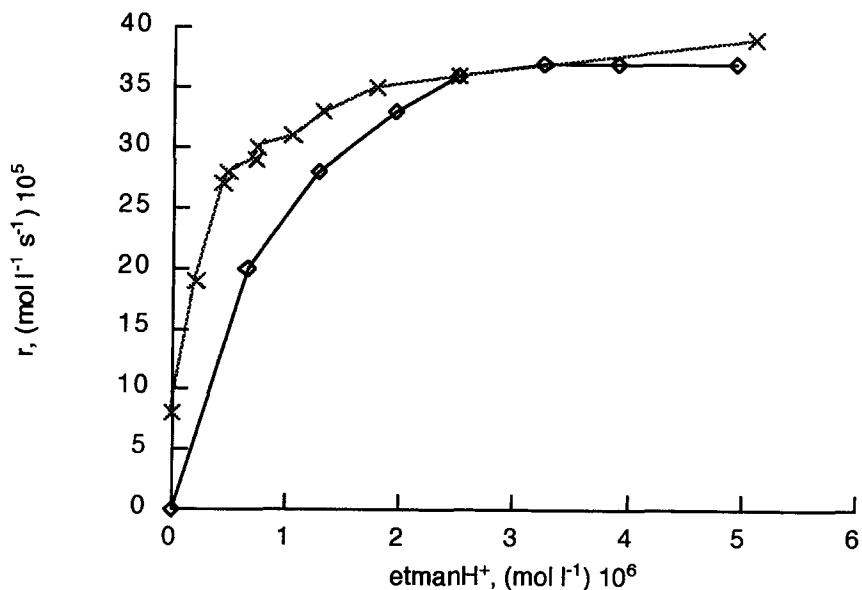


Fig. 9. Influence of the protonated ester on the initial reaction rate of hydrogenolysis of ethylmandelate: upper curve was calculated from data of Fig. 7, the lower from data of Fig. 4(A).

reaction rate. The comparison between the two curves clearly indicates that the protonated substrate achieves the saturation of the catalyst surface at very low concentration ( $2.5 \times 10^{-6} \text{ mol l}^{-1}$ ).

As regard to point (iii), in order to verify whether mandelic acid, which forms upon hydrolysis of the starting ester, affects the reaction kinetic, several reactions were carried out in the presence of a

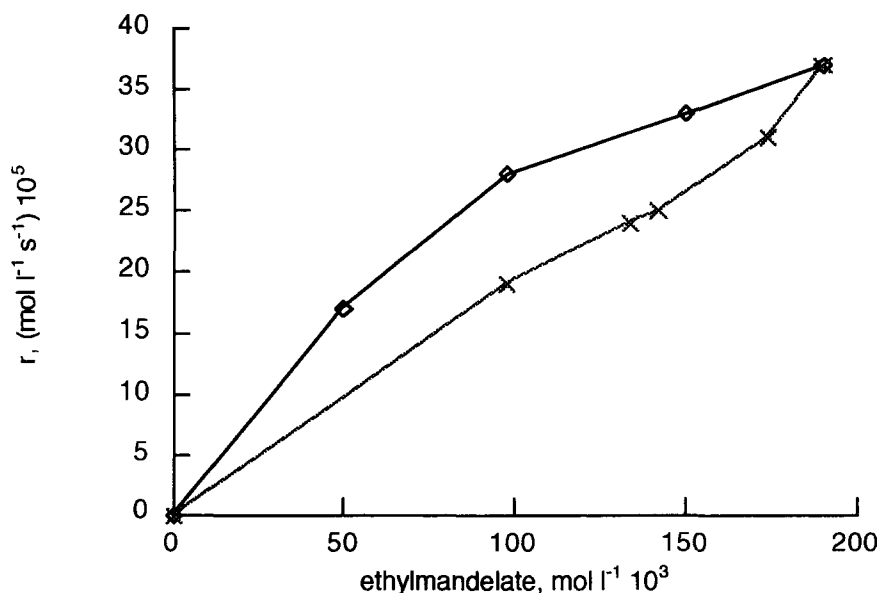


Fig. 10. Effect of the ethylmandelate concentration in the presence of phenylacetate: upper curve no phenylacetate, lower curve varying the concentration of phenylacetate, from 0 to 0.096 mol l<sup>-1</sup>. Run conditions the same of Fig. 4(A) and Fig. 6.

significant amount of mandelic acid (acid : ester=1 : 9 ratio). As the equilibrium of esterification of mandelic acid with ethanol solvent not achieved at time=0, it is possible to study the effect of the mandelic acid on the reaction initial rate. We found that the initial rate of reaction is practically the same as that observed when no acid was added, either in the HCl promoted reaction or in the unpromoted one. These facts suggest that the inhibiting effect of water is not due to the acid produced by the hydrolysis of the ester.

The effect of phenylacetate was studied carrying out the experiments with the overall concentrations of ethylmandelate and ethylphenylacetate equal to 0.192 mol l<sup>-1</sup>. The comparative result is plotted in Fig. 10, where the upper curve represents the effect of the concentration of the ester on the reaction rate at concentration of phenylacetate=0, while the lower line refers to the observed reaction rate when the concentration of the product varies from 0 to 0.096 mol l<sup>-1</sup>.

It can be noticed that the reaction rate is lower when the reaction is carried out in the presence of phenylacetate. The lowering can be attributed to the competitive adsorption between the phenylacetate ester and the protonated substrate on the catalyst surface.

### 3.2. Effect of cocatalysts

The promoting effect of HCl and of H<sub>2</sub>SO<sub>4</sub> are compared to those of other promoters in Fig. 11.

Only HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub> and LiCl have a significant promoting effect, while the others either are not able to promote the catalyst activity or completely inhibit the reaction. The enhanced activity of the catalyst measured in the presence of LiCl can be ascribed to the formation of the chlorided surface species mentioned above. In order to verify the effect of Li<sup>+</sup> cation, an experiment was carried out in the presence of LiClO<sub>4</sub>. As a matter of fact, LiClO<sub>4</sub> deactivates the catalyst as the reaction initial rate is lower than that measured without promoters. This can be due to competitive adsorption of the Li<sup>+</sup> cations [26]. In addition, we found that a reaction carried out in the presence of both H<sub>2</sub>SO<sub>4</sub> and LiCl gives an initial activity higher than that observed for the H<sub>2</sub>SO<sub>4</sub> cocatalyzed reaction and lower than that observed when HCl is employed as cocatalyst. These observations give further support to the hypothesis that competitive adsorption of Li<sup>+</sup> is likely to occur, thus preventing to achieve the same activity when HCl or the system H<sub>2</sub>SO<sub>4</sub>+LiCl are used. They also confirm the hypothesis that exist two distinct effects: one

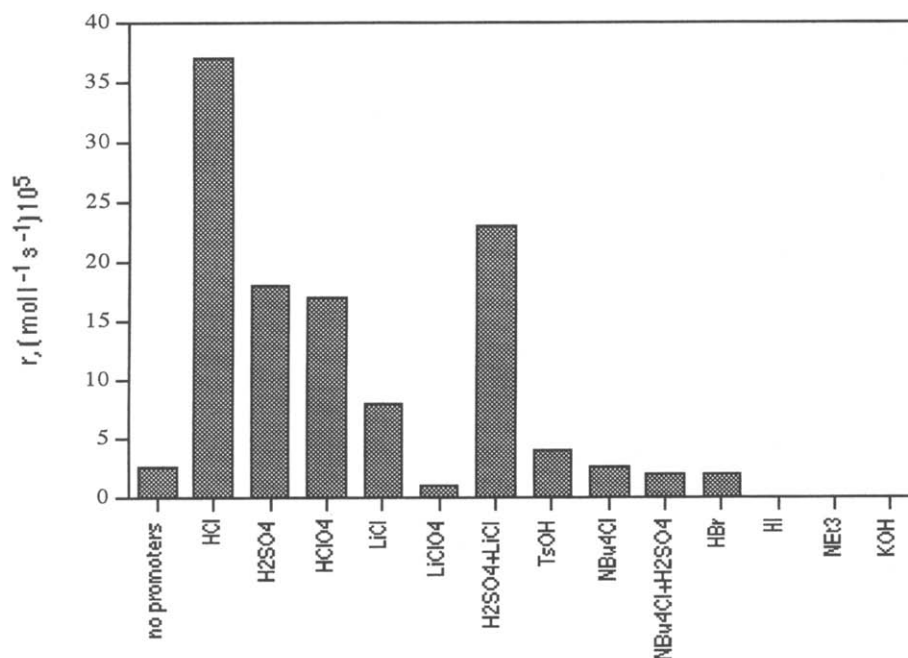


Fig. 11. Effect of promoters on initial rate of ethylmandelate hydrogenation. Run conditions:  $T=343$  K CEM:  $0.19 \text{ mol l}^{-1}$ ; solvent: 50 ml EtOH;  $[\text{Pd}]=9.6 \cdot 10^{-4} \text{ mol l}^{-1}$ ;  $P_{\text{H}_2}=97$  kPa;  $P_{\text{tot}}=170$  kPa;  $[\text{H}_2\text{O}]=0.085 \text{ mol l}^{-1}$ .

ascribable to the protonation of the substrate, and the other due to the formation of chlorided superficial species highly active in the hydrogenation of the substrate. It is interesting to note how *p*-toluensulfonic-acid, which is a strong acid, is not an efficient promoter. This effect could be ascribed to the phenyl group 'hiding' catalyst sites.

From Fig. 11 it appears that HBr and HI do not favour or inhibit the reaction, probably because of the strong absorption of the halogenide which prevents the other species to interact with the metal surface. Note also that NEt<sub>3</sub> and KOH inhibit the reaction.

### 3.3. Effect of catalysts microstructure

The results discussed were obtained employing Engelhard ESCAT 11 catalyst, which has the metal distributed into the bulk of the granule of the activated carbon. In order to check the effect of catalyst microstructure two other types of catalysts were used, with different microstructure. Engelhardt ESCAT 10 Pd/C 5% has the same metal distribution as that of ESCAT 11 but differs for the carbon support which is a peat derived carbon with a high percent of mesopores. Engelhard ESCAT

Table 2  
Chemisorption of CO

Catalyst	Metal distribution on carbon	Metal dispersion Pd <sub>s</sub> /Pd <sub>tot</sub>	CO absorbed ml/g Pd	$r \text{ mol l}^{-1} \text{s}^{-1} 10^5$	TOF s <sup>-1</sup>	E <sub>act</sub> <sup>a</sup> kJ mol <sup>-1</sup>
Escat 11	Bulk	0.28	51.1	37	27	42±4
Escat 10	Bulk WPS <sup>b</sup>	0.29	61.2	40	28	44±4
Escat 111	Eggshell	0.21	44.3	28	27	43±4

<sup>a</sup> Apparent activation energy.

<sup>b</sup> WPS wide pores support.

111 Pd/C 5%, is a catalyst with the metal 'eggshell' distributed.

The chemisorption of CO was studied in order to understand whether metal dispersion influences the activity of the active sites of the catalysts. The results reported in Table 2 show that the catalyst chemisorption is related to their activity. However, turnover frequency is the same for each catalyst and consequently, the catalytic activity of the surface palladium atoms are not appreciably influenced by the metal dispersion. Thus dispersion of the metal does not affect the activity of the sites. The apparent activation energy of the three catalysts is almost the same (ca. 43 kJ mol<sup>-1</sup>). Such an evidence is a further indication that catalyst surface activity is practically the same.

Even though the metallic dispersion does not change during the activation phase, as stated by X-ray diffraction measurements (unpublished data), the solubilization and re-deposition of the metal may induce a re-distribution of the metal on the support. Such an hypothesis can explain the independence of the reaction rate on catalyst microstructure.

#### 4. Conclusions

In the hydrogenation of the ethyl ester of mandelic acid catalysed by Pd/C the acid cocatalysts, hydrochloric or sulphuric acid, play an important role. The initial reaction rate reaches a maximum upon increasing hydrochloric acid concentration, thus, at low concentration, the acid has a promotional effect and, at higher concentration, also an inhibiting effect. The concentration of protonated ester as a function of the hydrochloric concentration has been estimated from equilibrium constant data. Since the trend of the concentration of the protonated species parallels the trend of the reaction rate, it is suggested that the protonated species plays a key role related to the catalyst activity. It is proposed that from this species, adsorbed on the catalyst surface, a molecule of water is displaced by a hydride anion formed upon activation of molecular hydrogen by palladium: the protonation of the hydroxyl group of the starting substrate would provide a easier way for the substitution step.

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