Solvent effects in liquid phase Fries rearrangement of phenyl acetate over a HBEA zeolite

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A kinetic study of phenyl acetate transformation was carried out in a batch reactor over a HBEA zeolite (framework Si/Al ratio of 11) at 160°C, sulfolane or *n*-dodecane being used as solvents. Whatever the solvent, phenyl acetate undergoes a monomolecular rearrangement into *o*-hydroxyacetophenone, an autoacylation into *p*-acetoxyacetophenone plus phenol and a hydrolysis into phenol. *p*-hydroxyacetophenone which appears as a secondary product results from the acylation of phenol with phenyl acetate. The initial reaction rates and the product distribution depend very much on the solvent. This can be explained by the large difference in the strength of adsorption between the polar sulfolane and the non-polar dodecane solvents on the active acid sites.

Keywords: zeolite beta; autoacylation; molecular rearrangement

1. Introduction

The Fries rearrangement of phenyl acetate (PA) leads to a mixture of *o*- and *p*-hydroxyacetophenones (*o*- and *p*-HAP) which are useful intermediates for the manufacture of pharmaceuticals. The use of conventional Friedel–Crafts catalysts, such as $AlCl_3$, causes important environmental problems and a considerable effort is being devoted to the development of solid acid catalysts, in particular of zeolite catalysts [1–14]. The Fries rearrangement can be catalyzed in the gas phase by acid zeolites. Unfortunately, the deactivation is very rapid due to carbonaceous deposits and to dehydroxylation of the zeolite with transformation of PA into phenol and acetic acid [9,14]. Consequently, the selectivity to hydroxyacetophenones is very poor.

The stability and the selectivity of zeolites are better when the Fries rearrangement is carried out in the liquid phase [5,7,8]. Mechanisms have been proposed for the formation of hydroxyacetophenones and of the main side products: phenol (P) and *p*-acetoxyacetophenone (*p*-AXAP). *o*- and *p*-HAP would be formed through different pathways: *o*-HAP from the intramolecular rearrangement of PA, *p*-HAP from an intermolecular reaction involving PA and an available phenol molecule. *p*-AXAP could result from various reactions, in particular from an intermolecular reaction between two PA molecules [8]. In liquid phase, solvents which are often used for solubilizing reactants and products, for facilitating heat transfer, for limiting the formation of carbonaceous compounds, etc. can also influence the rate and the selectivity of the desired transformation [7,15–17]. Thus, in PA transformation over a BEA zeolite it has been shown that the solvent polarity causes an increase in the selectivity to *p*-HAP and to phenol [7].

The aim of this paper is to confirm and to explain the effect of solvents on the rate and selectivity of zeolite catalyzed PA transformation. A kinetic study of PA transformation carried out over a HBEA zeolite both in a polar (sulfolane) and a non-polar solvent (*n*-dodecane) shows that differences in rate and selectivity are due to the strong adsorption of sulfolane. Mechanisms of formation of hydroxyacetophenones (*o*- and *p*-HAP), of *p*-AXAP and of phenol are discussed.

2. Experimental

The HBEA zeolite (Si/Al = 11, unit cell formula: $H_5Na_{0.3}Al_{5.3}Si_{58.7}O_{128}$) was provided by PQ Zeolites (CP 811-DL-25). Phenyl acetate (PA), sulfolane and *n*-dodecane (Aldrich, purity > 99%) were dried on magnesium sulfate and distilled before use [18]. The transformation of PA was carried out at 160°C in a flask equipped with a cooler and a magnetic stirrer (600 rpm). The standard conditions were the following: 100 mg of catalyst previously activated for 10 h at 500°C under dry air flow, a solution containing 20 mmol of PA (about 2.5 cm^3) and 6.6 cm^3 of sulfolane or dodecane solvent (PA concentration = $2.2\ mol\ \ell^{-1}$). The activated catalyst was introduced in the solution at 50°C (since sulfolane is solid at room temperature), stirred for 30 min and then the reactor was transferred in a bath at 160°C. For the kinetic study, the amounts of catalyst and of PA were kept constant (100 mg and 20 mmol), the concentration of PA being changed by using different amounts of solvent. Small samples of the reaction mixture (about 0.1 cm^3) were taken at various reaction times, diluted with methylene chloride and analyzed by gas chromatography on a 25 m capillary column of CP Sil5 CB. Blank tests (without catalyst), both the transformations of the PA–solvent mixture and of PA added with the solvent put in contact with the catalyst during one night, were carried out. No formation of HAP and of *p*-AXAP was observed.

3. Results and discussion

3.1. *Reaction products and mode of formation*

Whatever the solvent, phenyl acetate (PA) is transformed into *o*- and *p*-hydroxyacetophenones (*o*-HAP and *p*-HAP), into *p*-acetoxyacetophenone (*p*-AXAP) and into phenol (P). *o*-HAP, *p*-AXAP and P are apparently primary products, *p*-HAP a secondary product, only formed for reaction times longer than 2 h with the sulfolane solvent and 1 h with dodecane (fig. 1). This suggests that *o*-HAP and *p*-HAP are formed through different mechanisms [8]; *o*-HAP could result from an intramolecular rearrangement of PA while the formation of *p*-HAP involves the participation of one primary product in addition to PA.

p-AXAP and P can result from PA autoacylation:

$$2\text{PA} \rightarrow p\text{-AXAP} + \text{P} \qquad (1)$$

However, the production of phenol is greater than is expected from reaction (1). Thus, part of the phenol results from other reactions such as the decomposition of PA (reaction (2)) or/and the reaction of PA with traces of water (reaction (3)) or with the zeolite hydroxyl groups:

$$\text{PA} \rightarrow \text{P} + \text{CH}_2\text{=C=O} \quad \text{(ketene)} \qquad (2)$$

$$\text{PA} + \text{H}_2\text{O} \rightarrow \text{P} + \text{CH}_3\text{COOH} \qquad (3)$$

For simplification, the production of this excess phenol will be called hence-forward PA hydrolysis.

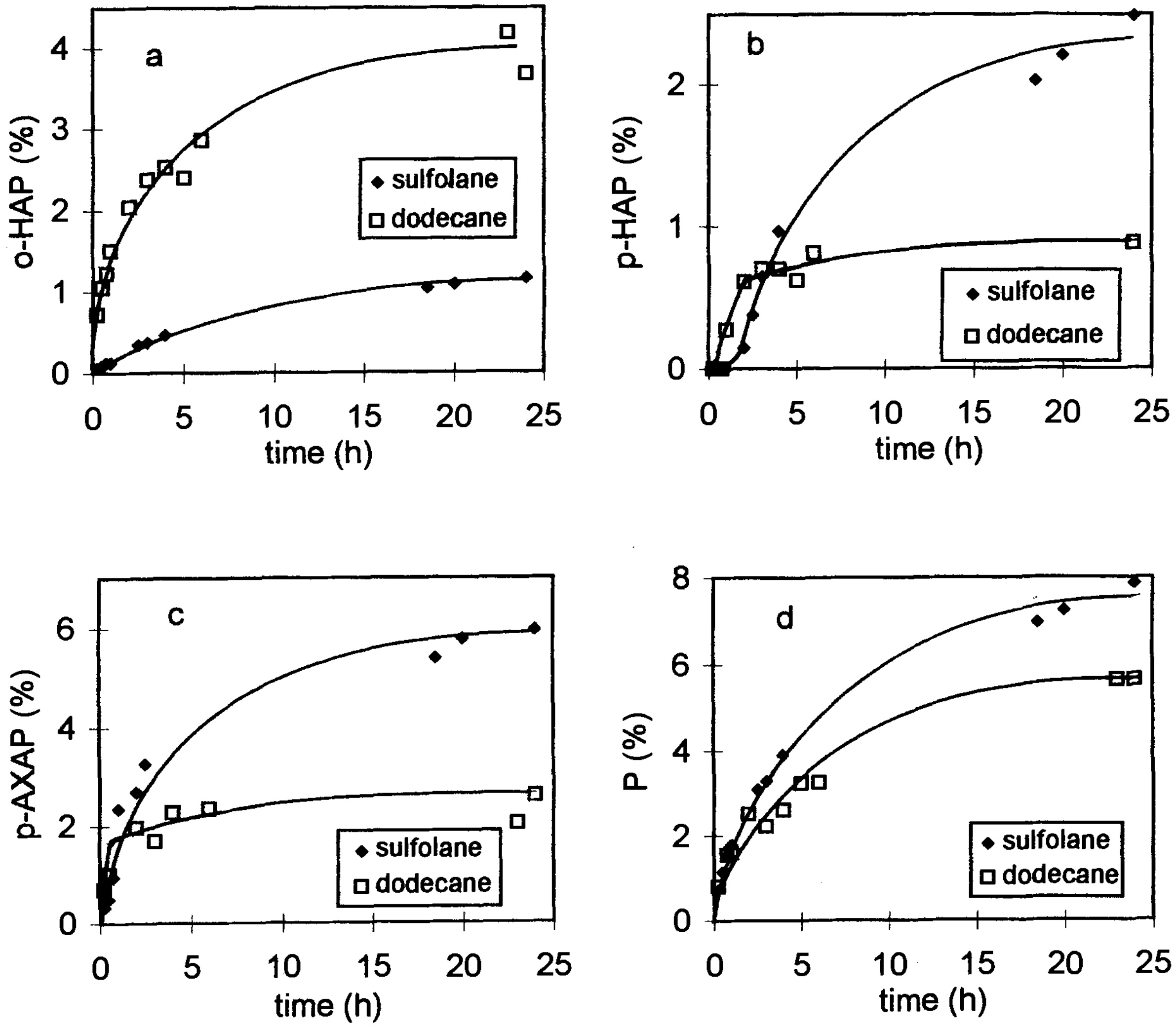

Fig. 1. Transformation of phenyl acetate (PA) into *o*-hydroxyacetophenone: *o*-HAP (a), into *p*-hydroxyacetophenone: *p*-HAP (b), into *p*-acetoxyacetophenone: *p*-AXAP (c) and into phenol: P (d) under standard conditions: 100 mg of zeolite, 160°C, $C_{\text{PA}} = 2.2$ mol ℓ^{-1}. Effect of the solvent on PA conversion (%) into the various products versus reaction time (h).

The secondary formation of p-HAP can be explained either by an acylation of phenol with PA (reaction (4)):

$$P + PA \rightarrow p\text{-HAP} + P \qquad (4)$$

or by decomposition or hydrolysis of p-AXAP, i.e. through reactions identical to those proposed to explain the excess formation of phenol (reactions (5) and (6)):

$$p\text{-AXAP} \rightarrow p\text{-HAP} + CH_2{=}C{=}O \qquad (5)$$

$$p\text{-AXAP} + H_2O \rightarrow p\text{-HAP} + CH_3COOH \qquad (6)$$

Isomerization of o-HAP into p-HAP is quite unlikely since no m-HAP is observed.

To discriminate between the two schemes of p-HAP formation (from secondary transformation of P or of p-AXAP) the transformation of a mixture of PA (2.2 M) with P (0.6 or 1.3 M) in sulfolane or in dodecane was investigated. This low concentration of P was chosen to limit the change in the solvent concentration. Whatever the solvent, p-HAP appears as a primary product (fig. 2) showing that, most likely, p-HAP results from reaction (4). Furthermore, no increase in the production of o-HAP is observed, which confirms [8] that o-HAP results mainly from an intramolecular transformation of PA. There is even a decrease observed which could be due to the competition of phenol with PA for adsorption on the acid sites.

3.2. *Influence of the solvent on the rate and on the selectivity of PA transformation*

Fig. 1 shows that the conversion of PA into o-HAP is much slower (7 times) initially in sulfolane than in dodecane. The initial production of p-AXAP is also slower (about twice) in sulfolane but after 1 h reaction, p-AXAP formation is faster in sulfolane than in dodecane. p-HAP formation begins sooner in dodecane but after 5 h becomes more significant in sulfolane than in dodecane. Lastly, the initial rate of PA transformation into phenol (via autoacylation and hydrolysis of PA) does not depend on the solvent. However, after 1 h, the transformation of PA into phenol becomes more significant in sulfolane than in dodecane.

The product distribution depends very much on the solvent. Thus, for long reaction times (hence at high PA conversion) the p/o-HAP ratio is much greater in sulfolane than in dodecane. Since p-AXAP can be easily transformed into p-HAP (by treatment with water [19]) it is also interesting to compare the ratios of (p-HAP + p-AXAP)/o-HAP in both solvents. With sulfolane as a solvent a great value of this ratio is obtained (7.5), this value being about 10 times greater than with dodecane (fig. 3). Therefore, it would be possible to prepare p-HAP with a high selectivity (around 90% in the $o + p$-HAP mixture) by using a sulfolane solvent [19].

3.3. *Kinetic study*

To understand the solvent effect, a kinetic study of PA transformation was carried out in dodecane and in sulfolane. As an example, the influence of the PA concentration on the conversion into o-, p-HAP, p-AXAP and excess phenol (hydrolysis) in sulfolane is shown in fig. 4. The greater the concentration of PA, the greater the production of o-, p-HAP and of p-AXAP, while the rate of hydrolysis is practically independent of the PA concentration. Identical conclusions can be drawn from the PA transformation in n-dodecane. However, the effect of the PA concentration is always more significant in sulfolane: apparent orders with respect to PA are close to 1 for the initial o-HAP formation and to 2 for the initial p-AXAP formation in sulfolane against about 0.5 and 1.5 in n-dodecane. p-HAP being a secondary product, it is not possible to calculate a reaction order. However, again, the effect of PA concentration is more significant in sulfolane than in dodecane.

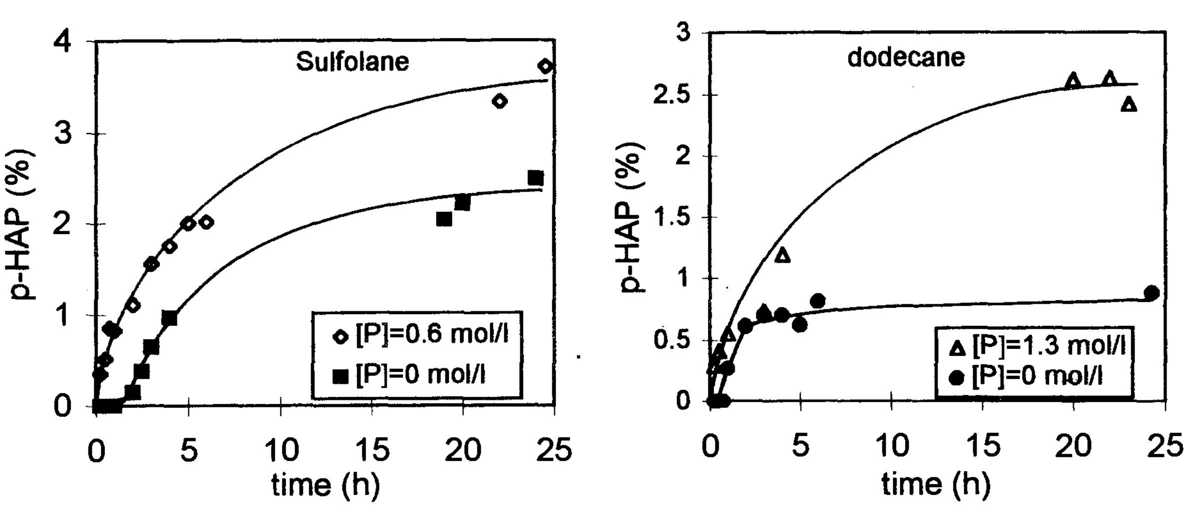

Fig. 2. Influence of phenol on the conversion of PA ($C_{PA} = 2.2$ mol ℓ^{-1}) into p-HAP in sulfolane and in dodecane.

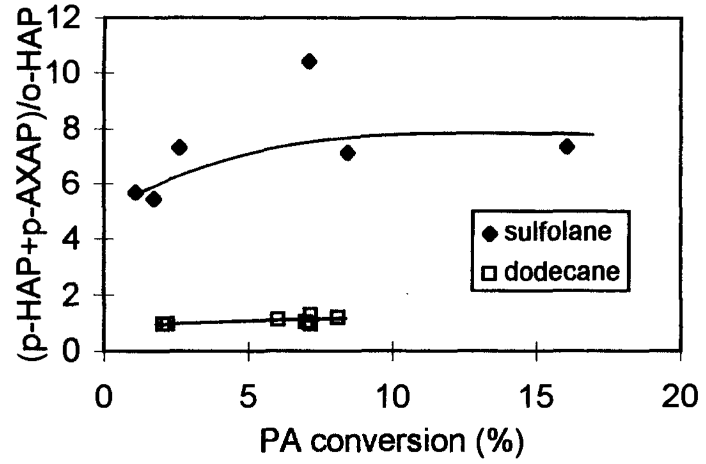

Fig. 3. Transformation of PA under standard conditions with sulfolane and with dodecane as solvents. (p-HAP + p-AXAP)/o-HAP versus PA conversion.

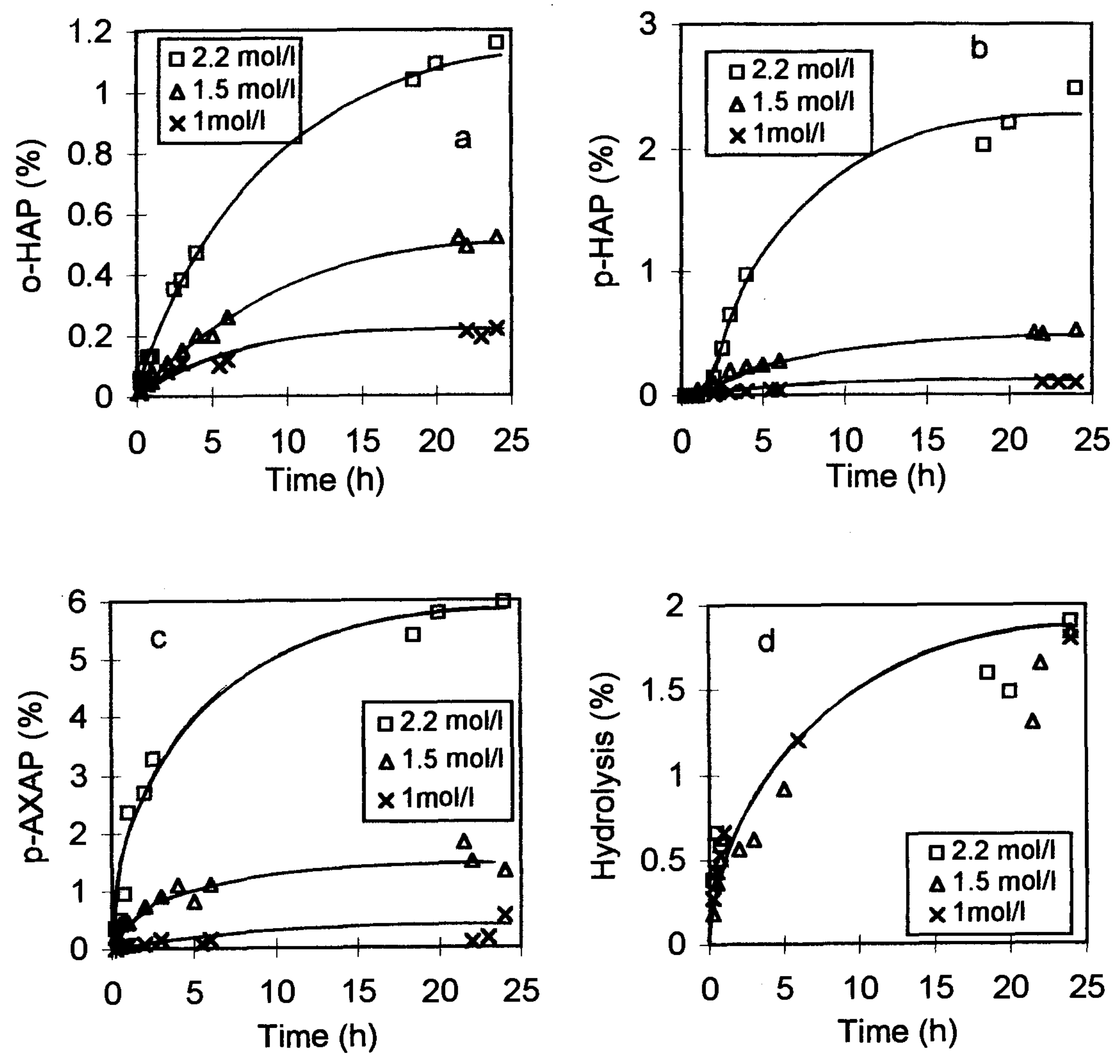

Fig. 4. Transformation of PA in sulfolane for various values of PA concentration. Conversion of PA into o-HAP (a), p-HAP (b), p-AXAP (c) and into phenol through hydrolysis (d) versus reaction time.

The difference between reaction orders found in sulfolane and in *n*-dodecane is quite likely due to differences in adsorption of the solvents on the acid sites: sulfolane would compete with PA and the reaction products to adsorb on the acid sites whereas the adsorption of *n*-dodecane can be considered as negligible. This can be demonstrated by considering the formation of *o*-HAP and of *p*-AXAP.

The intramolecular rearrangement of PA into *o*-HAP would involve the following steps:

$$\mathrm{PA} + \mathrm{X} \rightleftharpoons \mathrm{PA{-}X} \tag{a}$$

$$\mathrm{PA{-}X} \rightleftharpoons o\text{-}\mathrm{HAP{-}X} \tag{b}$$

$$o\text{-}\mathrm{HAP{-}X} \rightleftharpoons o\text{-}\mathrm{HAP} + \mathrm{X} \tag{c}$$

where X is the active acid site. Most likely, step b is the limiting step of this rearrangement. Indeed adsorption–desorption of PA and *o*-HAP (steps a and c) which are basic molecules are facile steps. With this mechanism, the initial rate of *o*-HAP formation can be written:

$$v_{o\text{-HAP}} = \frac{k_\mathrm{b} K_\mathrm{a} \bar{C}_\mathrm{m} C_\mathrm{PA}}{1 + K_\mathrm{a} C_\mathrm{PA} + K_\mathrm{S} C_\mathrm{S}} \tag{7}$$

with k_b the rate constant of step b, K_a and K_S the equilibrium constants of adsorption of PA and of the solvent and $\bar{C}_\mathrm{m}$ the total concentration in active sites.

The dodecane solvent adsorption being negligible

$$v_{o\text{-HAP}} = \frac{A C_\mathrm{PA}}{1 + K_\mathrm{a} C_\mathrm{PA}} \tag{8}$$

with the constant $A = k_\mathrm{b} K_\mathrm{a} \bar{C}_\mathrm{m}$. Fig. 5a shows that this equation is verified by the experimental results. Indeed $1/v_{o\text{-HAP}}$ versus $1/C_\mathrm{PA}$ is a straight line.

On the other hand, for PA rearrangement in sulfolane the solvent adsorption must be considered. Eq. (7) shows that the order value close to 1 for the formation of *o*-HAP in sulfolane can only be explained if $K_\mathrm{S} C_\mathrm{S}$ is much greater than $1 + K_\mathrm{a} C_\mathrm{PA}$.

$$v_{o\text{-HAP}} = \frac{A C_\mathrm{PA}}{K_\mathrm{S} C_\mathrm{S}} \tag{9}$$

Fig. 6a confirms that $v_{o\text{-HAP}} C_\mathrm{sulfolane}$ is proportional to C_PA. Moreover, the inhibiting effect of sulfolane, shown in eq. (9), explains why the formation of *o*-HAP is much slower in sulfolane than in dodecane.

The intermolecular transformation of PA into *p*-AXAP would occur through the following steps:

$$\mathrm{PA} + \mathrm{X} \rightleftharpoons \mathrm{PA{-}X} \tag{a}$$

$$\mathrm{PA{-}X} + \mathrm{PA} \rightleftharpoons p\text{-}\mathrm{AXAP} + \mathrm{P{-}X} \tag{b'}$$

$$(\text{or } p\text{-}\mathrm{AXAP{-}X} + \mathrm{P})$$

$$\mathrm{P{-}X} \rightleftharpoons \mathrm{P} + \mathrm{X} \tag{d}$$

where b′ is the limiting step.

The equation of the initial rate which takes into account the adsorption of the solvent is:

$$v_{p\text{-AXAP}} = \frac{k_\mathrm{b} K_\mathrm{a} \bar{C}_\mathrm{m} C_\mathrm{PA}^2}{1 + K_\mathrm{a} C_\mathrm{PA} + K_\mathrm{S} C_\mathrm{S}}, \tag{10}$$

which can be simplified into eq. (11) when dodecane (whose adsorption is negligible) is used as a solvent:

$$v_{p\text{-AXAP}} = \frac{A' C_\mathrm{PA}^2}{1 + K_\mathrm{a} C_\mathrm{PA}} \tag{11}$$

with $A' = k_{\mathrm{b}'} K_\mathrm{a} \bar{C}_\mathrm{m}$. Eq. (11) is verified in fig. 5b by plotting $C_\mathrm{PA}/v_{p\text{-AXAP}}$ versus $1/C_\mathrm{PA}$.

Because of the strong adsorption of sulfolane the rate of *p*-AXAP formation in this solvent is:

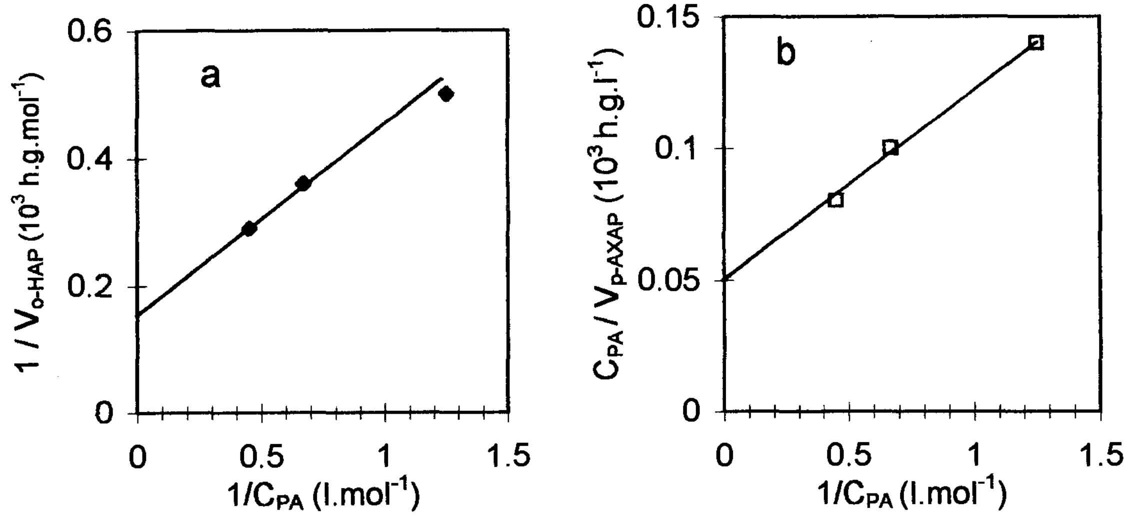

Fig. 5. Transformation of PA in dodecane. Verification of eq. (8) (a): Plot of the reverse of the initial rate of PA transformation into *o*-HAP: $1/v_{o\text{-HAP}}$ (10^3 h g mol^{-1}) as a function of the reverse of PA concentration (ℓ mol^{-1}) (◆). Verification of eq. (11) (b): Plot of $C_\mathrm{PA}/v_{p\text{-AXAP}}$ (10^3 h g ℓ^{-1}) as a function of $1/C_\mathrm{PA}$. $v_{p\text{-AXAP}}$ is the initial rate of PA transformation into *p*-AXAP (□).

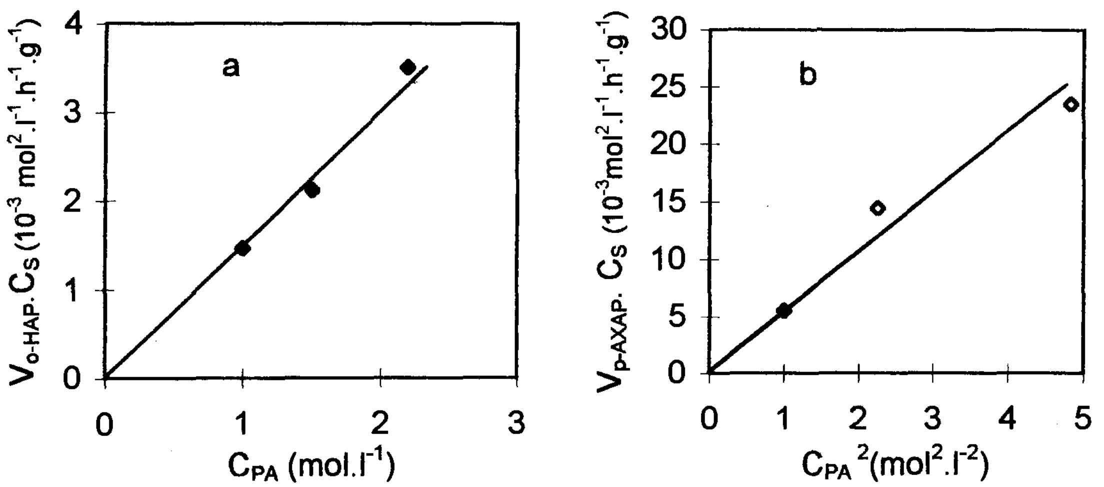

Fig. 6. Transformation of PA in sulfolane. Verification of eq. (9) (a): Plot of the product of the initial rate of PA transformation into *o*-HAP by the sulfolane concentration: $v_{o\text{-HAP}} C_S$ (10^{-3} mol^2 ℓ^{-1} h^{-1} g^{-1}) as a function of PA concentration C_{PA} (mol ℓ^{-1}). Verification of eq. (12) (b): Plot of $v_{p\text{-AXAP}} C_S$ (10^{-3} mol^2 ℓ^{-1} h^{-1} g^{-1}) as a function of the square of PA concentration C_{PA}^2 (mol^2 ℓ^{-2}).

$$v_{p\text{-AXAP}} = \frac{A' C_{PA}^2}{K_S C_S}, \qquad (12)$$

which is verified in fig. 6b. Again, because of the adsorption of sulfolane, the initial rate of *p*-AXAP formation is greater in dodecane than in sulfolane (fig. 1).

The values of K_a and K_S can be estimated separately from figs. 5a and 6a (*o*-HAP formation) and from figs. 5b and 6b (*p*-AXAP formation). Identical values of K_a and K_S were found from both experiments: 0.65 ℓ mol^{-1} for K_a and 2.4–2.6 ℓ mol^{-1} for K_S. The fact that K_S is about four times larger than K_a explains, at the same time as the higher solvent concentration, why sulfolane has a strong inhibiting effect on the initial formation of *o*-HAP and of *p*-AXAP.

However, fig. 1 shows that after long reaction times, *p*-AXAP formation is faster in sulfolane than in dodecane, a constant level being obtained after 2 or 3 h reaction in dodecane. The same is furthermore observed for all the products formed in dodecane. This means that the catalyst deactivation is faster in dodecane than in sulfolane. Most likely, this is due to a faster formation or trapping of heavy secondary products in the zeolite pores. This proposal is pending checking by comparing the compositions of the heavy products trapped in the zeolite pores during PA transformation in dodecane and in sulfolane.

4. Conclusion

From this kinetic study of phenyl acetate conversion in the liquid phase on a HBEA zeolite the following conclusions can be drawn:

(i) Whatever the solvent (dodecane or sulfolane), *o*-hydroxyacetophenone, *p*-acetoxyacetophenone and phenol appear as primary products, *p*-hydroxyacetophenone as a secondary product. As confirmed by the effect of the addition of phenol to phenyl acetate, *o*-hydroxyacetophenone results from the intramolecular rearrangement of phenyl acetate, *p*-acetoxyacetophenone from an intermolecular autoacylation of phenyl acetate with simultaneous production of phenol and *p*-hydroxyacetophenone from acylation of phenol with phenyl acetate. Part of the phenol is also formed by hydrolysis or decomposition of phenyl acetate.

(ii) Large differences are observed in the product distribution in sulfolane and in dodecane solvents. In particular, sulfolane favors significantly the formation of the para products. The comparison between the initial rates of product formation in both solvents and of their variations with the phenyl acetate concentration shows that sulfolane competes with phenyl acetate for adsorption on the acid sites. However, if because of its strong adsorption, sulfolane limits the initial rate of phenyl acetate transformation, it limits also the catalyst deactivation. These effects of the solvent polarity are similar to those found in the cyclohexylation of phenol over an ultrastable Y zeolite [16].

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