Benzoylation of 1,2-dimethoxybenzene with benzoic anhydride and substituted benzoyl chlorides over large pore zeolites

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Abstract

The benzoylation of 1,2-dimethoxybenzene (veratrole) with benzoic anhydride and substituted benzoyl chlorides has been investigated in the liquid phase (chlorobenzene as solvent) over the H-forms of various zeolites. H-Y and H-BEA have been shown to be efficient catalysts in such a reaction, and led to the selective formation of the corresponding dimethoxybenzophenones. The effect of various experimental parameters on the initial rate of the reaction of veratrole with benzoic anhydride over H-Y zeolite has been studied, leading to propose a suitable mechanism based on the difference of adsorptions of the aromatic substrate and the acylating agent. Moreover, the study of the reaction of veratrole with a series of substituted benzoyl chlorides (4-CH$_3$, 4-OCH$_3$, 4-*tert*-butyl, 4-Cl, 2-Cl and 2-Br benzoyl chlorides, respectively) over the same H-Y zeolite led to conclude that, due to the high reactivity of the aromatic substrate, the electrophilicity of the acylating agent does not play a relevant role under the given heterogeneous conditions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The interest of zeolites in the production of fine chemicals stands both in replacement of liquid acids to lower corrosion of equipment and pollution and in achievement of specific selectivities in given products. Several reviews have now appeared dealing with the use of such solid catalysts in organic reactions [1–5]. The acylation of aromatic substrates is of a particular interest for making intermediates which are widely used for the production of pharmaceuticals, perfumes, dyes, insecticides and others [6]. Zeolites have been shown, during the past decade, to be adequate and efficient catalysts especially in acylation reactions of a variety of aromatic substrates [7 and references therein]. The earliest studies of one of us on the acylation of toluene and *p*-xylene with straight-chain aliphatic acids catalyzed by CeNa-Y zeolites [8] have been extended more recently by our two groups towards the acetylation of various aromatics, such as benzene and alkylbenzenes [9,10], tetraline [11] and dimethoxybenzene isomers [7]. Benzoylation constitutes an important class among acylation reactions, due to the commercial importance of benzophenone and its substituted analogues, especially as additives in the perfumery industry [12]. Various acidic zeolites,

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among which zeolite beta was shown to be efficient, have been used in the liquid phase benzoylation of some mononuclear and polynuclear aromatics [13–16] by one of us. It is known that the ability of aromatic nuclei to undergo acylation is greatly enhanced by the presence of electron-donating substituents [17]. This is especially the case for the acylation of anisole, for which the acidity of zeolites is sufficient enough to carry out the reactions under moderate conditions [18–23]. For this reason, aryl ethers constitute an interesting class of aromatic derivatives as starting materials for acylation reactions. Surprisingly, only a few papers deal with acetylation or acylation of activated disubstituted aromatics, among them the acetylation of veratrole (1,2-dimethoxybenzene) has been studied, either in the presence of zeolites [24] or cation exchanged clays [25]. In a recent work [7], some of us were able to show that the use of large pore zeolites, such as H-Y and H-BEA, in the acetylation reaction of 1,2-, 1,3- and 1,4-dimethoxybenzenes with acetic anhydride allowed the development of a selective procedure for the preparation of the corresponding dimethoxyacetophenones in convenient yields. Moreover, we also evidenced the efficiency of the zeolite H-BEA in the liquid phase propionylation of 1,2-dimethoxybenzene (veratrole) to produce selectively the 3,4-dimethoxypropiophenone [26].

The present work deals with the results obtained in the benzoylation reaction, over various acidic zeolites and under liquid phase conditions, of the 1,2-dimethoxybenzene with benzoic anhydride and with various substituted benzoyl chlorides. Attention has been especially focused to the kinetic study of the benzoylation reaction over the most active H-Y zeolite, in order to propose an adequate mechanism of the benzoylation reaction under heterogeneous conditions, and to the study of the substituent effect on the acylating agent on the initial rate of the reaction.

2. Experimental

2.1. Catalysts and reactants

The H-FAU (H-Y) (Si/Al = 15) and the beta sample, H-BEA (Si/Al = 12.5) were from PQ Corporation (CBV 720 and CP 810 B-25, respectively). The H-MOR (Si/Al = 11) was from Zeocat, Montoir de Bretagne (ZM 510). The properties of the catalysts are listed in Table 1. The same programme was applied in the activation of the different samples. The calcination was performed at 500°C for 6 h with a heating rate of 60°C h^{-1} from R.T. to 500°C. All the calcinations were performed in a flow of dry air.

1,2-Dimethoxybenzene (veratrole) was a pure sample (99%) commercially available from Aldrich. Benzoic anhydride, 4-CH$_3$, 4-OCH$_3$, 4-*tert*-buyl, 4-Cl, 2-Cl and 2-Br benzoyl chlorides were purchased from Aldrich and Fluka (98–99%). Chlorobenzene was pure analytical grade from Aldrich, and was used after drying over molecular sieves.

2.2. Catalytic experiments and analytical method

The reactions were carried out under atmospheric pressure in a 100 ml round bottom flask equipped with a condenser, a dropping funnel, a thermometer and a stirring mechanism. The typical reaction with benzoic anhydride as acylating agent was carried out as follows: a solution of 1.38 g of 1,2-dimethoxybenzene (10 mmol, 0.2 M) in 50 ml chlorobenzene was introduced in the flask and magnetically stirred (600 or 1000 rpm) under nitrogen atmosphere. The freshly activated catalyst (0.5 g) was added and the reaction mixture was allowed to heat to reflux of chlorobenzene (130°C); 2.26 g (10 mmol) of benzoic anhydride was then added slowly through the addition funnel, and the mixture was stirred. Zero time was taken at

Table 1
Properties of catalysts

Zeolite	Si/Al (molar ratio)	Pore structure (nm)	BET surface area (m^2 g^{-1})	Acidity (meq. H$^+$ g^{-1})[a]
H-FAU	15	0.74 × 0.74	665	0.56
H-BEA	12.5	0.55 × 0.55	679	1.03
		0.76 × 0.64		
H-MOR		0.65 × 0.7		
	11	0.26 × 0.57	494	1.15

[a] Measured by thermodesorption of ammonia.

the end of the addition (it was verified that the order of introduction of the reactants had no effect on the conversion of aromatic). Samples were periodically collected and analyzed by gas chromatography (Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector, capillary column HP-1, 25 m × 0.2 mm, 0.33 mm film thickness, carrier gas hydrogen).

The corresponding reactions, using the 4- or 2-substituted benzoyl chlorides as acylating agents, were performed under the same standard conditions. For the GC analysis, the samples were previously hydrolyzed with an appropriate amount of water; the two phases were separated and the organic phase was analyzed as above.

2.3. Isolation and identification of the products

The products were isolated from the reaction mixture after 8 h. The catalyst was filtered out and the solvent was removed by evaporation in a rotary evaporator. The crude solid was purified through a silica gel column chromatography, using cyclohexane/ethyl acetate as eluent, followed by recrystallization (cyclohexane). The structure of the products was confirmed by comparison with authentical samples available from Aldrich whenever it was possible, by GC-MS analysis (Hewlett-Packard 5890, with a 5970A series mass selective detector) together with ^{1}H and ^{13}C NMR. The purity of the products was con-

Table 2
Benzoylation of veratrole with benzoic anhydride over zeolites

Zeolite	Reaction time (min)	Conversion of veratrole (%)
H-Y	60	75
	480	90
H-BEA	60	23
	480	29
H-MOR	60	2
	480	4

firmed through the melting points and microelemental analysis.

3. Results and discussion

3.1. Influence of the zeolite structure

The benzoylation reaction of 1,2-dimethoxybenzene with benzoic anhydride over acidic zeolites led to 3,4-dimethoxybenzophenone as the only benzoylated product, as shown in Fig. 1 which represents the concentration profiles of veratrole and product with reaction time over H-Y zeolite.

Table 2 shows the conversion of veratrole at 1 and 8 h of reaction under the same experimental conditions in the presence of three zeolites having a similar Si/Al molar ratio (between 10 and 15) but various structures.
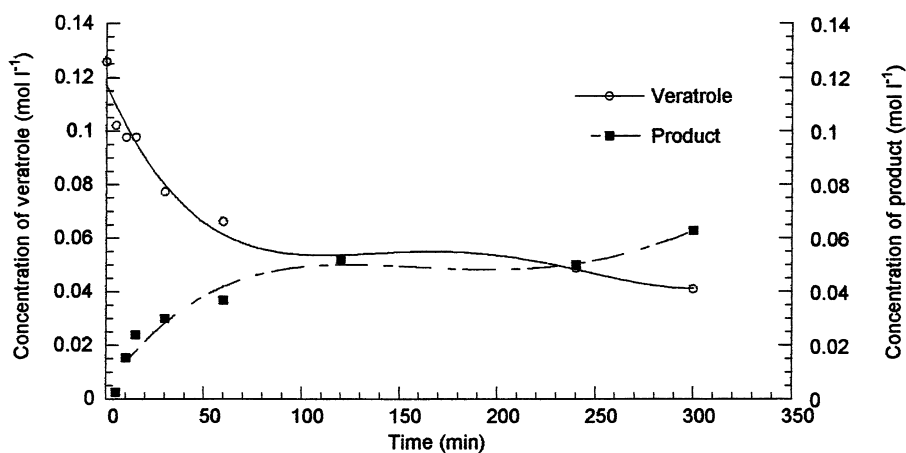

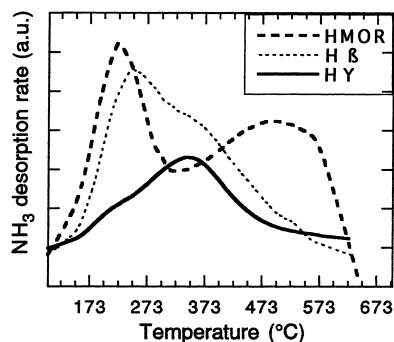Fig. 1. Disappearance of veratrole and formation of product vs. time.

Fig. 2. NH$_3$-TPD profiles of the three samples of zeolites.

H-Y appears to be the best catalyst in terms of activity (75% conversion of veratrole after 1 h), while H-MOR exhibits a very low activity.

As shown in Table 1, the total acidity of these three zeolites decreases in the order: H-MOR > H-BEA > H-Y. NH$_3$-TPD profiles for the three samples of zeolites are shown in Fig. 2. The results are standardized, therefore, the intensities of the peaks are comparable in all cases.

These profiles consist of two peaks: one appears at a low temperature range around 250°C and another appears at a high temperature range around 350–400°C for H-Y and H-BEA or 550°C for H-MOR. The low and high temperature peaks correspond to the weak

and strong acid sites, respectively. H-MOR presents the stronger sites, however, its catalytic activity is only very weak. H-BEA 12.5 exhibits a high number of weak sites and a number of strong acid sites slightly higher than H-Y 15. Nevertheless, H-Y is more active. Consequently, the higher activity of H-Y can be only related to the large pores tri-dimensional zeolite network and the presence of supercages, whereas the acid catalyzed reaction is more difficult to occur within the framework of the other zeolites, respectively interconnected channels of zeolite BEA and uni-dimensional structure of the mordenite, despite their strong acid sites.

3.2. Influence of the parameters of the reaction

The influence of various parameters on the veratrole conversion on the initial rate (determined by the slope at the origin of the veratrole concentration curve versus time) over H-Y (Si/Al = 15) is reported.

3.2.1. Effect of the agitation speed
The effect of the speed of agitation was studied in the range 600–1000 rpm as shown in Fig. 3 under otherwise similar conditions.

There was no significant change in the conversion after 6 h of reaction, indicating that there was no resistance to external mass transfer. All further reactions were conducted at 600 rpm.
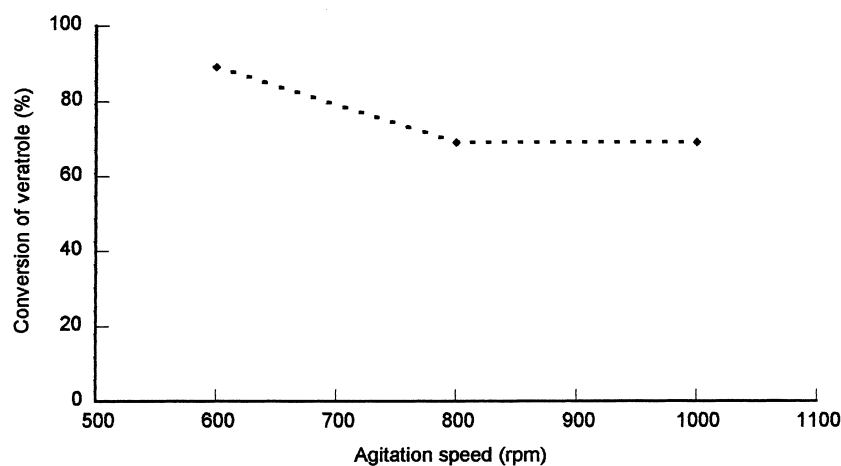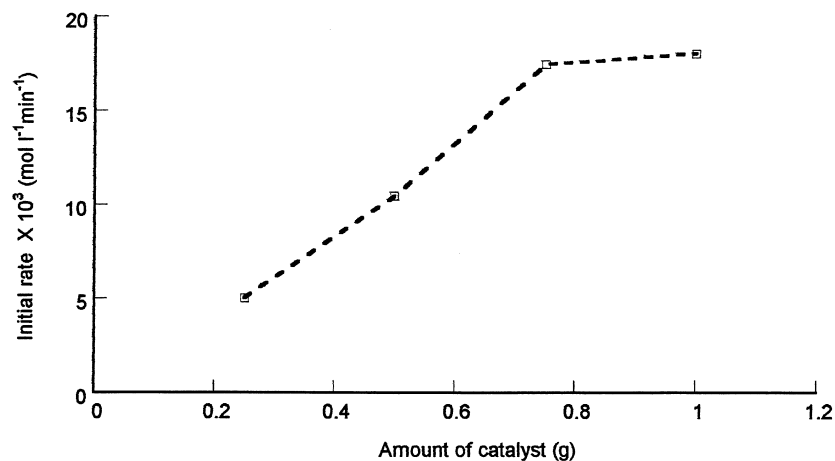

Fig. 3. Effect of agitation speed.

Fig. 4. Effect of catalyst concentration on the initial rate of the reaction.

3.2.2. Effect of the amount of catalyst

The catalyst mass was varied from 0.25 to 1 g. It is found that the initial activity is proportional to the amount of catalyst up to 0.8 g (Fig. 4). At higher catalyst amount, there is no more increase in the initial rate; consequently, the catalyst is being used to less than its maximum capacity, and diffusion limitation is operative.

Further experiments were therefore, carried out with 0.5 g of catalyst in the absence of mass transport limitation.

3.2.3. Effect of reactant concentrations

For kinetic purposes, the effect of mole ratio of reactants is properly established by varying concentrations. The initial concentration of benzoic anhydride was varied in the range of 0.1–$0.6\,\text{mol}\,l^{-1}$ by keeping constant the initial concentration of veratrole at $0.2\,\text{mol}\,l^{-1}$ and the initial rate of the reaction was plotted as a function of the initial concentration of benzoic anhydride as shown in Fig. 5.

The initial rate increases with increasing the initial veratrole concentration up to $0.2\,\text{mol}\,l^{-1}$. Beyond
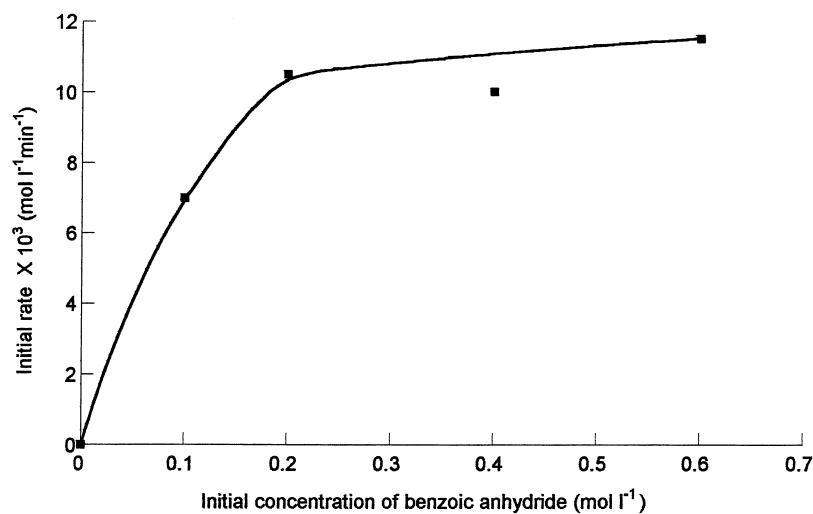

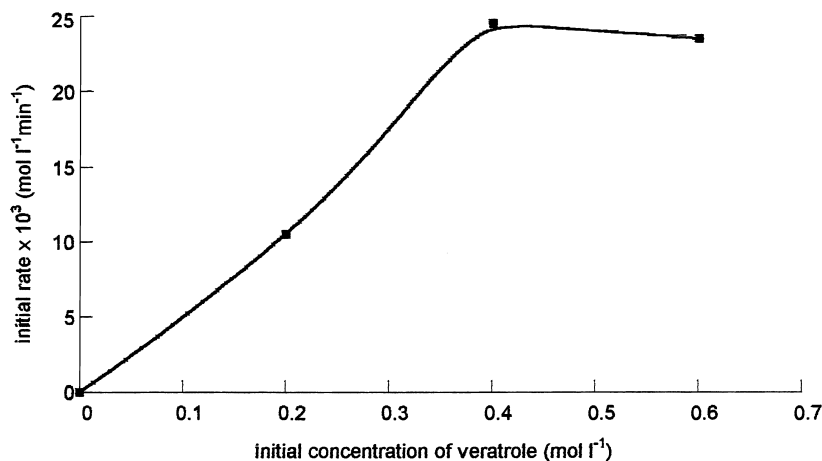Fig. 5. Profile of the initial rate of the reaction vs. benzoic anhydride concentration.

Fig. 6. Profile of the initial rate of the reaction vs. veratrole concentration.

this value, the initial rate of reaction is found to be quasi-independent of the initial veratrole concentration, showing zero order dependence on the concentration of acylating agent.

On the other hand, the same trends are observed for the variation of initial reaction rate versus initial concentration of veratrole at a constant initial concentration of benzoic anhydride ($0.2 \, mol \, l^{-1}$) (Fig. 6). The maximum of initial rate ($24.5 \times 10^{-3} \, mol \, l^{-1} \, min^{-1}$) is obtained for $0.4 \, mol \, l^{-1}$ in veratrole and $0.2 \, mol \, l^{-1}$ in benzoic anhydride.

3.3. Proposition of mechanism

Generally, kinetic studies reported in the [2] for alkylation or acylation of aromatics on acidic zeolites suggest that an Eley–Rideal mechanism is operative.

According an Eley–Rideal type mechanism, the considered reaction takes place between benzoic anhydride (B) compulsory adsorbed on the catalyst site to form the surface electrophile and veratrole (V) from the liquid phase. Then, the initial rate equation is the following:

$$r_0 = \frac{kw\lambda_B[B]_0[V]_0}{1 + \lambda_B[B]_0} \tag{1}$$

where r_0 is the initial rate of reaction, k the rate constant, w the catalyst amount (i.e. the number of catalytic sites), λ_B the equilibrium adsorption constant of benzoic anhydride and $[B]_0$ and $[V]_0$ the initial con-

centration of benzoic anhydride and veratrole, respectively.

At high initial concentrations of B, $\lambda_B[B]_0 \gg 1$, and thus, Eq. (1) reduces to $r_0 = k'[V]_0$ with $k' = kw$. Thus, the reaction is zero order in benzoic anhydride and first order in veratrole. This behavior is not totally observed in our experimental results. It is true for high initial concentration of benzoic anhydride (Fig. 5), but the plot of initial rate versus initial veratrole concentration is not linear for high initial concentration and presents a "plateau", hence the proposed mechanism and the kinetic law are not correct. A Rideal type mechanism kinetic equation cannot adequately represent the chemical process. As emphasized by Corma [3]: "it is difficult in the case of zeolite catalysts to assume a Langmuir–Rideal type mechanism in the strict sense, since any molecule within zeolite pores is going to be subjected to the electric field gradients and even to electronic confinement effects". Thus, one has to consider that the aromatic substrate must be adsorbed, but that such an adsorption at a protonic site generates a species with a significant degree of positive charge and the attack of such a species on a positively charged carbocation would not be expected. In previous papers [7,27], we have proposed that adsorbed aromatic substrates constitute like a catalyst poison, hindering the adsorption of the acylating agent. Consequently, the initial rate of reaction is modified as given below:

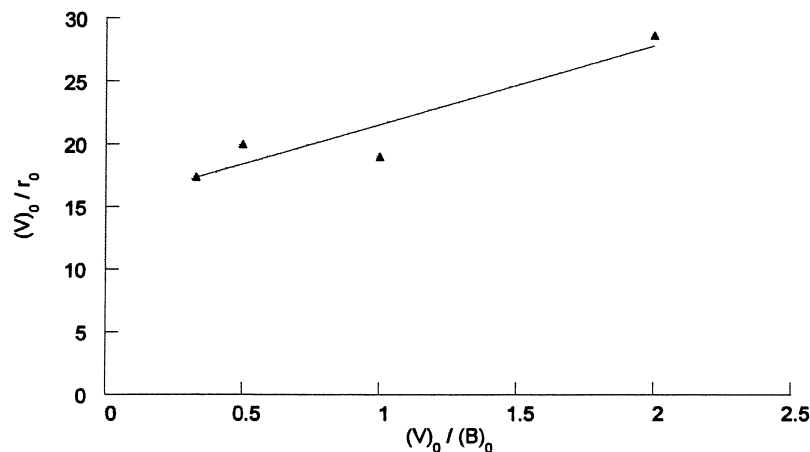$$r_0 = \frac{kw\lambda_B[B]_0[V]_0}{1 + \lambda_B[B]_0 + \lambda_V[V]_0} \tag{2}$$

Fig. 7. Plot of $[V]_0/r_0$ vs. $[V]_0/[B]_0$.

This assumption appears to be valid and corresponds to the experimental data i.e. an initial rate independent of $[V]_0$ for higher concentrations in veratrole (at $[B]_0 = $ constant, $\lambda_V[V]_0 >> 1 + \lambda_B[B]_0$ and consequently $r_0 = $ constant) and vice versa, independent of $[B]_0$ for higher concentrations of benzoic anhydride.

From linearization of Eq. (2), the plot of $[V]_0/r_0$ against $[V]_0/[B]_0$ yields a slope of $\lambda_V/(kw\lambda_B)$ and an intercept of $1/(kw)$ from which the adsorption coefficient ratio λ_V/λ_B could be established. Such a plot is shown in Fig. 7.

The fit is correct and λ_V/λ_B is found to be ~0.5. This value indicates that the adsorption of benzoic anhydride is twice that of veratrole and shows that, for two polar reactants, the competitive adsorption is in favor of the larger molecule in the intracrystalline microporous volume [28]. This result explains that the maximum initial rate is obtained for $0.4\,mol\,l^{-1}$ in veratrole and $0.2\,mol\,l^{-1}$ in benzoic anhydride.

3.4. Comparison benzoic anhydride–benzoyl chloride

The reactivity of benzoic anhydride is higher than that of the corresponding chloride. The initial rate of veratrole consumption is $10.5 \times 10^{-3}\,mol\,l^{-1}\,min^{-1}$ with benzoic anhydride and $6.6 \times 10^{-3}\,mol\,l^{-1}\,min^{-1}$ with benzoyl chloride. Such a result is in agreement with those obtained in the benzoylation of toluene over solid superacids [29]. As suggested by Derouane in a

very interesting review about zeolites as solid solvents [30], this difference of behavior can be attributed to a stronger adsorption of benzoic anhydride because of its molecular weight about twice that of benzoyl chloride.

3.5. Substituent effect

The reaction of veratrole with a series of substituted benzoyl chlorides was carried out at $130°C$ over H-Y, the most active catalyst. In all cases, the corresponding substituted benzophenone was obtained with satisfactory yield; the results are given in Table 3.

The mechanism of Friedel–Crafts acylation of aromatics over zeolites involves firstly the formation of an electrophilic intermediate which attacks at the aromatic ring in the rate-determining step to form a

Table 3

Benzoylation of veratrole with 4- or 2-R substituted benzoyl chlorides over H-Y zeolite (Si/Al = 15)

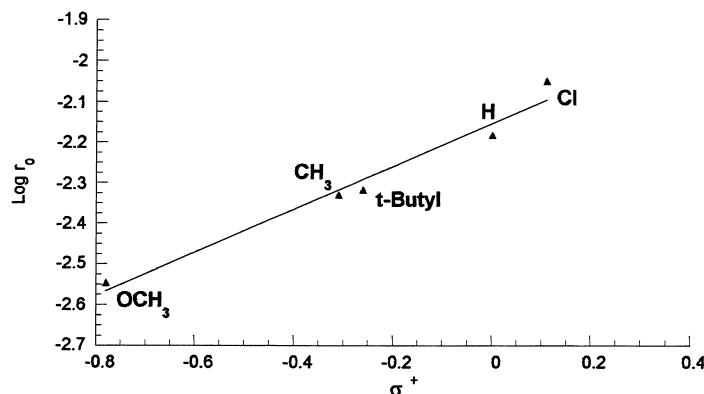| R	Initial rate $\times 10^3$ $(mol\,l^{-1}\,min^{-1})$	σ_p^+
4-H	6.6	0
4-CH3	4.7	−0.31
4-OCH3	2.8	−0.78
4-t-Butyl	4.8	−0.26
4-Cl	8.9	+0.11
2-Br	10.8	
2-Cl	12.2	

Fig. 8. Hammett relationship (log r_0 vs. σ^+) in the benzoylation reaction of veratrole with substituted benzoyl chlorides over H-Y zeolite (Si/Al = 15).

σ-complex. The Hammett ρ–σ^+ relationship (Fig. 8) shows a linear correlation with a weak positive slope of 0.5, which indicates a weak variation of the positive charge between the benzoyl cation and the transition state.

Nevertheless, from the observed results, it is obvious that the effect of the substituent on the initial rate is not much significant, as only a factor of 3 is observed between OCH_3 and Cl at the p-position. The more electron-donating substituent (OCH_3, $\sigma^+ = -0.78$) is reflected by the lower initial rate ($r_0 = 2.8 \times 10^{-3}$ mol l^{-1} min^{-1}). In contrast, the presence of the Cl electron-withdrawing substituent ($\sigma^+ = +0.11$) leads to an increase of the initial rate ($r_0 = 8.9 \times 10^{-3}$ mol l^{-1} min^{-1}). Such a weak variation has been already observed in the case of the thiophen benzoylation over large pore zeolites [31].

It is well-known that electron-donating substituents on the benzoyl cation decrease its electrophilicity; in contrast, the presence of electron-withdrawing substituents increases the electrophilicity. Thus, in that case, the electrophilicity of the acylating agent does not play a major role, because veratrole, which is a strong nucleophile, reacts with the electrophile whatever it is. The rate of the attack of the benzoyl cation on the aromatic ring, which is the slow step of the reaction, is not significantly modified by its electrophilicity.

The position of the substituent in benzoyl chlorides influences also the initial reaction rate. The o-Cl substituent leads to the highest initial rate although the

inductive effect of o-Cl unstabilizing the electrophilic intermediate is stronger than p-Cl. A "field effect" stabilizing the positive charge of the electrophilic intermediate by the electron cloud of the chlorine atom at the o-position has been assumed [21] in order to explain the higher reactivity of 2-Cl benzoyl chloride.

Finally, the Br substituent at the o-position leads to a slight decrease of the initial rate compared with the Cl at the same position; such a result can be logically attributed to the steric hindrance of the bromine atom.

4. Conclusion

Large pore zeolites, such as H-Y and H-BEA, have been shown to be efficient catalysts in the benzoylation reaction of 1,2-dimethoxybenzene with benzoic anhydride and substituted benzoyl chlorides, leading to the selective formation of the corresponding dimethoxybenzophenones. The effect of the various experimental parameters, in particular the mole ratio of the reactants, has been studied in the reaction of veratrole and benzoic anhydride over H-Y zeolite. Such a kinetic study especially indicated that the adsorption of benzoic anhydride was twice that of veratrole, allowing to confirm a modified Eley–Rideal type mechanism, already encountered and demonstrated in other aromatic electrophilic substitution reactions under heterogeneous conditions and based on the competitive adsorption of the aromatic substrate and acylating agent over the active sites of the zeolite catalyst. The

present work thus, clearly confirms the Derouane assessment [28] that "the availability of the reactants in the intracrystalline volume of the zeolites where the active sites are located depends on adsorption equilibria, which regulate reaction rate and catalyst performance". Moreover, the study of the reaction of veratrole with a series of substituted benzoyl chlorides (4-CH$_3$, 4-OCH$_3$, 4-*tert*-butyl, 4-Cl, 2-Cl and 2-Br benzoyl chlorides, respectively) over the same H-Y zeolite indicated that the effect of the substituent on the initial rate of the reaction was not significant, as only a factor of 3 is observed between OCH$_3$ and Cl at the *p*-position. Such a result leads to conclude that, under the given heterogeneous conditions, the electrophilicity of the acylating agent does not play a relevant role; this is mainly due to the high reactivity of the activated aromatic substrate.

Acknowledgements

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