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# Kinetic study and reaction mechanism of the hydroxyalkylation of aromatic compounds over H-BEA zeolites

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## Abstract

Hydroxyalkylation of various carbocyclic aromatic compounds has been carried out in the presence of dealuminated H-form BEA zeolites. A kinetic study has been realized by varying several reaction parameters such as catalyst weight, initial concentration in aromatic reactants, temperature, substituent effects on aromatic substrates. The experimental results obtained allowed to propose a 'poisoned Eley–Rideal' reaction mechanism, where the adsorbed aromatic substrate does not react with a molecule of chloral, but acts as a poison of the reaction. The ratio of the adsorption constants of the two reactants has been determined. Anisole was found to be more strongly adsorbed than chloral. Moreover, it has also been shown that this electrophilic aromatic substitution reaction follows a Hammett-type correlation, with a strong negative  $\rho$ -value of  $-4$ . The presence of a strong electron-donating substituent on the aromatic ring not only increases the reaction rate, but also favors the formation of the undesired bisarylalkanes. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydroxyalkylation; Anisole; Chloral; H-BEA zeolites; Kinetics; Eley–Rideal mechanism

## 1. Introduction

In a previous work [1], we have reported on the hydroxyalkylation of anisole by carbonyl compounds over protonic zeolites. We have shown in particular that the reaction with a deactivated reactant such as chloral led to the corresponding *ortho*- and *para*-carbinols at 293 K. It has also been shown that for the hydroxyalkylation reaction to work selectively, a prerequisite was to avoid the presence of an electron-donating group on the carbonyl compound. Among the zeolites studied, the H-BEA with

a Si/Al ratio of 12.5 exhibited both high activity and high selectivity towards the *para*-carbinol, i.e. 4-methoxy- $\alpha$ -trichloro benzylic alcohol.

The main purpose of the present work was then to investigate more deeply the kinetics of the hydroxyalkylation of anisole with chloral in the presence of H-BEA zeolites and to propose a mechanism of the reaction.

## 2. Experimental

### 2.1. Materials

Anisole (99%) was purchased from Aldrich, chloral (>97%) from Fluka. Phenol (99.5%) was supplied from Prolabo and toluene (HPLC grade) from SDS.

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Table 1  
H-BEA zeolites used for hydroxyalkylation of anisole with chloral

H-BEA sample origin	Si/Al	Acidity (meq H <sup>+</sup> g <sup>-1</sup> )
PQ-CP 811	12.5	0.92
PQ-CP 814	25	0.84
Dealuminated PQ-CP 811	43	0.44

## 2.2. Catalysts

Dealuminated H-form BEA zeolites were obtained from PQ zeolites. The different data concerning the samples used, origin, and Si/Al ratios as well as their acidity measured by thermodesorption of ammonia are reported in Table 1. The catalysts were calcined overnight at 773 K in flowing air (300 ml min<sup>-1</sup>) prior to use.

## 2.3. Reaction procedure

The hydroxyalkylation of aromatic compounds with chloral was carried out in a 50 ml stirred glass reactor operating in the batch mode. The general procedure was as follows: the freshly calcined catalyst (0.25–3 g) was stirred at the required temperature for 5 min in the presence of chloral (240 mmol). The agitation speed was 1250 rpm. Zero time was set when the aromatic compound (0–65 mmol) was added to the suspension of catalyst in chloral.

## 2.4. Analyses

Analyses were performed by high performance liquid chromatography (HPLC) using a Shimadzu LC-6A pump equipped with a UV spectrophotometer SPD-6A detector at 270 nm and controlled by a PC software package (ICS). A Merck RP 18 (C18) column was

used and the mobile phase was an acetonitrile/water mixture (50/50 by volume) at 0.7 ml min<sup>-1</sup> constant flow.

## 2.5. Determination of the initial reaction rates

The initial reaction rates are deduced from the experimental curves of carbinol concentration versus reaction time by determination of the slope at the origin. Taking into account the total volume of the reaction mixture, the initial rates are then converted into mole per second units.

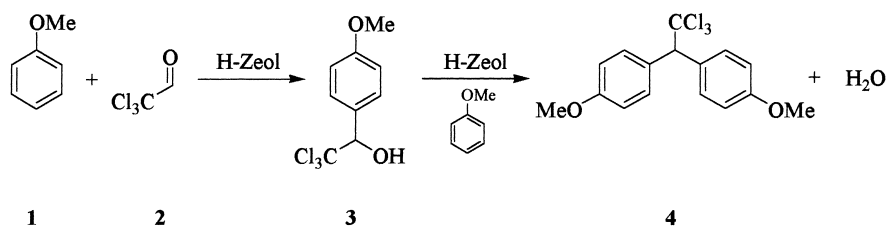
## 3. Results and discussion

### 3.1. Reaction scheme

The general reaction scheme for the condensation of chloral (**2**) with anisole (**1**) on zeolites is given below (Scheme 1). The carbinol (**3**) can, once formed, undergo further reaction with another molecule of anisole to form bisaryllalkane (**4**).

Under the following experimental conditions, 17.5 mmol (2 ml) of anisole; 240 mmol (25 ml) of chloral; 323 K; 1 g of H-BEA (Si/Al = 12.5); 1250 rpm, the hydroxyalkylation of anisole with chloral in the presence of a H-BEA zeolite (Si/Al = 12.5) leads selectively to the corresponding carbinol as shown in Fig. 1, which presents a typical concentration versus time profile for the disappearance of anisole and appearance of 4-methoxy- $\alpha$ -trichlorobenzyl alcohol (or *p*-carbinol). The *pp'*-bisaryllalkane is detected only as traces.

As previously reported, the H-BEA zeolite is the best catalyst for the formation of the desired carbinol. The selectivity towards carbinol, defined as the ratio [*p*-carbinol]/[consumed anisole], is higher than 95%



Scheme 1. Hydroxyalkylation of anisole with chloral in the presence of H-form zeolites.

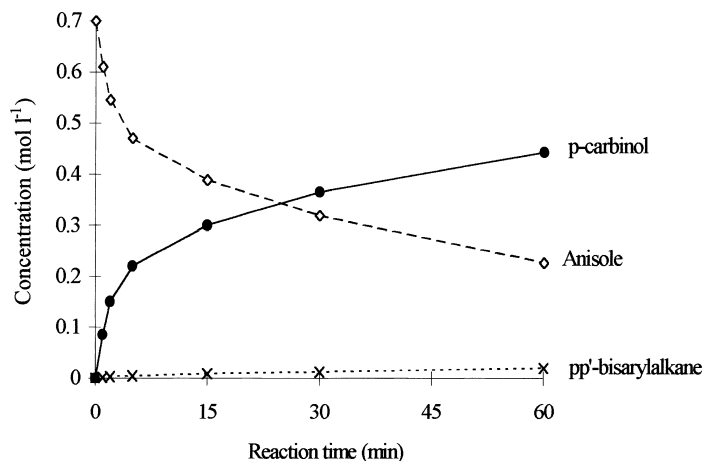


Fig. 1. Plots of disappearance of anisole ( $\diamond$ ) and appearance of the two reaction products, *p*-carbinol ( $\bullet$ ) and *pp'*-bisarylalkane ( $\times$ ) vs. reaction time (anisole: 17.5 mmol (2 ml); chloral: 240 mmol (25 ml); 323 K; H-BEA (Si/Al = 12.5): 1 g; 1250 rpm).

and, among the two possible carbinol isomers capable of being formed, only the *para*-isomer is obtained.

### 3.2. Influence of the catalyst weight

We examine now the influence of the catalyst weight on both the selectivity in the *p*-carbinol and the initial rate which is the slope of the curve substrate concentration versus time at 0 time. The results are reported in Table 2.

When the catalyst weight increases, a slight decrease in carbinol selectivity is observed as it can be expected in the case of successive reactions. The initial reaction rate increases proportionally to the catalyst weight ( $r_0 = 8 \cdot 10^5 \times w$ ). It is verified that the reaction is first-order with respect to the catalyst.

A catalyzed first-order reaction is characterized by a kinetic rate  $k_r$  and a mass transport factor  $k_m$ . The

rate of reaction is given by  $r = w \times k_r \times A_S$  with  $A_S$ : concentration of A at the catalyst surface;  $k_r$ : first-order rate constant and  $w$ : catalyst weight.

The rate of mass transfer from the bulk liquid to the surface of the solid catalyst is given as:  $r_m = k_m \times (A_1 - A_S)$ , in which  $A_1$  is the concentration of A in the bulk liquid. At the steady state, these two reactions are identical and we can write  $r = A_1 \times k_r k_m \times w / (k_r w + k_m)$  and its reciprocal:  $A_1/r = 1/k_m + 1/(k_r \times w)$ .

In the plot of the reciprocal of the initial reaction rate versus the reciprocal of the catalyst weight (Fig. 2),

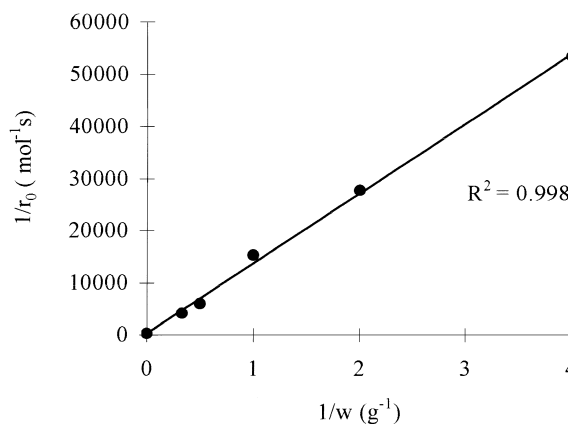


Fig. 2. Plot of the reciprocal of the initial reaction rates vs. the reciprocal of the catalyst weight.

Table 2  
Influence of the catalyst weight on the initial rates of appearance of the *p*-carbinol<sup>a</sup>

Catalyst weight (g)	0.25	0.5	1	2	3
Selectivity <sup>b</sup> in carbinol (%)	98	98	97	95	95
$r_0 \times 10^5$ (mol s <sup>-1</sup> )	1.9	3.6	6.5	16.6	24.3

<sup>a</sup> Anisole: 17.5 mmol (2 ml); chloral: 240 mmol (25 ml); 323 K; H-BEA (Si/Al = 12.5): 0.25–3 g; 1250 rpm.

<sup>b</sup> At 15% conversion of anisole.

Table 3  
Influence of the reaction temperature on the initial rates of formation of the *p*-carbinol<sup>a</sup>

Reaction temperature (K)	273	298	323	348
Selectivity <sup>b</sup> in <i>p</i> -carbinol (%)	100	98	97	95
$r_0 \times 10^5$ (mol s <sup>-1</sup> g <sup>-1</sup> )	1.1	3.6	6.5	13.3

<sup>a</sup> Anisole: 17.5 mmol (2 ml); chloral: 240 mmol (25 ml); 273–348 K; H-BEA (Si/Al = 12.5); 1 g; 1250 rpm.

<sup>b</sup> At 15% conversion of anisole.

if  $A_1$  is constant, the y-intercept, which is the reciprocal of  $k_m$ , is very small compared to the slope. Under our experimental conditions (1250 rpm, 1 g of catalyst, 323 K), mass transport limitation can be said to be absent and the kinetic regime is controlling the reaction.

### 3.3. Influence of the reaction temperature

The influence of the temperature on the reaction rates was investigated in the range 273–348 K. Table 3 shows the results performed at different reaction temperatures. The selectivity in *p*-carbinol slightly decreases when the temperature increases, bisaryllalkanes being formed in significant amounts at high temperatures. The apparent activation energy calculated by the Arrhenius law is 25 kJ mol<sup>-1</sup> (Fig. 3). Such a value is close to the upper limit for a diffusion-controlled reaction, but is not really unexpected from the previous results and the particularly high stability of the carbenium ion intermediates [1].

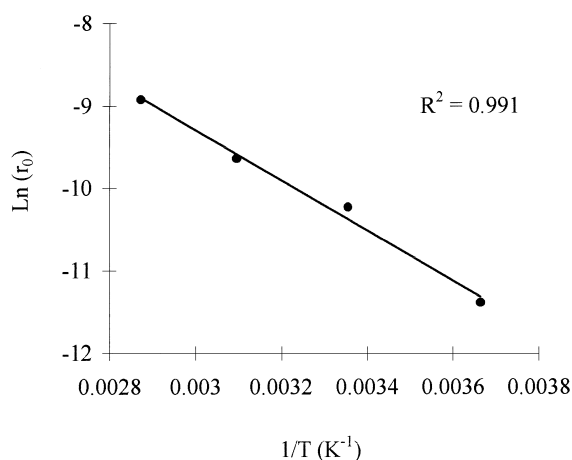


Fig. 3. Arrhenius plot for the formation of the *p*-carbinol.

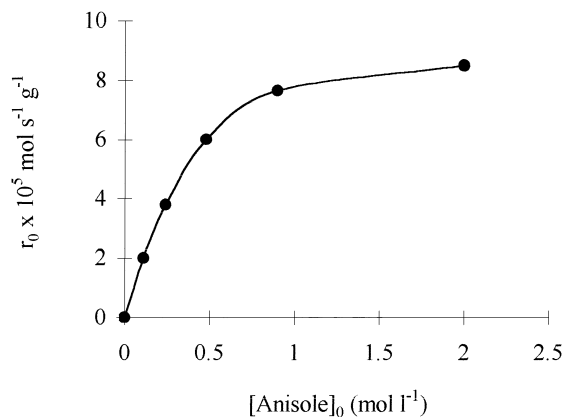


Fig. 4. Plot of the initial reaction rates vs. the initial concentration of anisole.

### 3.4. Influence of the initial concentration in anisole

In order to gain further understanding of the reaction mechanism, we have measured initial rates at different initial concentrations in anisole, while the amount of chloral used as solvent was kept constant (in excess in any case, 25 ml). Fig. 4 shows the initial reaction rate evolution with the initial concentration in anisole.

As can be seen from Fig. 4, the initial rate increases up to  $8.10^5$  mol s<sup>-1</sup> g<sup>-1</sup> for  $[\text{anisole}]_0 = 1$  M, then reaches a level off for higher anisole initial concentrations. Such a curve is not typical of a Langmuir–Hinshelwood mechanism for which the reaction occurs between two reactants competitively adsorbed on the same type of sites. Taking into account our experimental results, a new rate law is proposed in the discussion.

### 3.5. Influence of the Si/Al ratio

Hydroxyalkylation of anisole by chloral was studied over a series of H-BEA zeolites with different Si/Al ratios (12.5, 25 and 43). The initial reaction rates for the appearance of the *p*-carbinol are reported in Table 4. It can be seen from this table that the activity increases up to a Si/Al ratio equal to 25 and then becomes stabilized for higher ratios, the selectivity remaining unchanged.

The initial rates for all samples are now plotted versus the Al content of the H-BEA zeolites (Fig. 5). This figure also reports the total acidity provided by

Table 4  
Influence of Si/Al ratio (H-BEA) on the initial rates of formation of the *p*-carbinol<sup>a</sup>

Si/Al (H-BEA)	12.5	25	43
Selectivity <sup>b</sup> in carbinols (%)	98	98	98
$r_0 \times 10^{-5}$ (mol s <sup>-1</sup> g <sup>-1</sup> )	6.5	15.3	17.5

<sup>a</sup> Anisole: 17.5 mmol (2 ml); chloral: 240 mmol (25 ml); 323 K; H-BEA (Si/Al = 12.5): 1 g; 1250 rpm.

<sup>b</sup> At 15% conversion of anisole.

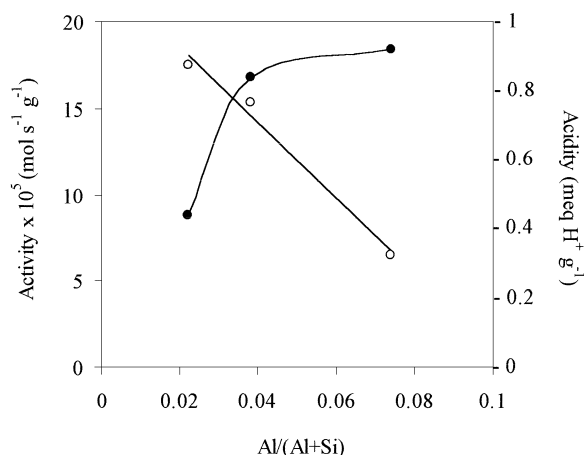


Fig. 5. Catalytic activity and acidity of H-BEA zeolites as a function of Al content.

NH<sub>3</sub>-TPD (Table 1) against the Al content. No correlation is found between activity and acidity of the catalysts.

From the standardized NH<sub>3</sub>-TPD profiles for the three samples of H-BEA zeolites (Fig. 6), the intensities of the peaks can then be compared. These profiles consist of two peaks: one at low temperature around 550 K and the other one at high temperature around 700 K. The low and high temperature peaks correspond to the weak and strong acid sites, respectively. The H-BEA 12.5 zeolite exhibits more weak than strong acid sites, whereas the reverse is observed for the two other H-BEA zeolites 25 and 43. The profiles of the ammonia TPD spectra for these two latter zeolites indicate that the acid sites are of comparable strength but their number is different. If we consider now the turnover frequencies (TOF), calculated by dividing the initial reaction rate by the number of acid sites as determined by TPD of ammonia, we can

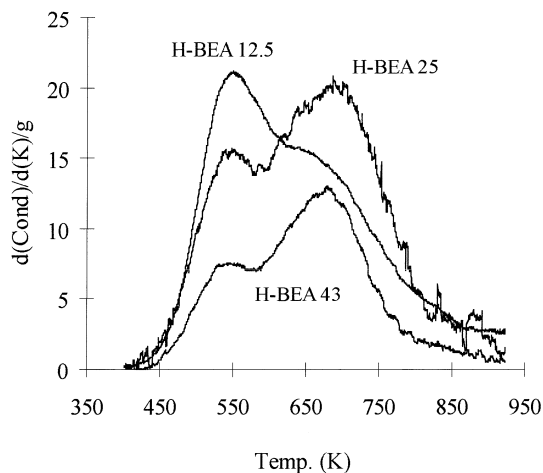


Fig. 6. NH<sub>3</sub>-TPD profiles for H-BEA zeolite samples.

see that the activity per site increases linearly from Si/Al = 12.5 to 43 (Fig. 7). The TOF number was expected to be constant for H-BEA 25 and H-BEA 43, if it only depends on the acidic strength of the site. In the absence of more precise data on these catalysts no conclusion can be drawn.

### 3.6. Substituent effects on the aromatic compound

As we have shown in other reactions of aromatic electrophilic substitution in the presence of zeolites [2,3], the reactivity of substituted compounds

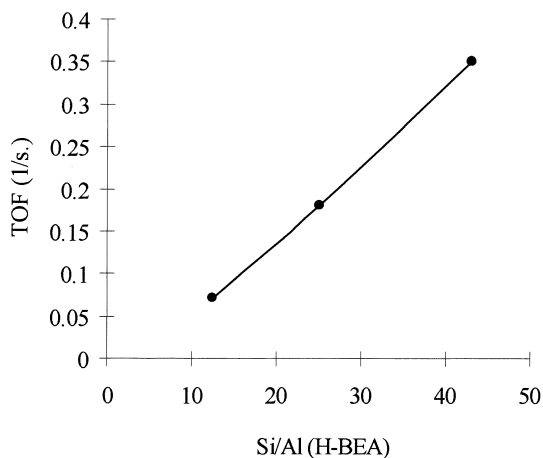


Fig. 7. TOF (s<sup>-1</sup>) vs. Si/Al ratio for H-BEA zeolite samples.

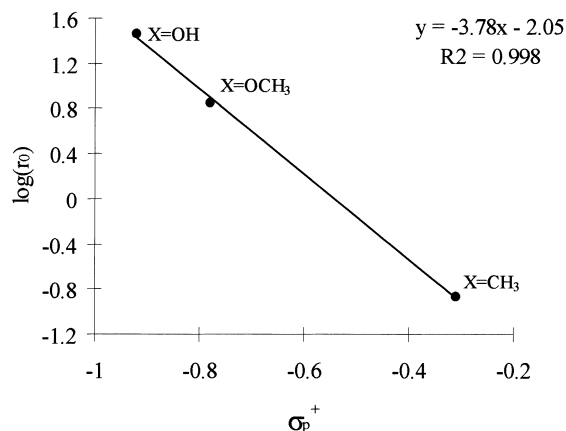


Fig. 8. Hammett relationship for the hydroxyalkylation of phenol, anisole and toluene.

(toluene, anisole, phenol) obeys a Hammett  $\rho$ - $\sigma$  relationship. The plot of the logarithms of the initial reaction rates against substituent constants  $\sigma_p^+$  gives a straight line correlation (Fig. 8) and a large negative value of  $\rho$  ( $-3.8$ ). The initial rates of reaction increase with the increasing electron-donating character of the substituent, indicating that the rate-determining step is favored by electron donation to the reaction center. The negative  $\rho$ -value indicates an important charge development in the highest energy transition state, which resembles the Wheland intermediate.

### 3.7. Proposition of mechanism

The hypothesis of adsorption on Brønsted sites for both chloral and anisole is to be ruled out because two species positively charged could not react together in agreement with our previous work. We assume that chloral and anisole compete on the acidic sites because of the basic character of anisole. Adsorbed anisole does not react and only acts as a poison. It is then assumed that anisole physisorbed in the intracrystalline space reacts with chemisorbed chloral. Such an assumption leads to the corresponding rate equation as follows (Eq. (1)).

$$r = k \times \Theta_C \times [A] \quad (1)$$

with  $\Theta_C = (\lambda_C[C]) / (1 + \lambda_C[C] + \lambda_A[A])$ , where  $\lambda_C$  and  $\lambda_A$  are the adsorption coefficients of chloral and

anisole, respectively. Consequently,  $r_0$  is converted into Eq. (2).

$$r_0 = k \times w \frac{\lambda_C[C]_0[A]_0}{1 + \lambda_C[C]_0 + \lambda_A[A]_0} \quad (2)$$

Such a rate expression reveals that the order with respect to anisole passes from unity (for  $\lambda_A[A]_0 \ll (1 + \lambda_C[C]_0)$ ) to zero (for  $\lambda_A[A]_0 \gg (1 + \lambda_C[C]_0)$ ) when the initial concentration increases. The profile of the curve depicted in Fig. 4 is in agreement with this assumption and the corresponding model is named by the authors 'poisoned Eley-Rideal'. By linearizing Eq. (2), we obtain Eq. (3).

$$\frac{1}{r_0} = \frac{1}{k} \times \frac{1}{[A]_0} + \frac{1}{k} \times \frac{\lambda_A}{\lambda_C} \times \frac{1}{[C]_0} \quad (3)$$

From Eq. (3), and if the initial concentration in chloral is considered as constant (in fact, it slightly varies because of the dilution effect of chloral by anisole), the plot of the reciprocal of initial reaction rates as a function of the reciprocal of the initial concentration, or molecules number, of anisole must be linear. Indeed, Fig. 9 shows a linear relationship ( $R^2 = 0.997$ ), except at the highest anisole amount where chloral concentration cannot be really considered as constant.

From both slope and intercept, the adsorption constant ratio  $\lambda_A/\lambda_C$  can then be calculated; a  $\lambda_A/\lambda_C$  ratio of 13 is found. This value indicates that anisole is more strongly adsorbed on the catalytic sites than chloral. Such a result is in good agreement with the

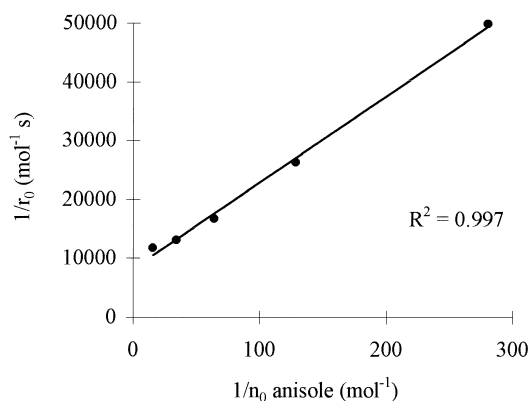


Fig. 9. Plots of the reciprocal of the initial reaction rates ( $\text{mol}^{-1} \text{s}$ ) vs. the reciprocal of the initial anisole molecules number ( $\text{mol}^{-1}$ ).

basicity constants of the different reactants, given as the  $pK_a$ 's of the conjugate acids,  $-6.5$  for anisole [4],  $-10.2$  for acetaldehyde [5] and less than  $-10$  for chloral as far as the presence of a chloro substituent reduces the basicity substantially. Moreover, the fact that anisole is more adsorbed than chloral is in accordance with recent papers of Derouane [6,7]: “adsorption equilibria favor the adsorption of the larger (or more polar) molecules in the intracrystalline microporous volume”. Other authors [8] also cited the strong adsorption of anisole on zeolites. It could then be proposed a mechanism in which chloral and anisole are adsorbed on acidic sites of the zeolite, but where the chemisorbed electrophile reacts with physisorbed anisole to form a  $\sigma$ -complex. The rearomatizing deprotonation of the arenium ion leads to the carbinol and a proton which regenerates the acidic site on the catalyst.

#### 4. Conclusion

Under mild conditions (273–298 K) and in the presence of a H-BEA zeolite with a Si/Al ratio of 12.5, the condensation of chloral with anisole leads to 4-methoxy- $\alpha$ -trichlorobenzyl alcohol with a selectivity over 98%.

The kinetic law presented in this paper is a ‘poisoned Eley–Rideal mechanism’ in which anisole present in the liquid phase reacts with a molecule of adsorbed chloral, whereas the adsorbed anisole acts as a poison of the reaction. Such an assumption well agrees with the experimentally measured kinetic rates. Anisole was found to be more strongly adsorbed than chloral.

Once again, the electronic effects observed confirm that this reaction is an electrophilic aromatic substitution which follows a  $\rho$ - $\sigma^+$  Hammett relationship with a large negative  $\rho$ -value.

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