Mono-N-methylation of Primary Amines with Alkyl Methyl Carbonates over Y Faujasites. 2. Kinetics and Selectivity

Maurizio Selva,* Pietro Tundo, and Alvise Perosa
Dipartimento di Scienze Ambientali dell’Università Ca’ Foscari, Calle Larga S. Marta 2137, 30123 Venezia, Italy

Received June 14, 2002

In the presence of a Na-exchanged Y faujasite, the reaction of primary aromatic amines 1 with 2-(2-methoxyethoxy)methylmethyl carbonate [MeO(OCOCMe2)CH2O(OCOCMe2)2, 2a] yields the corresponding mono-N-methyl derivatives ArNHMe with selectivity up to 95%, at substantially quantitative conversions. At 130 °C, the reaction can be run under diffusion-free conditions and is strongly affected by the solvent polarity: for instance, in going from xylene (εs = 2.40) to triglyme (εs = 7.62) as the solvent, the pseudo-first-order rate constant for the aniline (1a) disappearance shows a 5-fold decrease. In DMF (εs = 38.25), the same reaction does not occur at all. Competitive adsorption of the solvent and the substrate onto the catalytic sites accounts for this result. The behavior of alkyl-substituted anilines ZC6H4NH2 [Z = Me, Et, Pr, Bu, (Bu)2, (Bu)3] and p-alkoxylanilines p-ZC6H4NH2 [Z = OMe, OEt, OPr, O-] clearly indicates a steric effect of ring substituents: as diffusion of the amine into the catalytic pores is hindered, the reaction hardly proceeds and the mono-N-methyl selectivity (S,M/D) drops as well. Moreover, the strength of adsorption of the amine onto the catalyst influences the rate and the selectivity as well: the reaction of p-anisidine and p-toluidine— despite the higher nucleophilicity of these compounds—is slower and even less selective with respect to aniline. From a mechanistic viewpoint, the intermediacy of carbamates ArN(Me)CO2R and dimethyl carbonate shows that the reaction outcome can be improved by tuning the amphoteric properties of the catalyst: in going from CsY to the more acidic LiY zeolite, methylation is not only more selective (S,M/D ratio increases from 77% to 84%) but even much faster (CsY, conversion of 36% after 22 h; LiY, conversion of 43% after 7 h).

Introduction

The direct mono-N-alkylation of primary amines is not usually performed with conventional alkylation procedures because competing overalkylation reactions lead to mixtures of secondary and tertiary amines along with the corresponding ammonium salts. This is particularly the case for N-methylation reactions.

A few years ago, we reported that a very high mono-N-methyl selectivity can be attained when primary aromatic amines 1 are allowed to react with dimethyl carbonate (DMC) as the alkylation agent in the presence of alkali-metal-cation-exchanged faujasites as the catalysts (Scheme 1). Typically, at 120−150 °C (P = 2−6 bar), the formation of alkyl-substituted anilines 3—even deacti- vated ones (XC6H4H) with X = p-O2N, p-CN, o-MeO2C)—

SCHEME 1

\[
\text{ArNH}_2 + \text{MeOCO}_2\text{Me} \xrightarrow{\text{Y-zeolites}} \text{ArNHMe} + \text{MeOH} + \text{CO}_2
\]

130-150 ºC, 5.8 bar

Ar = p-OC6H4H, p-NCC6H4H, p-CH2OCC6H4H, 2,6(CH2)2C6H4

takes place with a selectivity of 92−98%, at conversions of 72−93%.

More recently, we demonstrated that this alkylation procedure is a general one: anilines react with different dialkyl carbonates 2 to yield the corresponding mono-N-alkylated derivatives XCl2H2NHR (X = H, Cl, NO2; R = Me, Et, Bu, allyl) with a selectivity of 90−97% in good to excellent yield (68−94%). It was also observed that the reaction can be conveniently carried out at atmospheric pressure with the use of high-boiling-point unsymmetrical dialkyl carbonates ROCO2R′ [R = Me, Et; R′ = MeO(CH2)2O(CH2)2; 2b and 2c, respectively]; a chemoselectivity of up to 99% toward N-methylation and N-ethylation was achieved (Scheme 2).


Mono-N-methylation of Primary Amines

**Results and Discussion**

**Mono-N-methylation of Aniline.** (i) Experimental Conditions. As aforementioned, selective mono-N-methylations of amines can be achieved at atmospheric pressure with the use of unsymmetrical methyl alkyl carbonates ROCO₂Me. This is advantageous (with respect to DMC) for the setup of a kinetic investigation because reactions can be monitored more easily in conventional glass reactors.

Accordingly, the mono-N-methylation of aniline (1a) with 2-(2-methoxyethoxy)ethyl methyl carbonate [MeO-(CH₂)₂O(CH₂)₂OCO₂Me, 2a] was investigated as a model reaction (eq 1).

\[
\text{PhNH₂} + \text{ROCO₂Me} \xrightarrow{\text{NaY}} \text{PhNHMe} + \text{ROH} + \text{CO₂}
\]

\[1a \quad 2a \]

\[R = \text{MeO}(\text{CH₂})₂O(\text{CH₂})₂\]

Initial experiments were carried out using solutions (0.45 M, 5 mL) of 1a in triglyme [MeO(CH₂)₂O(CH₂)₂] which were made to react at 130 °C (atmospheric pressure) with different amounts of 2a [molar ratio 2a:1a (W) in the range of 2–6] in the presence of the faujasite NaY with the catalyst [weight ratio (Q) NaY:1a = 0.5]. The conversion of aniline was monitored by GLC over a period of 8 h for each run.

Figure 1 reports the results.

As the W ratio increases from 2 to 4, the conversion rises as well from 40% to 80%. Then, further increments in the quantity of 2a (W ≥ 4) do not have any appreciable effect on the reaction conversion, which is substantially unaltered (~80%). This may indicate that, at W ≥ 4, the concentration of the carbonate adsorbed by the zeolite is a constant during the reaction, which is substantially unaltered (~80%). This may indicate that, at W ≥ 4, the concentration of the carbonate adsorbed by the zeolite is a constant during the reaction.

\[\text{Conversion} (\%)\]

\[\text{molar ratio } 2a:1a\]

\[\text{Figure 1. Mono-N-methylation of aniline with } 2a \text{ at } 130 \, ^\circ\text{C: reaction conversions after } 8 \, \text{h.}\]

In all cases reported in Figure 1, the mono-N-methyl selectivity is 99%.

(ii) Order and Regime of Reaction. Under the conditions of point i, reaction 1 was run using a W ratio of 5, and with the addition of n-tetradecane as the internal standard.

Figure 2a reports both the disappearance of aniline and the formation of its N-methyl derivative. At a high conversion (>70%), the mass balance falls within a 5% range because of the concurrent formation of PhN(R)Me [R = MeO(CH₂)₂O(OC₂Me), ≤1%, by GC] along with a unidentified byproduct (≤4%).

If one considers that the concentration of the carbonate adsorbed by the zeolite is a constant during the reaction, a simplified rate law equation can be used (eq 2, where \(k' = k[2a]^p\)).

\[
v = \left(\frac{[1a]}{dt}\right) = k'[1a]^p[2a]^q = k'[1a]^p
\]

\[2\]

Accordingly, the decay of aniline follows a first-order rate law (Figure 2a). This is confirmed by Figure 2b, which shows that the concentration of aniline (determined by GC) fits the integrated expression of eq 2 with \(p = 1\) well, i.e., \(\ln([1a]/[1a]_0) = k't\) \([1a]_0\) and \([1a] = \text{concentrations of } 1a\text{ at } t = 0\) and at a later time t, respectively. The resulting plot gives a straight line (r > 0.99) whose slope is the pseudo-first-order rate constant \(k_{obs}\) for the disappearance of the substrate (\(k_{obs} = 4.9 \times 10^{-3} \text{ min}^{-1}\)).

However, before the discussion of any kinetic result, it was compulsory to establish the regime under which reaction 1 occurred: in fact, especially zeolite-catalyzed processes (where the inner cages of the catalyst have sizes comparable to those of the reactant molecules) could be seriously limited by diffusion phenomena.

To this scope, the formal treatment for heterogeneous catalytic reactions was applied: the effect of both the catalyst weight and the stirring rate on the kinetic constant \((k_{obs} \text{ in eq } 2)\), as well as the activation energy of the process, were considered.
reaction 1, were investigated. Under the conditions of Figure 2 (T = 130 °C, W = 5), two sets of experiments (I and II) were carried out: reaction 1 was run (a) by varying the Q ratio (weight ratio NaY:1a) in the range of 0.5-1.5 and (b) at a Q of 0.5, with different stirring rates of 600 and 1000 rpm. The constant k_{obs} was determined in all cases, and each reaction was repeated twice to check the reproducibility.

In the first set (I), it was found that k_{obs} increased linearly with the catalyst amount (Figure 3a), while set II showed that k_{obs} was substantially independent of the stirring rate (k_{obs} = 5.0 \times 10^{-3} and 4.9 \times 10^{-3} min^{-1} at 600 and 1000 rpm, respectively).

Moreover, under the conditions of Figure 2 (W = 5, Q = 0.5), reaction 1 was investigated in the range of temperature from 130 to 150 °C, and an activation energy of 48 kJ mol^{-1} was calculated from the corresponding Arrhenius plot (ln(k_{obs}) = ln A - E_{act}/RT; Figure 3b). This value was well above the threshold of 25 kJ mol^{-1} accepted for chemically controlled reactions. To summarize, the data of Figure 3 as well as the effect of the stirring on the reaction rate allowed the conclusion that reaction 1 was not diffusion controlled under the examined conditions. Hence, the kinetic treatment could be validated.

(iii) Effect of the Solvent. To investigate the influence of the solvent polarity, the mono-N-methylation of aniline with carbonate 2a was carried out in the presence of aprotic reaction media having dielectric constants either higher or lower with respect to that of triglyme (r = 7.62): in

(12) As reported by Simpson et al., the most appropriate analysis of this effect for zeolites is the approach of Weisz-Prater. This model, however, was not applicable for reaction 1 because the diffusional coefficients (D) of the reactants were not available. (a) Simpson, M. F.; Wei, J.; Sundaresan, S. Ind. Eng. Chem. Res. 1996, 35, 3861. (b) Weisz, P. B.; Prater, C. D. Adv. Catal. 1954, 6, 143.

(13) Values of k_{obs} are averaged over two runs: at any given Q, the two k_{obs} values were within a maximum of a 10% deviation from each other.

particular, N,N-dimethylformamide (DMF, εr = 38.25) and xylene (εr = 2.40) were employed. Experiments were run under the conditions previously reported (130 °C, Q = 0.5, and W = 5), and in all cases, solutions (0.4 M, 5 mL) of aniline in the given solvent were used. n-Tetradecane and ethylene glycol di-n-hexyl ether (n-C14H30OCH2CH2O-n-C6H13) were the internal standards for reactions with xylene and DMF, respectively. Reaction 1 was also performed in the presence of only the carbonate 2a with no additional solvent.

As described above (point ii), pseudo-first-order rate constants (kobs) were evaluated for the disappearance of aniline. The results are reported in Table 1.

The data clearly show that although the reaction selectivity is not affected by solvent polarity, the nature of the solvent has a dramatic effect on the reaction rate. As the dielectric constant increases, kobs markedly drops (entries 1–3), to the point that it is no more determinable in the more polar medium (DMF) where the reaction is inhibited (after 8 h, conversion was 3%, entry 4). By contrast, the fastest reaction takes place when no additional solvents are used (entry 5).

The rationale for this behavior can be found in the large difference in the strength of adsorption between polar and apolar solvents onto the zeolite. Polar compounds such as DMF interact strongly with the polar environment (i.e., a silicoalumininate structure) of the inner cages of the faujasite, while the apolar xylene is hardly retained. Consequently, the polar solvent itself becomes the major competitor of aniline for the active sites of the catalyst, and the corresponding reaction rate falls.

This explanation may also account for the outcome in the absence of added solvents (entry 5): the higher rate constant is due to a 2-fold effect of the relatively low polarity of 2a (εr = 6.14), and of the lack of competitive phenomena of adsorption.

However, regardless of the solvent used, the reaction proceeds toward the formation of only mono-N-methylaniline: once the reactant amine is adsorbed, the very high selectivity is induced by the structure/polarity features of the catalyst.

Similar effects have also been described for the cyclo-

TABLE 1. Influence of the Solvent Polarity in the N-Methylation of Aniline with 2a

<table>
<thead>
<tr>
<th>solvent</th>
<th>kobs × 10⁻²</th>
<th>convn (%)</th>
<th>SM,D (%)</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 xylene</td>
<td>2.40</td>
<td>2.29</td>
<td>98</td>
<td>99</td>
</tr>
<tr>
<td>2 triglyme</td>
<td>7.62</td>
<td>0.49</td>
<td>85</td>
<td>99</td>
</tr>
<tr>
<td>3 triglyme with nondried NaY</td>
<td>7.62</td>
<td>0.42</td>
<td>79</td>
<td>99</td>
</tr>
<tr>
<td>4 DMF</td>
<td>38.25</td>
<td>naᵇ</td>
<td>3</td>
<td>99</td>
</tr>
<tr>
<td>5 c</td>
<td>6.14ᵇ</td>
<td>2.41</td>
<td>100</td>
<td>99</td>
</tr>
</tbody>
</table>

ᵃ kobs values are averaged over two reactions carried out for each solvent. ᵇ na = not available. ᵇ The reaction was run with only the carbonate 2a in a 5-fold molar excess with respect to aniline. No additional solvent was used. ᵇ The dielectric constant of 2a was determined as reported in the Experimental Section. ᵇ SM,D: N-Methyl selectivity defined as [PhNH(CH3)]/(PhNH2). ᵇ Yield of 3a (N-methylaniline) determined by GC.

The rationale for this behavior can be found in the large difference in the strength of adsorption between polar and apolar solvents onto the zeolite. Polar compounds such as DMF interact strongly with the polar environment (i.e., a silicoalumininate structure) of the inner cages of the faujasite, while the apolar xylene is hardly retained. Consequently, the polar solvent itself becomes the major competitor of aniline for the active sites of the catalyst, and the corresponding reaction rate falls.

This explanation may also account for the outcome in the absence of added solvents (entry 5): the higher rate constant is due to a 2-fold effect of the relatively low polarity of 2a (εr = 6.14), and of the lack of competitive phenomena of adsorption.

However, regardless of the solvent used, the reaction proceeds toward the formation of only mono-N-methylaniline: once the reactant amine is adsorbed, the very high selectivity is induced by the structure/polarity features of the catalyst.

Similar effects have also been described for the cyclo-

TABLE 2. Reaction of 1a, 1b, and 1b' with 2a at 130 °C in the Presence of NaY

<table>
<thead>
<tr>
<th>entry</th>
<th>amine</th>
<th>x (Å)</th>
<th>y (Å)</th>
<th>NaY:Y (g/g)</th>
<th>solvent</th>
<th>t (h)</th>
<th>SM,D (%)</th>
<th>yield (%)</th>
<th>kobs × 10⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>4.34 1.17 0.5</td>
<td>0.5</td>
<td>xylene</td>
<td>3</td>
<td>98</td>
<td>99</td>
<td>2.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 b</td>
<td>4.34 1.81 6.44</td>
<td>0.5</td>
<td>xylene</td>
<td>7</td>
<td>66</td>
<td>94</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 c</td>
<td>4.60 1.86 7.89</td>
<td>0.5</td>
<td>xylene</td>
<td>7</td>
<td>56</td>
<td>85</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 d</td>
<td>1.5</td>
<td>xylene</td>
<td>7</td>
<td>88</td>
<td>81</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 b'</td>
<td>0.5</td>
<td>triglyme</td>
<td>7</td>
<td>94</td>
<td>na</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 b'</td>
<td>1</td>
<td>triglyme</td>
<td>7</td>
<td>51</td>
<td>93</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 b'</td>
<td>1</td>
<td>triglyme</td>
<td>16</td>
<td>76</td>
<td>88</td>
<td>na</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Weight ratio between the catalyst NaY and the amine 1. ᵇ SM,D defined as in Table 1. ᵇ Not available.

hexylation of phenol over USHY faujasites, and for the Fries rearrangement of phenyl acetate over HBEA zeolites: in both cases, the authors claimed that reaction rates were strongly depressed in the presence of polar solvents able to adsorb onto the acidic sites of the catalysts.

Finally, it should be noted that only a modest decrease of the catalytic activity is observed when the reaction is carried out with a faujasite not preliminarily dried (compare entries 2 and 3): the amount of water (5–7 wt %) adsorbed by the catalyst may account for this result.

Mono-N-methylation of p-Alkyl- and p-Alkoxysterminated Anilines. Our previous results suggested that the adsorption of anilines and dialkyl carbones onto the cages of Y zeolites, and consequently the selectivity of the mono-N-alkylation reactions, could be controlled by the pore size and amphoteric properties of the catalysts. To understand this phenomenon, a comparative study on a homologous series of anilines was undertaken. In particular, p-alkyl- and p-alkoxylanilines p-ZC6H4NH2 (Z = Me, Et, Pr, n-Bu (1b–e); Z = OMe, OEt, OPo, O-n-Bu (1b′–e′)) appeared to be appropriate substrates to describe the influence of both the bulkiness and the electronic properties of the substituents.

p-Toluidine and p-Anisidine. At first, the reactivities of the smallest terms of the two series, p-toluidine (1b) and p-anisidine (1b′), were compared. At 130 °C, solutions (5 mL, 0.3 M) of these amines in xylene or trimylene as the solvent were made to react with the carbonate 2a (in a 5-fold molar excess with respect to the amine) and the zeolite NaY. n-Dodecane (in xylene) and diethylene glycol diethyl ether (in trimylene) were used as internal standards. Pseudo-first-order rate constants (kobs) were evaluated as for aniline. The results are reported in Table 2.

For a convenient comparison, Table 2 also reports the result for 1a and an estimate of the molecular size of amines 1a, 1b, and 1b′ expressed through the dimensions x, y, and z of the smallest box able to fit in such compounds (columns 3–5; see also the Experimental Section).

---


(19) Zeolites are known to be hygroscopic solids. Before each reaction, the catalyst was dried with heating overnight at 70 °C and under vacuum (10 mm). This treatment was not applied in the case of entry 3 in Table 1. The dried zeolite showed a weight decrease in the range of 5–7% (determined through a gravimetric comparison between three dried and nondried samples).
In xylene as the solvent, the more nucleophilic amines 1b and 1b′ show a comparable reactivity (entries 2 and 3), but surprisingly, their methylation reactions appear much slower and even less selective with respect to aniline: this is especially true for p-anisidine (S_{M/D} = 85%, at 56% conversion; entry 3).

As for aniline, the reaction rate is also slowed with the increase of the solvent polarity (compare entries 3 and 4 and entries 5 and 6), though the selectivity is slightly improved (entries 3 and 6).

The steric requisites of 1b and 1b′ (x, y, z) indicate that these compounds should have relatively free access to the catalytic cages: Y faujasites possess, in fact, inner pores (supercages) 11.8 Å in diameter, which are connected through channels 7.4 Å in diameter. If so, the drop of the reaction rate observed for p-toluidine and p-anisidine would be mainly due to electronic effects of aryl substituents. Both amines 1b and 1b′ may diffuse and adsorb into the catalyst following the pattern proposed for aniline, with two sites of adsorption: on the first, the amine is held through H-bonds between amine protons and basic oxygen atoms of the zeolithic framework; on the second, the amine is pinned to the lattice, forming a π complex between the aryl ring and an acid cation (e.g., Na⁺). Since the strength of these interactions increases for electron-rich amines, the desorption of p-toluidine and p-anisidine as well as their mono-N-methyl derivatives is expected to be less favored with respect to aniline. This would account not only for the decrease of the rate, but also for the drop of selectivity described in Table 2.

However, although this electronic effect is relevant, the bulkiness of the aryl substituents plays an important role as well. This clearly emerges from the following experiments.

**p-Alkylanilines.** At 130 °C, solutions of p-alkylanilines 1c–e in xylene (0.3 M, 5 mL) were made to react with the carbonate 2a (2a:1 in a 5:1 molar ratio) in the presence of NaY (NaY:1 in a 0.5:1 weight ratio). n-Dodecane was used as the internal standard. In this case, the reactivity of different amines was compared through the evaluation of reaction conversions rather than kinetic constants.

Moreover, also highly hindered amines such as 3,5-di-tert-butyl- and 2,4,6-tri-tert-butylanilines (compounds 1f, g, respectively) were used as the substrates. At 160 °C, they were made to react with 2a in tryglime as the solvent under the conditions used for p-alkylanilines.

The results are reported in Table 3. As for Table 2, the dimensions x, y, and z of the smallest box able to fit in the amines 1a–g are also reported (columns 3–5).

The data show that the increase of the steric hindrance of the substituents immediately reflects on the reaction rate: in going from the p-methyl to the p-butyl group, the conversion drops from 66% to 9% after reaction times of 7 and 8 h (entries 2–5). Yet, as far as the reactant amines are allowed to migrate into the catalytic cages, the mono-N-methyl selectivity is rather constant (90–94%) at comparable conversions (entries 2–5).

The effect is much more drastic for compounds 1f–g, whose diffusion (if any) into the catalyst is severely hampered, undergoes a sluggish reaction even at 160 °C (entry 6), and despite the very low conversion (9%), the selectivity is only 82%: by-products of N,N-dimethylation (1%) and N-alkylation (ArNHR, R = MeO(CH2)2O(CH2)2; 3%) reactions are observed. This decrease of selectivity can be ascribed to the reaction taking place on the external surface of the zeolite.

Under the same conditions, 2,4,6-tri-n-butylaniline (1g), which cannot access the inner pores of the zeolite, does not react (entry 7). Given the steric crowding around the amine function, it is also in doubt whether compound 1g would be able to react at all with the carbonate.

**p-Alkoxylanilines.** Previous experiments on 1b (Table 2) suggested that selectivity could be improved in the presence of triglyme as the solvent. Moreover, reactions in triglyme could be run at a higher temperature with respect to xylene: this would have helped the investigation of more hindered alkoxyanilines whose reactivities were expected to be lower than that of 1b. Accordingly, solutions of p-alkoxyanilines 1c–e in triglyme (0.3 M, 5 mL).

### Table 3. Methylation of p-Alkylanilines 1c–e and Di- and Tri-tert-butyl-Substituted Anilines 1f,g with the Carbonate 2a

<table>
<thead>
<tr>
<th>entry</th>
<th>amine</th>
<th>x (Å)</th>
<th>y (Å)</th>
<th>z (Å)</th>
<th>zeolite hosting ability</th>
<th>solvent</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>conv (%)</th>
<th>S_{M/D} (%)</th>
<th>product (M + D) yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>aniline, 1a</td>
<td>4.34</td>
<td>1.17</td>
<td>5.59</td>
<td>yes</td>
<td>xylene</td>
<td>130</td>
<td>4</td>
<td>100</td>
<td>99</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>p-toluidine, 1b</td>
<td>4.34</td>
<td>1.81</td>
<td>6.44</td>
<td>yes</td>
<td>xylene</td>
<td>130</td>
<td>7</td>
<td>66</td>
<td>94</td>
<td>41</td>
</tr>
<tr>
<td>3</td>
<td>p-ethylaniline, 1c</td>
<td>4.64</td>
<td>1.91</td>
<td>8.08</td>
<td>yes</td>
<td>xylene</td>
<td>130</td>
<td>8</td>
<td>41</td>
<td>92</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>p-propylaniline, 1d</td>
<td>4.67</td>
<td>1.90</td>
<td>9.20</td>
<td>yes</td>
<td>xylene</td>
<td>130</td>
<td>8</td>
<td>27</td>
<td>89</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>p-butylaniline, 1e</td>
<td>4.81</td>
<td>1.93</td>
<td>10.62</td>
<td>yes</td>
<td>xylene</td>
<td>130</td>
<td>8</td>
<td>9</td>
<td>92</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>3.5-di-tert-butylaniline, 1f</td>
<td>6.56</td>
<td>4.38</td>
<td>8.71</td>
<td>c</td>
<td>triglyme</td>
<td>160</td>
<td>7</td>
<td>9</td>
<td>82</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>2,4,6-tri-tert-butylaniline, 1g</td>
<td>9.20</td>
<td>4.39</td>
<td>8.42</td>
<td>no</td>
<td>triglyme</td>
<td>160</td>
<td>8</td>
<td>9</td>
<td>82</td>
<td>6</td>
</tr>
</tbody>
</table>

a Except for aniline (see entry 1, Table 1), all reactions were run using solutions of the substrates in xylene or triglyme (0.3 M, 5 mL). The molar ratio 2a:1 was 5. The weight ratio NaY:1 was 0.5. All data were averaged over two consecutive runs. b The hosting ability was referred to as the possibility to fit the reagent into the zeolite cage, through the estimate of dimensions x, y, and z. c The size of compound 1f makes uncertain its diffusion through the zeolite channels (d = 7.4 Å). d Percentage of mono-N-methyl and di-N,N-methyl derivatives.

(20) Although aniline was made to react in a more concentrated solution (0.4 M, Table 1) with respect to 1b and 1b′ (0.3 M), this difference could not account for the observed variation of k_{ads} (entries 1–3).


(23) Some of the investigated amines were quite unreactive, and the corresponding k_{ads} values were not determinable.
TABLE 4. Methylation of p-Alkoxyanilines 1b′–1e′ with 2-(2-Methoxyethoxy)ethyl Methyl Carbonate

<table>
<thead>
<tr>
<th>entry</th>
<th>amine</th>
<th>x (Å)</th>
<th>y (Å)</th>
<th>z (Å)</th>
<th>zeolite hosting ability</th>
<th>t (h)</th>
<th>convn (%)</th>
<th>S_{M,O} (%)</th>
<th>product (M + D) yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b′</td>
<td>4.60</td>
<td>1.86</td>
<td>7.89</td>
<td>yes</td>
<td>5</td>
<td>73</td>
<td>86</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>1c′</td>
<td>4.59</td>
<td>1.83</td>
<td>9.03</td>
<td>yes</td>
<td>8</td>
<td>84</td>
<td>78</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>1d′</td>
<td>4.73</td>
<td>1.89</td>
<td>10.44</td>
<td>yes</td>
<td>8</td>
<td>22</td>
<td>93</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>1e′</td>
<td>4.72</td>
<td>1.89</td>
<td>11.63</td>
<td>yes</td>
<td>8</td>
<td>9</td>
<td>85</td>
<td>54</td>
</tr>
</tbody>
</table>

All reactions were run at 150 °C using solutions of the substrates (0.3 g) in tritylme (5 mL). The molar ratio 2a:1 was 5. The weight ratio NaY:1 was 1. All conversion data were averaged over two runs. *Defined as in Table 3. Percentage of mono-N-methlated and di-N,N-methlated products.

5 mL) were made to react at 150 °C with the carbonate 2a (2a:1 in a 5:1 molar ratio) in the presence of NaY (NaY:1 in a 1:1 weight ratio). n-Tetracane was used as the internal standard. The reactivities of different amines were compared through the evaluation of reaction conversions rather than kinetic constants. All products were identified by GC/MS analyses.

The results are reported in Table 4.

Although a direct comparison between Tables 3 and 4 is not possible, p-alkoxyanilines show the same trend as described for p-alkylanilines. The increase of steric hindrance of para-substituents (from p-MeO to p-BuO groups) results in a striking drop of the reaction conversion (from 84% to 9% after 8 h; entries 1–5).

Also the mono-N-methyl selectivity is comparable between the two sets of amines (p-alkyl and p-alkoxy amines) when their bulkiness is considered. For example, p-propyl- and p-ethoxyanilines, for which very similar molecular sizes are estimated (see x, y, and z of entries 4 in Table 3 and 2 in Table 4), show S_{M,O} values of 90% and 92% at conversions of 45% and 43%, respectively. Likewise, p-butyl- and p-propoxylanilines exhibit an analogous behavior (entries 5 of Table 3 and 3 of Table 4).

On the whole, the data of Tables 2–4 are all consistent with the following facts: (i) Steric effects are crucial for the reaction rate. The methylation rate of para-substituted anilines is markedly slower with larger substituents, but as long as the diffusion of amines is allowed into the catalytic supercages of NaY, the reaction may take place with comparable mono-N-methyl selectivities (at similar conversions) for all the tested substrates. Otherwise, if diffusion is inhibited or severely limited, the reaction hardly occurs and selectivity drops as well.

(ii) Within limits, the more nucleophilic the amine is, the slower its reaction is as well. Electronic effects of the substituents alter the rate of adsorption/desorption of both reagents and products into the catalyst. This seems to affect primarily the methylation rate, but also influences selectivity: the geometric features of the zeolite cage can shape the formation of the mono-N-methyl derivative on the condition that the migration of reagent and product through the catalytic pores is not hampered by electronic effects. (iii) Although preliminary, the estimation of the molecular size of the reactants through the simple device of the smallest box seems to offer a good prediction of the reaction outcome as both rate and selectivity are concerned.

Mono-N-methylation of Anilines. Reaction Mechanism. In a preliminary mechanistic investigation, the mono-N-methyl selectivity of the reaction of anilines with DMC has been explained through Scheme 3.2

An amine (1) is initially adsorbed into a zeolite cage, where it reacts with DMC to form a carbamate [ArNHCO2Me (4), eq a]. Due to its polarity, the corresponding anion 4 is held into the zeolite pores where both methylation and demethoxycarbonylation reactions take place (eqs c and d). Two observations strengthen this mechanistic scheme: (i) the occurrence of small amounts (1–5%) of compound 4 and ArN(Me)CO2Me (5) in the reaction of anilines with DMC; (ii) when PhNHCO2Me was made to react with DMC, it was first converted into PhN(Me)CO2Me, which in turn gave PhNHMe.

This mechanism sounded reasonable also for the reactions of anilines with the carbonate 2a. However, all the attempts to confirm the presence of the corresponding carbamates ArNHCOCO2R and/or ArN(Me)CO2R (R = MeO(CH2)2O(CH2)2) failed.

Apparently, the only striking difference between the reactions of DMC and of the carbonate 2a was that the former was reacted in a closed vessel (autoclave), while the latter was reacted at atmospheric pressure. To rule out such a distinction, aniline was also made to react at 130 °C with 2a (1a:2a in a 1:9 molar ratio) in an autoclave in the presence of NaY (weight ratio NaY:1a = 1). Under these conditions, the carbonate 6a [PhN(Me)CO2R, R = MeO(CH2)2O(CH2)2] was finally observed in a 2% yield (Scheme 4).24

SCHEME 4. Reaction of Aniline with the Carboxylate 2a: Composition of the Reaction Mixture after 5 h at 130 °C

<table>
<thead>
<tr>
<th>reaction</th>
<th>product</th>
<th>96%</th>
<th>2%</th>
<th>2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhNH2</td>
<td>RCOOCH2</td>
<td>NaY, 130 °C Autoclave</td>
<td>PhNH2(CH3)</td>
<td>PhNHR + PhN(CH3)CO2R</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6a</td>
</tr>
</tbody>
</table>

This result not only supported the similarity of the reaction mechanism of DMC and of the carbonate 2a, but also suggested that the presence of the intermediate carbamates 4–6 (formed reversibly through reactions a, c, and d of Scheme 3) could be controlled by the CO2 released from the reaction. For this reason, the demethoxycarbonylation reaction of these moieties could perhaps

(24) The product 4a was characterized by GC/MS analysis of the reaction mixture. The structure was then confirmed by its synthesis from the transesterification of PhN(Me)CO2Me with MeO(CH2)2O(CH2)2OH catalyzed by K2CO3 (see the Experimental Section).
be faster at atmospheric pressure. A beneficial effect of the CO$_2$ pressure has been recently reported by us also in the synthesis of methyl carbamates from aliphatic amines and DMC.\textsuperscript{25} However, there are presently no clear reasons why the formation of compound 6a was so chemoselective (not even a trace of PhN(Me)CO$_2$Me was detected).

Finally, it should be noted that if Scheme 3 applies, the relationship among the rate constants for methoxy-carbonylation (a), methylation (c), and demethoxy-carbonylation (d) reactions may also control selectivity, and explain the first-order disappearance observed for aniline (Figure 2), which may appear even too simple given Scheme 3.

**N-Methylation of Benzylamine.** In general, the reactions of primary aliphatic amines with conventional alkylation agents are much less selective than those of anilines.\textsuperscript{26} We experienced this behavior also in the use of dimethyl carbonate as a methylaing agent:\textsuperscript{2} for example, at 130 °C, the reaction of benzylamine with DMC catalyzed by NaY yielded the corresponding mono-N- and di-N-methyl derivatives in equal amounts even at very low conversions (≤10%).

With the aim of improving the mono-N-alkyl selectivity of such processes, two facts could be exploited: (i) the high basicity and nucleophilicity of aliphatic amines could be used to run reactions under milder conditions; (ii) the amphoteric properties of Y faujasites were tunable (by changing their metal cations).\textsuperscript{27} Accordingly, the use of different MY zeolites (M = Li, Na, K, Cs) could have modified the reaction outcome.

Initial experiments were carried out at 90 °C and atmospheric pressure. Benzylamine (7; 0.3 g, 2.8 mmol) was made to react with either dimethyl carbonate (20 mL, as a reagent/solvent) or the carbonate 2a (xylene solutions, 0.4 M, 5 mL; 2a:7 in a 5:1 molar ratio) in the presence of NaY (weight ratio NaY:7 = 1). For comparison, the reaction with 2a was also run at 130 °C.

The results are reported in Table 5.

In the case of DMC, it should be first noted that the mono-N-methyl selectivity—although not as satisfactory as for anilines—is significantly improved with respect to previous results at a higher temperature.\textsuperscript{2,28} On NaY, S$_{MD}$ increases from 38% (at 130 °C, entry 2) to 63% (at 90 °C, entry 1b) at comparable conversions (75% and 67%). To our knowledge, the best procedure for the direct mono-N-alkylation of benzylamine claims selectivities up to 85%, though only with sparingly reactive alkyl bromides RBBr (R = n-C$_4$H$_9$ and n-C$_8$H$_{17}$).\textsuperscript{29}

As for DMC, also in the case of the carbonate 2a, the reaction temperature has a drastic effect on the monoalkyl selectivity: at comparable conversions (46–49%), S$_{MD}$ is 75% and 63% at 90 and 130 °C, respectively (entries 3 and 4).

In view of these data, the N-methylation of benzylamine was investigated in the presence of DMC and a series of MY zeolites (M = Li, Na, K, Cs) under the conditions previously described (7, 0.3 g; DMC, 20 mL; weight ratio MY:7 = 1).\textsuperscript{30} These catalysts were prepared by exchange of NaY with aqueous solutions of alkali-metal salts.

The results are also reported in Table 5.

Both the reaction rate and selectivity appear markedly affected by the nature of the catalyst, and in general, LiY and NaY faujasites allow more rapid and selective reactions with respect to KY and CsY. After 7 h, reactions with LiY/NaY show benzylamine conversions up to 44% with an S$_{MD}$ of 84% (entries 1a and 5a), while with KY/CSY conversions are lower (33–36%) even after 22 h. Despite that, S$_{MD}$ ratios are lower as well (77–79%), entries 6b and 7b).

Figure 4 describes this situation in more detail for the LiY and CsY catalysts: when selectivity is reported vs conversion, the formation of mono-N-methylbenzylamine on LiY is better than on CsY. The effect of the Cs ion is even more surprising if one considers that CsY is actually a "mixed zeolite" which contains almost equal amounts of Cs$^+$ and Na$^+$ (Table 5, entry 7, ionic exchange of 56%).

The acid/base features of MY and the size of the metal cations seem to be the rationale for the results of Table 5 and Figure 4.

The basicity of these catalysts (due to the oxygen atoms of the zeolitic framework) can be increased by exchange with soft metal cations, and it follows the order Cs$^+$ > K$^+$ > Na$^+$ > Li$^+$.\textsuperscript{27} The Lewis acidity instead (due to metal cations) goes through the reverse sequence, and is higher for Li.$^+$\textsuperscript{27,31} In our case, the more acidic the zeolite, the better the reaction selectivity as well: the increased acidity may lower the nucleophilic character of the

### Table 5. N-Methylation of 7 with DMC and 2a in the Presence of MY Catalysts

<table>
<thead>
<tr>
<th>entry</th>
<th>MY exchange$^b$ (% carbonate$^c$)</th>
<th>carbonate$^c$ (°C)</th>
<th>t (h)</th>
<th>convn M/D</th>
<th>S$_{MD}$ ($^d$) (M/D)</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>NaY</td>
<td>DMC</td>
<td>90</td>
<td>7</td>
<td>44</td>
<td>84</td>
</tr>
<tr>
<td>1b</td>
<td>NaY</td>
<td>DMC</td>
<td>90</td>
<td>22</td>
<td>67</td>
<td>63</td>
</tr>
<tr>
<td>2a</td>
<td>NaY</td>
<td>DMC</td>
<td>130</td>
<td>3.5</td>
<td>75</td>
<td>38</td>
</tr>
<tr>
<td>3a</td>
<td>NaY</td>
<td>2a</td>
<td>90</td>
<td>7</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td>3b</td>
<td>NaY</td>
<td>2a</td>
<td>90</td>
<td>94</td>
<td>46</td>
<td>35</td>
</tr>
<tr>
<td>4a</td>
<td>NaY</td>
<td>2a</td>
<td>130</td>
<td>22</td>
<td>49</td>
<td>63</td>
</tr>
<tr>
<td>5a</td>
<td>LiY</td>
<td>DMC</td>
<td>90</td>
<td>7</td>
<td>77</td>
<td>38</td>
</tr>
<tr>
<td>5b</td>
<td>LiY</td>
<td>DMC</td>
<td>90</td>
<td>22</td>
<td>70</td>
<td>61</td>
</tr>
<tr>
<td>6a</td>
<td>KY</td>
<td>DMC</td>
<td>90</td>
<td>7</td>
<td>18</td>
<td>91</td>
</tr>
<tr>
<td>6b</td>
<td>KY</td>
<td>DMC</td>
<td>90</td>
<td>22</td>
<td>33</td>
<td>79</td>
</tr>
<tr>
<td>7a</td>
<td>CsY</td>
<td>DMC</td>
<td>90</td>
<td>7</td>
<td>19</td>
<td>92</td>
</tr>
<tr>
<td>7b</td>
<td>CsY</td>
<td>DMC</td>
<td>90</td>
<td>22</td>
<td>36</td>
<td>77</td>
</tr>
</tbody>
</table>

$^a$ Percentage of ionic exchange from NaY: the metal contents were evaluated through atomic adsorption (Na, K) and emission (Li, Cs).$^b$ For entries 1–4, DMC was used as a reagent/solvent (20 mL); for entry 5, a solution of benzylamine (0.4 M, 5 mL) in xylene was made to react with 2a (2a:7 = 5 molar ratio).$^c$ n-Tetradecane was the internal standard.$^d$ S$_{MD}$ = mono-N-methyl selectivity defined as in Tables 2–4. M = mono-N-methylbenzylamine and D = di-N,N-methylbenzylamine.

---

(30) The carbonate 2a was advantageous for high-temperature methylation reactions (T > 120 °C). However, since benzylamine was rapidly methylated also at a lower temperature (90 °C), DMC (a commercially available compound) could be used more conveniently at its reflux temperature (90 °C) and at atmospheric pressure.
Mono-N-methylation of Primary Amines

![Graph](image)

**FIGURE 4.** Reaction of benzylamine with DMC in the presence of LiY and CsY faujasites: mono-N-methyl selectivity vs conversion.

reactant amine so that N,N-dimethylation is disfavored. Also in the methylation of aniline with MeOH, it has been reported that LiY/NaY faujasites can catalyze both ring alkylation and N-alkylation reactions, while KY/CsY exclusively directs the reaction toward N-methylation.32

Steric hindrance of the metal cations may account for effects on the reaction rate. The drop of conversions observed with KY and CsY is reasonably due to the larger size of K+/Cs+ (with respect to Li+/Na+).32 These moieties may partially obstruct the zeolite channels in a way that the diffusion of reactants is hindered.

From a mechanistic viewpoint, the occurrence of methylv carbamates [both PhCH2,NHCO2Me and PhCH2N-(Me)CO2Me were observed in a 1−5% total yield] indicates that the pattern sketched out in Scheme 3 is perhaps active for benzylamine too. Though, the lower selectivity with respect to anilines cannot rule out a B3a2-type reaction where the amine directly attacks the methyl group of DMC.

**Conclusions**

In the presence of Y faujasites, the investigation of the mono-N-methyl selectivity in the reactions of primary amines with methyl alkyl carbonates allows the following considerations.

(i) Aniline. At 130 °C and atmospheric pressure, the liquid-phase methylation of aniline—the model compound for aromatic amines—with the carbonate 2a can be run with NaY under conditions free from diffusion limitations. Accordingly, the kinetic investigation of this reaction shows a clear effect of the solvent polarity: the rate constant decreases by a factor of 5 when the dielectric constant of the solvent increases from 2.40 (xylene) to 7.62 (triglyme). More polar solvents (DMF) inhibit the reaction. Competitive adsorption phenomena between the amines and the solvent for the active sites of the catalyst offer a good rationale for this behavior. Notwithstanding, much remains to be understood of the adsorption and activation of the organic carbonates.

A mechanistic similarity is plausible for the reactions of 2a and DMC. Although preliminary, this is based upon the intermediacy of carbamate species whose formation is probably dependent on the CO2 pressure generated throughout the reaction.

(ii) p-Alkyl- and p-Alkoxyanilines. With respect to scanty nucleophilic aromatic amines, the reaction of p-alkyl- and p-alkoxyanilines with 2a presents some synthetic limitations: the mono-N-methyl selectivity does not exceed 80% at conversions up to 85%. However, this investigation sheds light on the relationship between the steric demand of the zeolite cages and the steric/electronic effects of para-substituents. In particular, the shape of the zeolite pores may affect the mono-N-methyl selectivity, provided that the diffusion of reagents into the catalyst is fast enough. Accordingly, as long as the diffusion of these substrates is inhibited, both the selectivity and rate drop markedly.

(iii) Benzylamine. The reaction of benzylamine—a model for aliphatic amines—with both DMC and the carbonate 2a provides further insight for the improvement of the mono-N-methyl selectivity. By varying the amphoteric properties of the catalysts—in particular, by increasing their acid strength with the use of hard cations (Li+ and Na+)—better selectivity (due perhaps to the modification of the nucleophilicity of the amine) and reaction rate (due to the lesser hindrance of small ions) are achieved.

In view of this outcome, a further step in this area will be the preparation and use of faujasites in the protonic form (HY and HX).

Overall, this work has shown some of the main features of the methylation of primary amines with methyl alkyl carbonates and DMC, catalyzed with alkali-metal exchanged Y faujasites. The scenario is rather complex: the size of the amines feels the geometry of the catalyst, but the final mono-N-methyl selectivity arises from a synergetic effect between the double reactivity of organic carbonates (as methoxy/alkoxy carbonylating and methylylating agents) and the steric−amphoteric requisites of the zeolite cages.

**Experimental Section**

All compounds used were ACS grade and were employed without further purification. The zeolite NaY was available commercially. 2-(2-Methoxyethoxymethyl) methyl carbonate [MeO(CH2)2OCH2OCH2OOCO2Me, 2a] was prepared according to a procedure already reported and compared to an authentic sample.41 1H NMR spectra were recorded on a 300 MHz spectrometer, using CDCl3 as the internal standard. GLC and GC/MS (70 eV) analyses were run using 30 m capillary columns.

![Propoxyaniline](image)

**4-Propoxyaniline (1d)** was synthesized from p-nitrophenol according to known procedures.34 1H NMR (CDCl3): δ 6.76 (2H, d, J = 8.7 Hz, Ar), 6.65 (2H, d, J = 8.7 Hz, Ar), 3.86 (2H, t, J = 6.7 Hz, −OCH2−), 3.33 (2H, br s, NH2), 1.78 (2H, t, J = 6.7 Hz, −OCH2−), 1.03 (3H, t, J = 7.6 Hz, CH3). GC/MS (70 eV): m/z 151 (M+, 24), 109 ([M − CH3=]

---

CH₃CH₃, 100). 108 (33), 81 (11), 29 (11), 19 (42). IR (neat), cm⁻¹: 3354 (NH₂), 1236 (C–O–C).

Reaction of Aniline with 2a. Figure 2 and Table 1. A three-necked, jacketed, 25 mL round-bottomed flask fitted with a stopcock, an adapter for the withdrawal of samples, a reflux condenser capped with a N₂-containing rubber reservoir, and a magnetic bar was loaded with a solution of aniline (1a) (0.4 M, 5 mL) in a given solvent; in particular, xylene, tritylamine, and N,N-dimethylformamide were used. n-Tetradecane (0.6 mmol) or ethylene glycol di-n-hexyl ether (n-C₆H₁₃OCH₂CH₂O-n-C₆H₁₃, 0.45 mmol) was used as the internal standard for reactions with xylene, tritylamine or DME, respectively.

The organic carbonate 2a [MeOOC₂H₅]₂CH₂OCH₂OMe] and the faujasite NaY were added to the mixture (2a:1a = 5 molar ratio, 1a:NaY = 0.5 weight ratio), which was then degassed under vacuum and put under a N₂ atmosphere. The flask was heated at the desired temperature (130 °C) while the mixture was vigorously stirred. At intervals, samples (0.1 mL) were withdrawn and were analyzed by both GC and GC/MS.

Under these conditions, a reaction was also performed without any solvent and in the presence of ethylene glycol di-n-hexyl ether as the internal standard.

Figure 1, Tables 2–5. The above-described procedure was followed also for the experiments of Figure 1 and Tables 2–5 according to the molar and weight ratios reported there.

All reactions except those of amines 1f–g in Table 3 were carried out in the presence of an internal standard, which was (a) n-dodecane for reactions of p-alkylanilines or (b) n-tetradecane for reactions of p-alkylanilines and benzylamine. The molar ratio aminestandard was 2.5. Accordingly, calibration curves were built for each substrate, and used to follow the reaction by GC. In the case of aniline, a calibration curve was also made for the product N-methylaniline.

Table 5. Reactions with DMC. Under the conditions described above, benzylamine (0.3 g) was also made to react at 90 °C with DMC (20 mL) in the presence of different MY catalysts (M = Li, Na, K, Cs; 7aMY = 1 weight ratio). n-Tetradecane was the internal standard. The molar ratio aminestandard: standard was 2.5.

If not otherwise indicated, all reactions were repeated at least twice, and the data of the kinetic constants or conversions were averaged over two runs not differing more than 10% from each other.

N-Monomethyl and N,N-dimethyl derivatives of the investigated amines were identified by GC/MS. The methylated products of aniline, p-toluidine, p-ethylaniline, p-anisidine, and benzylamine (RNHMe, 3a–c, 3b, and 8; RNMe₂, 9a–c, 9b, and 10) were confirmed by comparison with authentic commercial samples. GC/MS spectra of all the other compounds are available in the Supporting Information.

Ethylene Glycol Di-n-hexyl Ether. This compound was prepared according to known procedures. The use of this standard was convenient for both its high boiling point and solubility in polar solvents.

Reaction of Aniline in an Autoclave. A stainless steel autoclave (150 mL of internal volume) was charged with aniline, the carbonate 2a (1a:2a = 9 molar ratio), and NaY (1a:NaY = 1 weight ratio). At rt and before the reaction, air was removed by a purging valve with a N₂ stream. The autoclave was then heated by an oil-circulating jacket while the mixture was kept under magnetic stirring. A thermocouple fixed onto the autoclave head checked the temperature throughout the reaction. After 5 h, the autoclave was cooled to rt, purged from CO₂, and finally opened. The reaction mixture was analyzed by GC and GC/MS.

Estimation of the Molecular Size of Amines 1a, 1b–g, and 1b′–e. The dimensions (x, y, z) of the smallest boxes able to fit compounds 1a, 1b–g, and 1b′–e were estimated with the use of Hyperchem Pro ver. 5.11. The calculation method was molecular mechanics using the MM+ force field (options electrostatic potential – bond dipoles, and cutoff – none), and the type of calculation was geometry optimization performed through the conjugate gradient method (Polak–Ribière algorithm with an RMS (root-mean-square) gradient of 0.1 kcal/(A mol)).

Carbamates. N-Benzyl methyl carbamate (PhCH₂NHCO₂Me, 7a) and N-methyl-N-benzyl methyl carbamate (PhCH₂NMeCO₂Me, 7b) were prepared according to known procedures. The synthesis of 6a [(PhNMe)₂CO₂R, Re = MeO(CH₂)₂O(CH₂)₆] was performed by adjusting a known transesterification reaction of N-phenyl methyl carbamate with alcohols. a jacketed, 25 mL round-bottomed flask was charged with N-methyl-N-phenyl methyl carbamate [PhNMe(CO₂Me), 0.2 g, 1.2 mmol], diethylene glycol monomethyl ether [MeO-(CH₂)₂O(CH₂)₆OH; 10 mL], and K₂CO₃ (0.83 g, 6 mmol). The mixture was magnetically stirred and heated at 130 °C. After 25 h, the carbamate 6a was observed in a very low yield (2%). No other products were obtained. Compound 6a was characterized by GC/MS analysis (70 eV): m/z 253 (M⁺, 20), 195 ([M – CH₂–CO₂Me]⁺), 137, 179 ([M – CH₂–CO₂Me]⁺ – O)⁻, 131, 151 ([M – CH₂–CO₂Me]⁺ – O)⁻, 100, 135 ([M – CH₂–CO₂Me]⁺ – O)⁻, 65, 107 (29), 106 ([M – CO₂- (CH₂)₆O(CH₂)₆OH]⁻), 49, 77 (44).

MY Catalysts. (a) Preparation and Characterization. Faujasites MY (M = Li, K, Cs) were prepared by an ionic exchange reaction of the commercially available NaY with aqueous solutions of MCl. The metal content of the catalysts was determined as follows: A Teflon-lined autoclave (200 mL) was charged with MY (0.1 g), milli-Q water (5 mL), aq H₂F (40%, 1.5 mL), and a mixture of aq HCl/HNO₃ (3:1 v/v; 3 mL). The autoclave was then dosed with a Teflon-lined cap, and heated in a microwave digestion rotor for 20 min (power ranging from 250 to 650 W). After being cooled to rt, the clear solution was transferred into a volumetric flask and diluted with milli-Q water to 50 mL. Then, analyses by atomic adsorption (kw(Na) = 589.0 nm; kW(K) = 766.5 nm) and emission (Li, Cs) were performed according to known procedures.

(b) Treatment. If not otherwise specified, before each reaction, all the catalysts MY were dehydrated by being heated at 65 °C under vacuum (10 mmHg) overnight.

Dielectric Constant of 2a. The dielectric constant of 2a was measured by a capacitor with circular plates (C₁meas) inserted into the circuit shown in Scheme 5.

\[ C_{\text{meas}} = C_0 \left( V_0 / V_{\text{meas}} - 1 \right) \]

\( V_0 = 200 \text{ mV}; C_0 = 255 \text{ pF}. \)

By applying a potential V₀ of 200 mV, and with a capacitor C₀ of 255 pF, the capacity of Cmeas was alternatively measured in air and after dipping the capacitor into the carbonate 2a (eq 3). Finally, the wanted dielectric constant was calculated from \( \epsilon_r = C_{2a/C_{\text{air}}} = 352/57 = 6.2 \).


Acknowledgment. Murst (Italian Ministry of University and Scientific and Technological Research) and INCA (Interuniversity Consortium Chemistry for the Environment) are gratefully acknowledged for financial support. Prof. G. Mistura (Department of Physics, University of Padova) and Prof. G. Rampazzo (Department of Scienze Ambientali, University of Ca’ Foscari, Venezia) are kindly acknowledged for their help in the measurement of dielectric constants and in the characterization of MY catalysts.

Supporting Information Available: GC/MS spectra for compounds 3d,e,f,c,d,e and 9d,e,f,c,d,e. This material is available free of charge via the Internet at http://pubs.acs.org.

J O026057G