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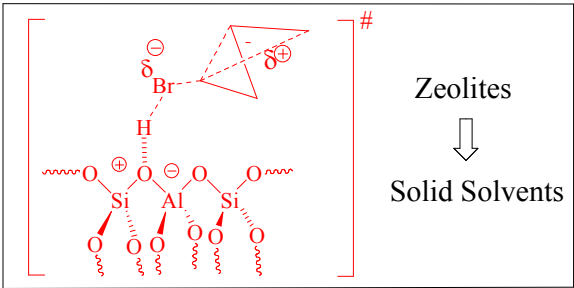
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COMMUNICATION

Solid Solvents: Activation Parameters for the Rearrangement of Cyclopropylcarbinyl Bromide on Mordenite Zeolite

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Rearrangement of cyclopropylcarbinyl bromide over proton and ammonium-exchanged Mordenite (H-MOR and NH₄-MOR) was studied at different temperatures. The product distribution analysis revealed a similar profile to what is found in solution, with prevalence of cyclobutyl over allylcarbinyl bromide. The activation parameters showed that compared with 80% aqueous ethanol solution, the zeolites present lower enthalpy of activation and higher entropy of activation, but yielding a significantly lower $\Delta G^\ddagger_{298}$. The results may be explained in terms of the ability of zeolites to serve as solid solvents, providing a polar nanoenvironment for ionic reactions to occur.

The interconversion of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl substrates can be explained in terms of the formation of bicyclobutonium cation.^{1,2} Deamination of cyclopropylcarbinylamine with nitrous acid give mixtures of cyclobutanol, cyclopropylcarbinol and allylcarbinol (figure 1), consistent with the formation of the bicyclobutonium cation, which has three possible positions for nucleophilic attack.³ The cyclobutyl and cyclopropylcarbinyl compounds are found in major proportions, being products of kinetic control, whereas the allylcarbinyl structure is found in minor proportion and is ascribed as product of thermodynamic control. Several works have established the role of the bicyclobutonium cation as intermediate in solutions.³

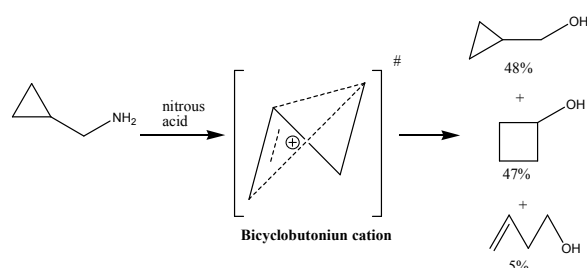


Figure 1. Deamination of cyclopropylcarbinylamines in nitrous acid solutions. Formation of the bicyclobutonium cation.

We have studied the rearrangement of cyclopropylcarbinyl halides to prove the formation of carbocations as discrete intermediates within the zeolite cavity.^{4,5} There is still some discussion⁶ whether ionic carbocations or covalent oxonium or alkoxy species (figure 2) are the real intermediates in zeolite-catalyzed reactions. Zeolites are crystalline aluminosilicates with pores of molecular dimensions.⁷ Their structures are constructed by the interconnection of tetrahedral SiO₄ and AlO₄⁻ units, forming pores and cages of different geometries. The presence of aluminum atom creates a negative charge that should be compensated. Thus, zeolites are cation-exchanged material and can be produced in the protonic form, acting as strong acids.⁸ These properties make zeolites important catalysts in oil refining and petrochemical.⁹

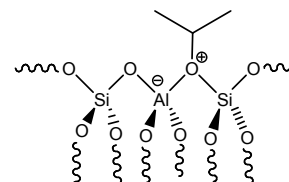


Figure 2. Structure of the alkoxy on zeolites.

Although equilibrium between the alkoxides and the respective carbocations has never been experimentally proven, some theoretical results indicate that the tert-butyl carbenium ion might be more stable than the respective alkoxy, depending on the temperature employed.⁹

In this work, we report an experimental study of the activation parameters for the rearrangement of cyclopropylcarbinyl bromide (CPC) on Mordenite (MOR) zeolite, with two different compensation cations (H⁺ e NH₄⁺). These experiments provide additional evidences for the role of zeolites as solid solvents, providing a local nanoenvironment for ionic reactions to occur.

The chemical analysis by X ray fluorescence (FRX) showed that no sodium was presented in the ammonium-exchanged zeolite. The Mordenite has a Si/Al ratio of 7.9 and 425 m²/g of specific surface area. Mordenite is a large-pore zeolite with about 6.5 to 7.0 Å of pore aperture. The kinetics coefficients were determined at four different temperatures assuming pseudo first-order kinetics (formation of the carbocation). The results are presented in table 1. The activation parameters were calculated from the kinetic constants and are shown in table 2, together with the parameters reported in the literature for the solvolysis in 80% aqueous ethanol.

Table 1. First-order kinetics coefficients for the rearrangement of CPC on Mordenite.

Temperature (°C)	k (10 ⁻² min ⁻¹)	
	NH ₄ -Mor	H-Mor
28	0,56 ± 0,05	0,63 ± 0,04
37	0,92 ± 0,04	0,82 ± 0,02
41	1,06 ± 0,05	1,09 ± 0,06
56	1,86 ± 0,06	1,33 ± 0,07

Table 2. Activation parameters of the rearrangement of CPC on Mordenite zeolite and EtOH/H₂O.

System	E _a (kcal/mol)	ΔH [‡] (kcal/mol)	ΔS [‡] (cal/mol.K)	ΔG [‡] ₂₉₈ (kcal/mol)
NH ₄ -Mor	8,3 ± 0,9	7,7 ± 0,3	-21,7 ± 1,0	14,2 ± 0,5
H-Mor	5,25 ± 0,1	4,6 ± 0,1	-26,0 ± 1,0	12,3 ± 0,5
EtOH/H ₂ O*	--	21,0 ± 0,3	-12,5 ± 1,0	24,7 ± 0,6

*Solvolysis in 80 % (v/v) EtOH/H₂O.¹⁰

At 28 °C, the rearrangement of CPC occurs faster over H-MOR than over NH₄-MOR, whereas at 56 °C there is an inversion in this order. This is due to the higher entropy of activation observed for the H-MOR zeolite. In contrast, the enthalpy of activation is higher on NH₄-MOR than in H-MOR. The correct interpretation of these parameters is not simple, as there is no similar study in the literature. We may suggest that the enthalpy of activation reflects the strength of the hydrogen bonding between the zeolite and the alkylhalide in the transition state. Therefore, the protonic zeolite interacts stronger with the substrate by hydrogen bonds, assisting the ionization of the bromide leaving group. In the ammonium-exchanged zeolite, the hydrogen atoms can make hydrogen bonds with the oxygen atoms of the framework, whereas this situation is not possible in the protonic zeolite. Thus, the intensity of the hydrogen bonds in the TS should be higher in the case of H-MOR than in NH₄-MOR (figure 3), explaining the enthalpy results.

The difference in the activation entropy is more intriguing. We may suggest that assistance by the ammonium cation may involve less distortion of the zeolite structure compared with the protonic zeolite. Partially because of the multiple hydrogen bonds between the NH₄⁺ cation, and the zeolite structure and partially because of the smaller loss in degree of freedom of the organic moiety, which could be closer to the framework oxygen atoms (figure 3).

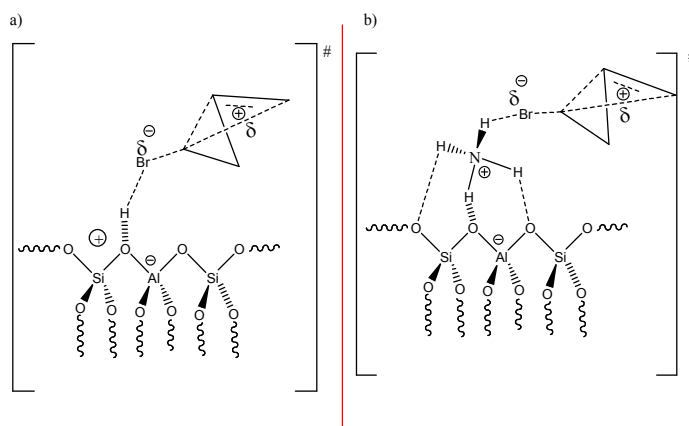


Figure 3. Proposed structure of the transition state for the ionization of cyclopropylcarbinyl bromide over the protonic zeolite (a), and ammonium-exchanged zeolite (b).

It is important to note that the calculated enthalpy of activation does not include the adsorption process, which is a step that precedes the ionization of the substrate (apparent enthalpy of activation). Therefore, the true enthalpy of activation must include this part and should be slightly higher than the values reported in table 2. The calculated enthalpy of adsorption of butyl bromides over sodium-exchanged zeolites was around - 5.5 kcal/mol.¹¹

There is no reported value for adsorption of alkyl bromides over ammonium or proton-exchanged zeolites. Nevertheless, the calculated enthalpy of adsorption of tert-butylchloride over sodium-exchanged zeolite is -10.4 kcal/mol,¹² whereas for adsorption of dichloromethane over proton-exchanged zeolite is -12.1 kcal/mol.¹³ Therefore, we may assume that the enthalpy of adsorption may not strongly depend on the counter cation of the zeolite, assuming a range between 5 to 8 kcal/mol for the alkyl bromides. Hence, the true enthalpy of activation may vary from 12.7 to 15.7 kcal/mol for NH₄-MOR and 9.6 to 12.6 kcal/mol for the H-MOR.

Compared with the data in 80% aqueous ethanol, the zeolites presented lower enthalpy of activation, but higher entropy of activation. This latter may be interpreted in terms of the distortion of the zeolite structure to interact with the transition state. Therefore, due to the rigid crystalline structure, higher degrees of freedom are lost relative to solution. For the difference in enthalpy of activation, again, it could be partially explained in terms of the intensity of hydrogen bonding in the transition state, which may be stronger on the zeolites rather than in the protic solvent medium. However, the local polarity may also influence this result. Although the polarity of the zeolites has been considered similar to the polarity of methanol-water solutions,¹⁴ there is no general discussion concerning the local polarity, near the active sites. We suggest that zeolites act as solid solvents, providing a high polar nanoenvironment for ionization of organic substrates, which is associated with their zwitterionic nature. The concept of zeolites as solid solvents has already been introduced by Derouane, to discuss partition coefficients of reactants inside and outside the zeolite porous system.^{15,16} Nevertheless, he did not use this term to account for the ionizing power of the zeolites.

The isomer distribution favors the formation of cyclobutyl bromide over the allylcarbinyl bromide, consistent with the kinetic

distribution. However, as the reaction goes through, the allylcarbinyll isomer becomes predominant, indicating that cyclobutyl bromide is reactive under the reaction condition.

Conclusions

The activation parameters for the rearrangement of cyclopropylcarbinyll bromide over H-MOR and NH₄-MOR were measured. It was shown that the zeolites presented significantly lower enthalpy of activation, associated with hydrogen bond assistance of the leaving group in the transition state, than 80% aqueous ethanol solution. On the other hand, the zeolites presented higher entropy of activation compared with solution, probably due to the distortion of the framework structure to accommodate the transition state. These results reinforces the concept of zeolites as solid solvents, providing a nanoenvironment for ionic reactions to occur.

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Notes and references

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† The zeolite NH₄-Mor was obtained by ion exchange of the Na-MOR (Zeolyst, CBV10A) with NH₄Cl solution (70 °C with agitation for 2 hours). The resulting solid (NH₄-MOR) was washed with distilled water until chloride free test with AgNO₃. The H-MOR zeolite was obtained from NH₄-MOR by calcination at 550 °C (5 °C.min⁻¹) for 60 min. About 308 mg of the zeolite was initially pretreated at 200 °C (5 °C.min⁻¹) for 60 minutes under N₂ atmosphere (40 mL.min⁻¹). Then, it was carefully transferred to the reaction medium, which already contained 6 mL of n-hexane at the desired temperature. A solution containing 100 µL of n-heptane (internal standard) and 100 µL (1mmol) of cyclopropylcarbinyll bromide (Sigma-Aldrich) was added to the system. To obtain the kinetics parameters, samples of 50 µL were collected from the reaction medium and diluted in 200 µL of n-pentane for further analysis by gas chromatography. Blank experiments with the cyclopropylcarbinyll bromide in n-hexane showed that no reaction occurs at the conditions used in this study, indicating that the rearrangement does not occur in the absence of the zeolite.

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