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Regioselectivity in Hydrocarbon Activation on Zeolite Y: Stereochemistry of H−D Exchange

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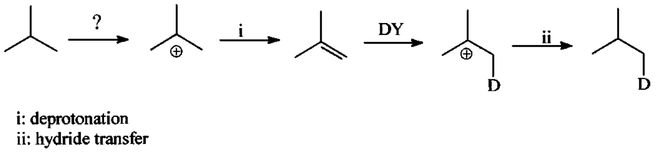
The H−D exchange between alkanes and zeolites normally proceeds with the formation of adsorbed carbenium ions and olefins as intermediates. Cycloalkanes were used to study the regioselectivity and stereochemistry of the elimination/protonation reactions on zeolites to establish the role of the framework in proton transfer reactions. A preferential exchange in the secondary equatorial position adjacent to the tertiary center, relative to the axial one was observed. This result is in agreement with recent theoretical calculations of elimination/protonation reactions occurring on the zeolite surface, which point out that an eclipsed conformation between the eliminating proton and the cationic center is necessary for the reaction to take place. Therefore, in cycloalkanes, the equatorial hydrogens can be better accommodated in the eclipsed orientation. This result is in opposition to what is observed for elimination/protonation reactions of cycloalkanes in solution, where the axial protons are easier eliminated. With *t*-butyl-cyclohexane an almost exclusive exchange at the methyl position was observed. This result cannot be explained by the present accepted mechanism involving olefins and carbenium ions. © 1997 Academic Press

INTRODUCTION

The mechanism of electrophilic alkane activation over zeolites and other solid acids is still open for debate. Although carbocations are believed to be intermediates in cracking, isomerization, and alkylation reactions over zeolites (1), their initial formation from alkane molecules is unclear. On the other hand, the mechanism of electrophilic alkane activation in liquid superacids involves the protonation of the C−C and C−H σ bonds to form pentacoordinated carbonium ions (2), characterizing alkanes as σ-donor bases. Mota and collaborators have shown (3, 4) that the H−D exchange between zeolite Y and 3-methylpentane occurs at 100°C, a temperature well below the cracking threshold. This reaction was previously used in the study of alkane activation in liquid superacid systems (5–7) to characterize the involvement of pentacoordinated carbonium ions. In DSO_3F/SbF_5 at −78°C, isobutane gives a regioselective exchange at the tertiary position (7), consistent with the formation of a tertiary pentacoordinated carbonium ion. At 0°C however, in $DF{-}SbF_5$, isobutane (8) and *n*-butane (9) exchange all protiums for deuterons at a very fast rate, in comparison with protolytic cleavage of σ C−H and C−C bonds.

The fact that *n*-hexane does not exchange with zeolite Y at the same conditions as the 3-methylpentane does, together with the apparent exchange in all the positions of 3-methylpentane, led Mota to propose a rearrangement of pentacoordinated carbonium ions over the zeolite surface (10, 11). However, Sommer and collaborators reinvestigated (12, 13) the H−D exchange between zeolites and alkanes and proposed a different chemistry. They found that, with tertiary alkanes, exchange does occur only in the primary and secondary positions adjacent to the tertiary carbon, which is never exchanged. Therefore, they proposed a mechanism of H−D exchange on zeolites similar to the mechanism of H−D exchange in sulfuric acid (14, 15), involving carbenium ions and olefins (Scheme 1). Later, Engelhardt and Hall (16) also reached the same conclusion, studying the exchange between perdeuterated isobutane and zeolite Y. Nevertheless, the initial formation of the tertiary carbenium ion could not be completely characterized in these studies.

It is interesting to point out that, although olefins are believed to be formed during the H−D exchange on zeolites, they are not normally observed in the recovered hydrocarbon, after the H−D exchange. Nevertheless, recent studies have indicated that the exchange rate is substantially increased when alkenes are added to the alkane feed



SCHEME 1. Mechanistic scheme for the H−D exchange on zeolites.

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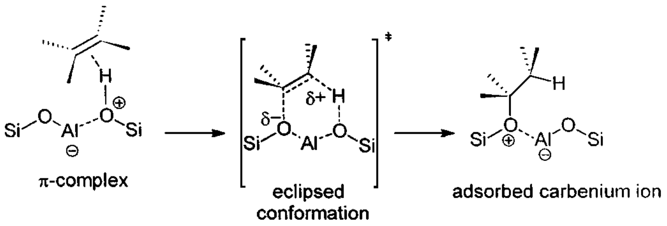


SCHEME 2. Schematic view of the protonation of alkenes on zeolites.

(17, 18) and that significant amounts of olefinic material remains adsorbed on the zeolite surface after the H–D exchange, as observed by solid state ^{13}C NMR analysis (17). These findings support the mechanistic pathway shown in Scheme 1. On the other hand, theoretical calculations (17–21) on the protonation of alkenes over zeolite catalysts, indicate that a π-complex between the double bond and the acidic hydrogen is initially formed and is followed by proton transfer, together with nucleophilic assistance from the framework oxygen to the electron-deficient carbon, to form an adsorbed carbenium ion (Scheme 2). One can observe that in the transition state, the adding proton and the assisting oxygen atom are on the same plane, making an eclipsed conformation. The microscopic reversibility principle (24) states that the transition state for the forward and reverse reaction must be the same. Hence, for proton elimination from an adsorbed carbenium ion, an eclipsed conformation should also be applied. For cycloalkanes this step may be greatly influenced by the hydrocarbon structure and the steric environment inside the zeolite pore. Therefore, a study of the stereochemistry of H–D exchange of cycloalkanes on zeolites can provide insights into this problem. In this work we wish to report some preliminary studies in this field.

EXPERIMENTAL PART

Materials

An ultrastable HUSY prepared at CENPES was used in this study. Some physical and chemical properties of the zeolite are shown in Table 1. The hydrocarbons were purchased from Aldrich Chemicals and Schuchardt Munchen. All the hydrocarbons showed purity greater than 99%.

TABLE 1

Chemical and Physical Characterization of the Zeolite HUSY

	HUSY
Global SAR[a]	5.3
Framework SAR[b]	9
Na_2O (wt%)	0.29
Area (m^2/g)	661
Micropore Volume (ml/g)	0.281

[a] SAR stands for the molar silica to alumina ratio.
[b] Measured by infrared according to Ref. (25).

Procedures

For the H–D exchange studies, two procedures were employed:

Procedure A. The exchange was carried out in an all-glass grease-free flow system. About 550 mg of the zeolite, in an U-type glass reactor, was pretreated in a flow of 38 ml/min of dry N_2 at 500°C for 30 min. Deuteration was then carried out with 3 mol% of D_2O in N_2 at 200°C for 60 min, followed by an additional N_2 purge of 15 min. The temperature was reduced to 100°C and the alkane (ca 2.5 mol% in N_2) was passed at a rate of 20 ml/min. The reacted hydrocarbon was collected in a precooled (−78°C) U-tube for 90 min and then transferred to NMR tubes for analysis.

Procedure B. A modified technique, employing a straight reactor, was also used for the less volatile hydrocarbons. Pretreatment and deuteration procedures were the same as in Procedure A. Nevertheless, the hydrocarbons (4 mmol) were added by means of a microsyringe, through a lateral inlet in the reactor, and collected downwards, by immersing a collector in an ice bath. The flow of N_2 in this case was 60 ml/min. The collected hydrocarbons were analyzed by NMR and GC/MS. This procedure also allowed the measurement of relative rates, by injecting an equimolar mixture of isomers.

Analysis

NMR analysis of the hydrocarbons were carried out on a Bruker 400 MHz and 500 MHz at Strasbourg and on a Varian VXR-300 at Cenpes. A detailed ^1H NMR analysis, in some cases including ^1H–^{13}C correlation and ^1H–^1H COSY experiments, of the hydrocarbons was carried out for the assignment of the chemical shifts. Quantitative and qualitative deuterium content was obtained by comparison of the 400 MHz ^1H and ^2H NMR spectra obtained after addition of an adequate amount of a $CF_2ClCFCl_2$ solution of a $CDCl_3/CHCl_3$ mixture used as internal standard.

GC/MS analysis were carried out in an HP 5988 A quadrupole equipment, with electron impact ionization (70 eV). Estimation of the degree of deuteration was done after correction for the natural abundance ^{13}C.

RESULTS

Six cycloalkanes were chosen to study the stereochemistry of H–D exchange on zeolites: methyl-cyclohexane, *t*-butyl-cyclohexane, *cis*-1,2-dimethyl-cyclohexane, *trans*-1,2-dimethyl-cyclohexane, *cis*-decalin, and *trans*-decalin.

Figure 1 shows the results of ^2H and ^1H NMR of methylcyclohexane after H–D exchange. Deuterium was mainly

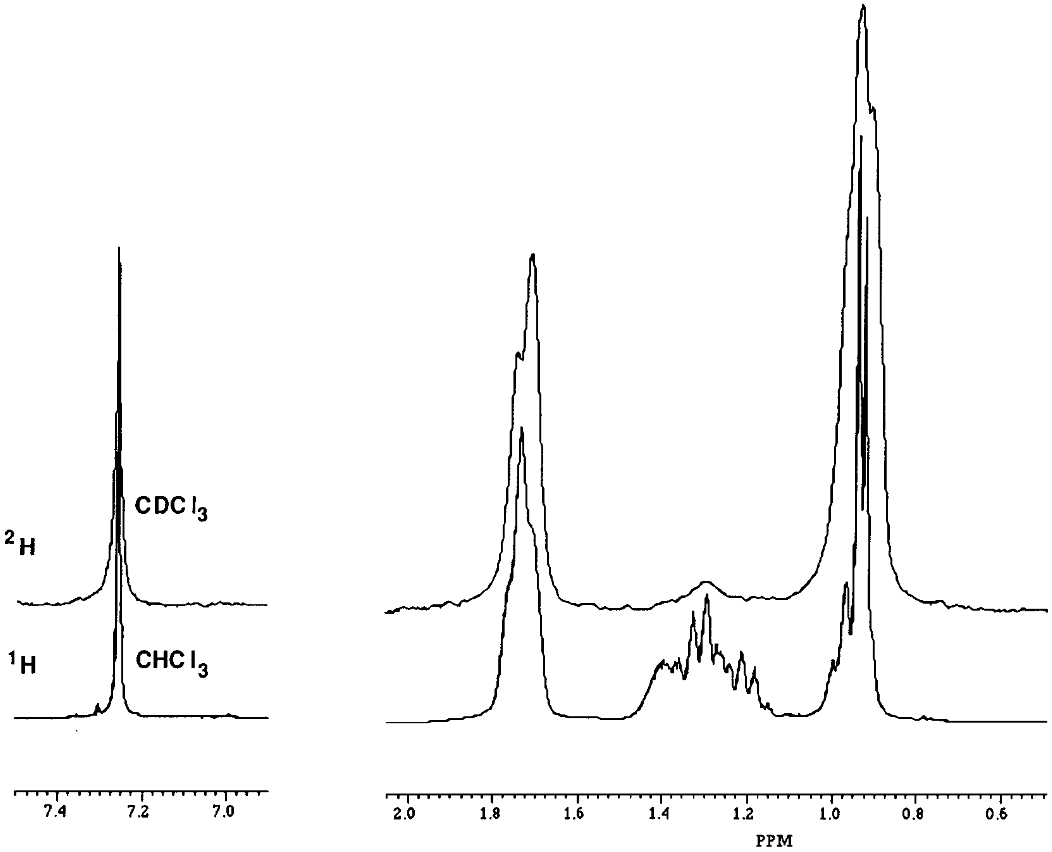


FIG. 1. ^1H and ^2H NMR spectra of methyl-cyclohexane exchanged on DUSY at 100°C.

incorporated at the methyl position (0.9 ppm). Unfortunately, all the equatorial protons overlap, impairing a precise evaluation. Nevertheless, the results indicated that equatorial protons (1.7 ppm) are significantly more exchanged, compared with axial protons (1.3 ppm), a fact which is in opposition to what is observed in liquid media, where axial protons are well known to be preferentially involved in elimination–reprotonation reactions (26) relative to the equatorial protons.

For the *t*-butyl-cyclohexane, Fig. 2 clearly shows the preferential exchange at the methyl groups (0.9 ppm). The other positions showed minor or negligible exchange. These data are surprising since no mechanism involving olefins can explain the exchange at the methyl position.

The ^1H and ^2H NMR spectra of *trans*-decalin after H–D exchange (Fig. 3) are consistent with exchange in all positions. However, for the hydrogens adjacent to the tertiary center, exchange at equatorial position (1.6 ppm) was fourfold higher than at the axial position (1.0 ppm). There was also a significant exchange at the tertiary position (0.9 ppm), consistent with elimination to form a *tetra*-substituted olefin. With *cis*-decalin, exchange was observed in all positions (Fig. 4), as in the case of the *trans* isomer. Nevertheless, no significant regioselectivity, among the equatorial and axial hydrogens, was observed, consistent with a rapid interconversion of two conformational structures, switching the axial and equatorial hydrogens. Gas chromatographic analysis indicated the formation of about 18% of *trans*-decalin, during the H–D exchange. This isomerization is consistent with the formation of a tertiary carbenium ion, followed by hydride transfer to give the thermodynamically more stable isomer.

The exchange with the *trans*-1,2-dimethyl-cyclohexane occurred almost exclusively in the methyl groups, at 0.9 ppm (Fig. 5). On the other hand, the *cis*-1,2-dimethyl-cyclohexane showed exchange (Fig. 6) in the methyl positions (0.9 ppm), as well as in the tertiary axial and equatorial positions (1.8 ppm) and axial and equatorial positions adjacent to the tertiary carbon (1.5 ppm). In this molecule, there is no resolution between the axial and equatorial positions.

Competitive experiments between *cis*- and *trans*-decalin and *cis*- and *trans*-1,2-dimethyl-cyclohexane revealed that the *cis* isomers are more reactive than the respective *trans* isomers. Considering first-order kinetics in the hydrocarbon, we found that, the *cis*-1,2-dimethyl-cyclohexane has an exchange rate 23-fold higher than the *trans* isomer. For the decalins, the difference is even larger. The *cis* isomer is 47 times more reactive than *trans*-decalin at 100°C.

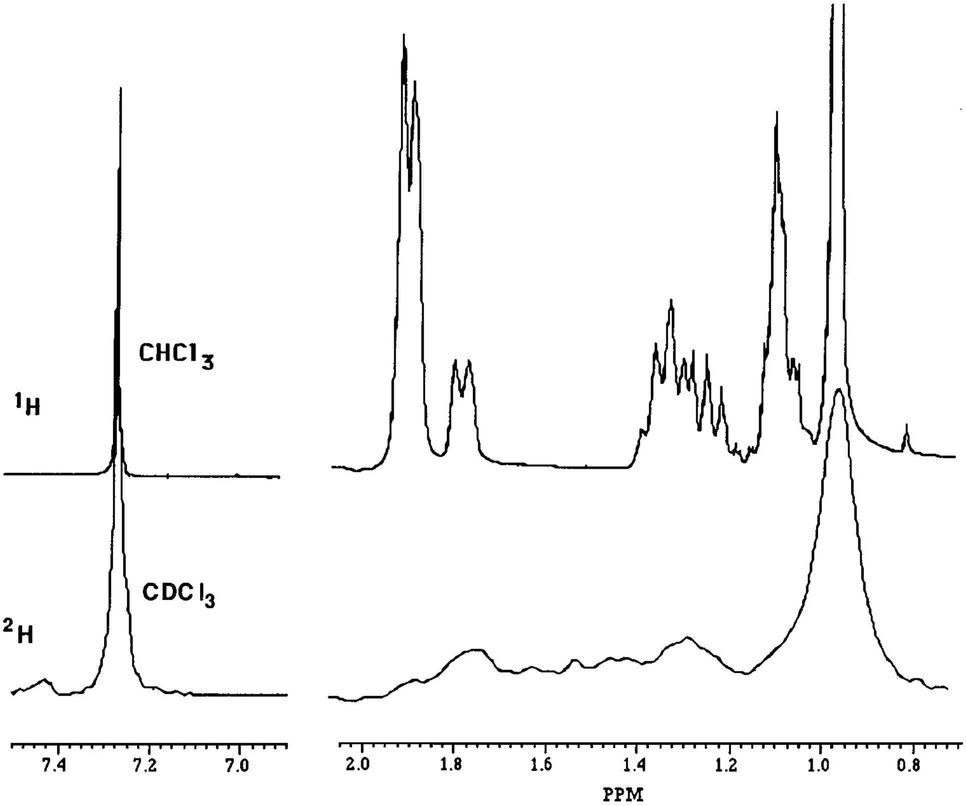


FIG. 2. ^{1}H and ^{2}H NMR spectra of *t*-butyl-cyclohexane exchanged on DUSY at 100°C.

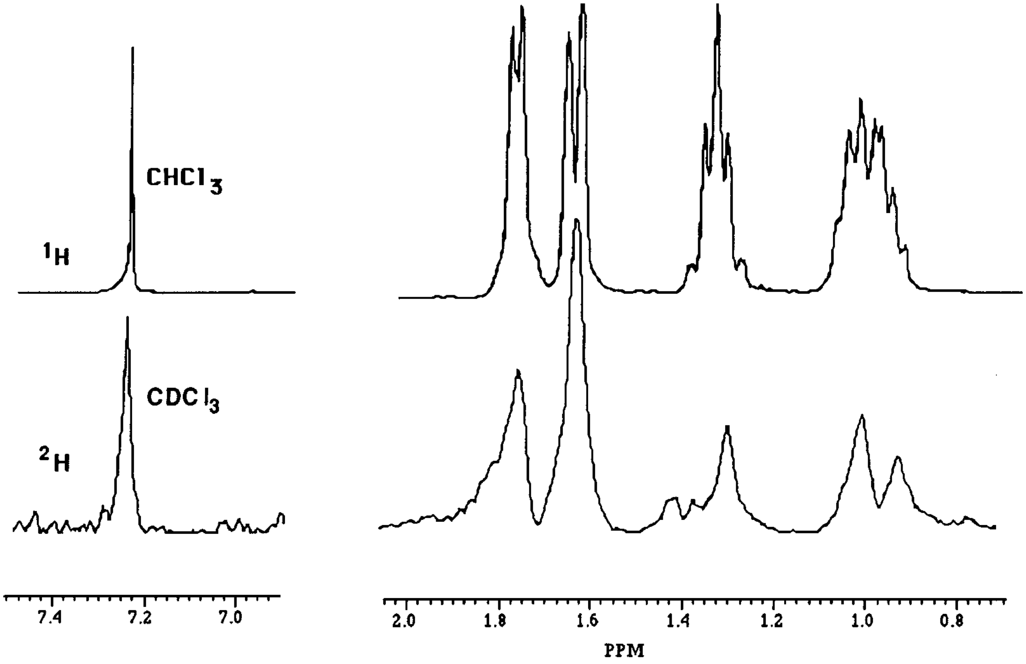


FIG. 3. ^{1}H and ^{2}H NMR spectra of *trans*-decalin exchanged on DUSY at 100°C.

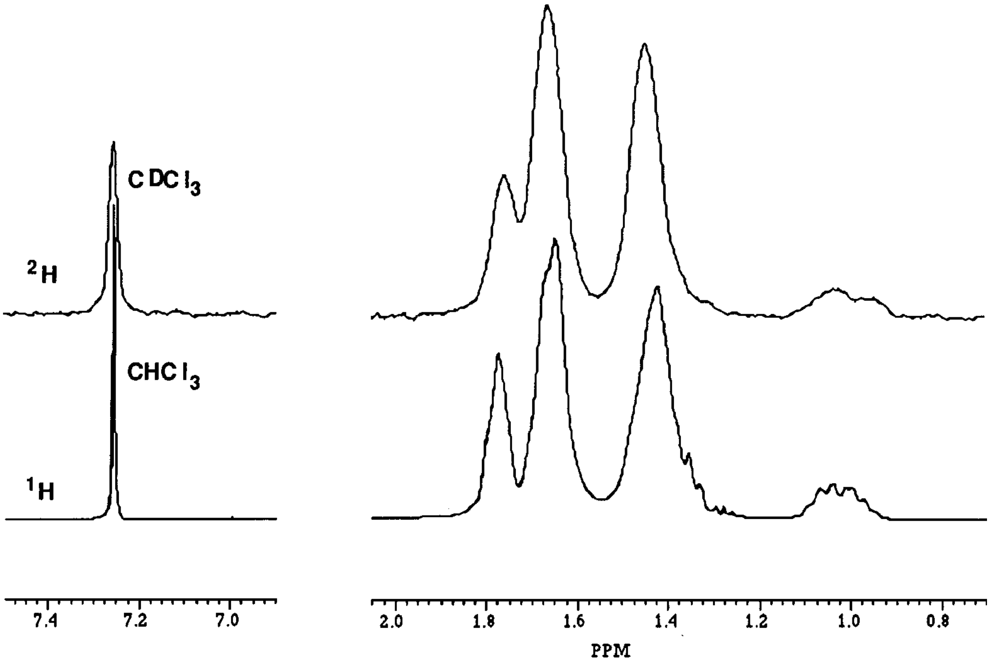


FIG. 4. ^{1}H and ^{2}H NMR spectra of *cis*-decalin exchanged on DUSY at 100°C.

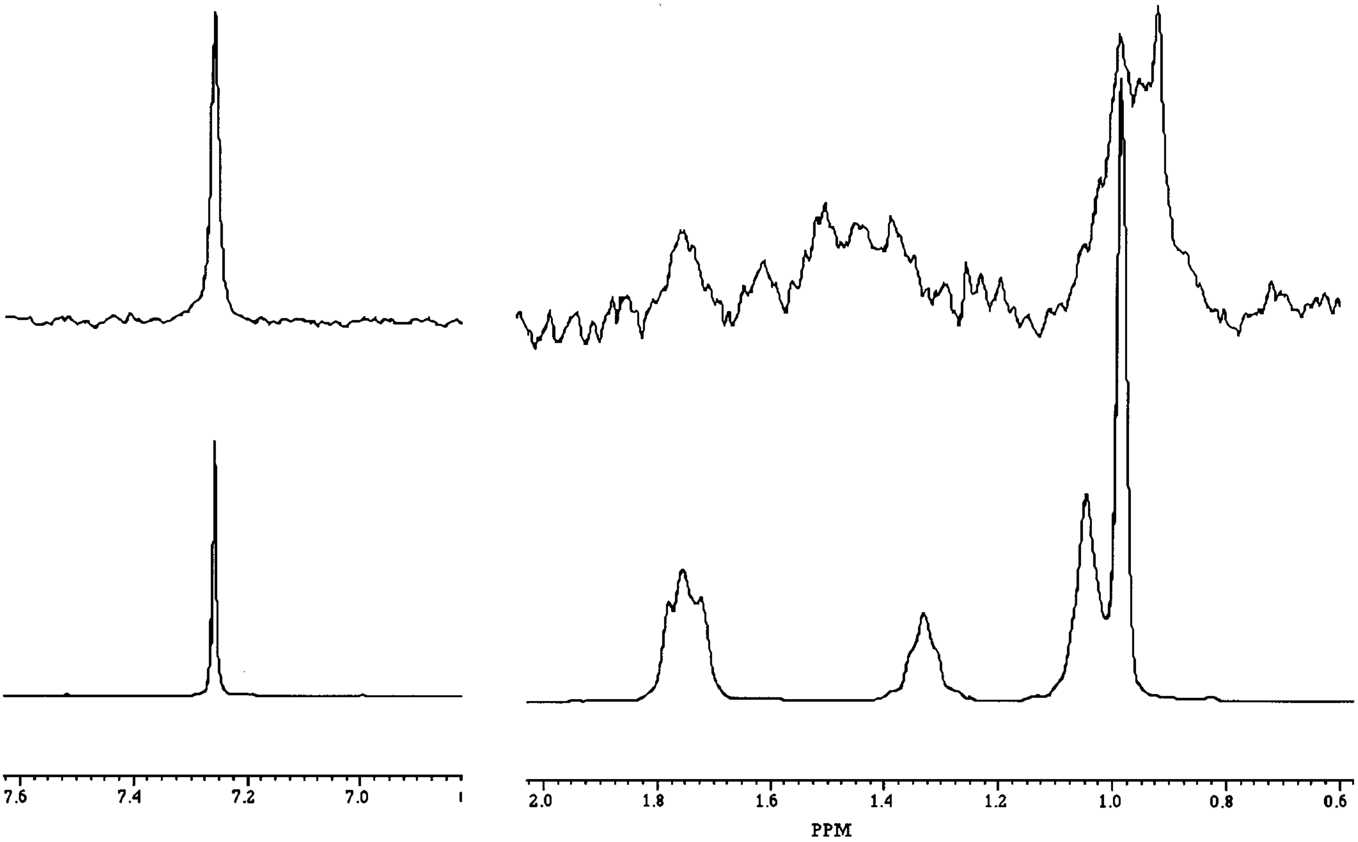


FIG. 5. ^{1}H and ^{2}H NMR spectra of *trans*-1,2-dimethyl-cyclohexane exchanged on DUSY at 100°C.

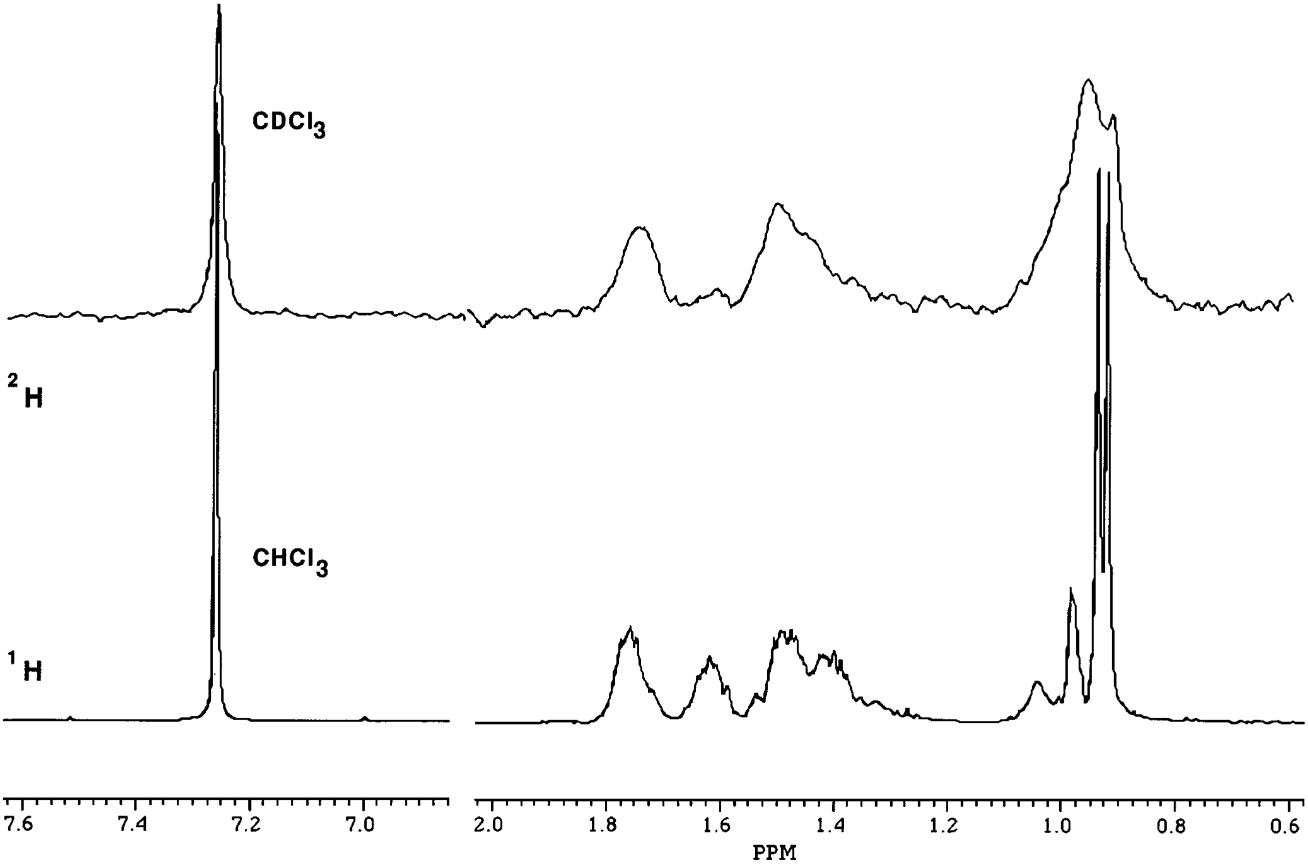


FIG. 6. ^1H and ^2H NMR spectra of *cis*-1,2-dimethyl-cyclohexane exchanged on DUSY at 100°C.

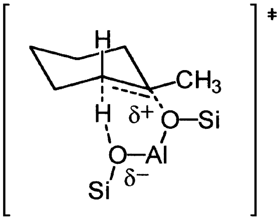
DISCUSSION

The most reasonable mechanism to explain the H–D exchange on zeolite involves elimination–reprotonation steps with adsorbed olefins and carbenium ions as intermediates (Scheme 1). In principle, the position of deuterium in the molecule, the regioselectivity, will be governed by these reactions. A mechanism involving adsorbed carbonium ions as intermediates seems improbable due to the lack of exchange of the methine hydrogen in tertiary alkanes (12, 13, 16–18) and by the fact that linear alkanes do not exchange under the same conditions (10–12) that tertiary alkanes do, indicating that secondary and primary C–H bonds are not easily protonated by the zeolite. Hence, the most reasonable pathway to explain the exchange results of tertiary alkanes over deuterated zeolite is the formation of an adsorbed tertiary carbenium ion, which can eliminate a proton to form an adsorbed olefin that can be protonated (deuterated) to give the adsorbed tertiary carbenium ion with deuterium incorporated in positions adjacent to the cationic center, according to the reaction sequence showed in Scheme 1. A final hydride transfer step affords the deuterated alkane and the adsorbed tertiary carbenium ion, which can reinitiate the cycle. This mechanism of H–D exchange on zeolites is similar to the exchange in sulfuric acid (14, 15) and do not involve adsorbed carbonium ions as intermediates.

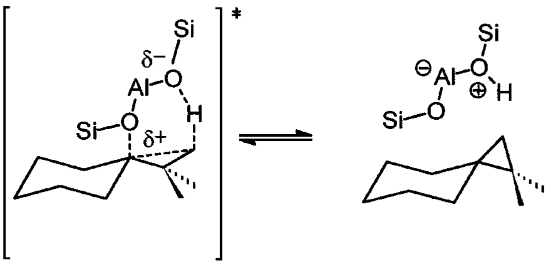
Recent results of H–D exchange on zeolites at temperatures lower than 100°C also support the mechanism shown in Scheme 1. For instance, adamantane, a rigid cyclic molecule where formation of a bridgehead olefin is virtually impossible, does not exchange with DUSY at room temperature (27), but it does with liquid superacids (28), selectively at the tertiary position. Yet, the H–D exchange of 2-methylpentane and 3-methylpentane with DUSY at 0°C, although showing rates significantly slower than at 100°C, presented (27) the same NMR spectral patterns, indicating exchange only at the secondary and primary positions adjacent to the tertiary center. In liquid superacids, at similar temperatures, there occurs (29) significant exchange at the tertiary position of isobutane, stressing the different mechanisms for exchange on zeolites and liquid superacids. Indeed, the existence of tertiary pentacoordinated carbonium ions as discrete intermediates in hydrocarbon reactions has been questioned, in view of a recent high level *ab initio* theoretical calculation (30). Thus, tertiary carbonium ions seem to straightforwardly decompose to the respective carbenium ion and hydrogen. Therefore, in the H–D exchange in liquid superacids, they are better described as transition states, coordinated with the counterion, rather than discrete intermediates. Evidences for this assumption comes from results (8) of isobutane exchange/ionization in DF/SbF$_5$ mixtures. As the acid strength increases, by increasing the amount of SbF$_5$, thus decreasing the coordinating ability of the counterion, the ionization to the *t*-butyl cation increases, relative to H–D exchange.

The protonation (deuteration) according to Scheme 1, follows the Markovnikov rule, with formation of the tertiary carbenium ion. However, as indicated by theoretical calculations (19–23) and shown in Scheme 2, it is expected that an eclipsed conformation, between the adding proton (deuteron) and the assisting oxygen from the framework, is formed in the transition state. Therefore, a regioselectivity among the hydrogens adjacent to the tertiary position should be expected.

With methyl-cyclohexane there is a great preference for exchange in the methyl and in the equatorial positions. Although the resolution of the NMR spectrum does not allow discrimination among the equatorial positions of the molecule, it can be inferred that most of the exchange takes place at the equatorial positions adjacent to the tertiary center, as the formation of the tertiary carbenium ion should be the preferred pathway. With *trans*-decalin the exchange of the equatorial hydrogen, adjacent to the tertiary center was fourfold preferred over the axial one, supporting the interpretation of the methyl-cyclohexane data. These results are in agreement with calculations of the olefin protonation–elimination reactions shown in Scheme 2, which indicated the need for an eclipsed conformation. In cycloalkanes the equatorial protons adjacent to the tertiary center can achieve an eclipsed conformation with the cationic center, allowing elimination and protonation (deuteration) reactions to take place (Scheme 3). The axial protons are more distant to the framework and interaction through an eclipsed conformation with the cationic center is very difficult and high in energy. With *cis*-decalin there was no selectivity for exchange in equatorial and axial positions. This is explained by the great flexibility of this molecule, interchanging the equatorial and axial hydrogens and making the achievement of an eclipsed conformation easier.



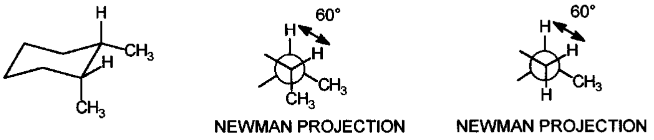
SCHEME 3. Possible transition state for protonation-elimination reactions of cycloalkanes on zeolites. Preferential exchange of the equatorial hydrogens.



SCHEME 4. Possible pathway for exchange in the methyl position of *t*-butyl-cyclohexane. Formation of a cyclopropane (spiro) intermediate.

An interesting observation arose from the exchange with *t*-butyl-cyclohexane, where an almost exclusive exchange at the methyl position was observed. This result cannot be explained by the general mechanism, shown in Scheme 1, for the H–D exchange on zeolites, as there is no possibility of eliminating a proton from the methyl group to form an olefin. A carefully inspection in the result of H–D exchange with *trans*-decalin also revealed that the axial hydrogens in β position with respect to the tertiary center (1.3 ppm) are exchanged (Fig. 3). Therefore, a 1,3-elimination-protonation process seems to be operating for *t*-butyl-cyclohexane and *trans*-decaline. We still do not have a definite explanation for this process. However, the involvement of adsorbed pentacoordinated carbonium ion cannot account for the observed results, since neopentane and neohexane (2,2-dimethylbutane), both having a quaternary carbon, did not exchange with DUSY under the same conditions. A feasible pathway would involve the formation of a cyclopropane ring, followed by protonation (deuteration) in the C–C bond, opening the ring (Scheme 4). Nevertheless, additional experiments must be carried out, before a clearer conclusion can be drawn. The exchange of the axial hydrogens in β position to the tertiary center (1.3 ppm) in *trans*-decalin can also be explained invoking a similar 1,3 elimination process, forming a bicyclo compound.

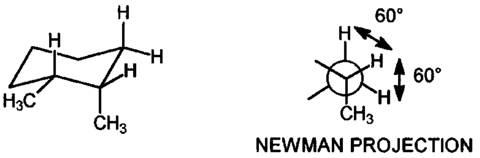
For the 1,2-dimethyl-cyclohexanes the situation is similar to the other cycloalkanes. In the *trans* isomer exchange is almost exclusive in the methyl group, as found for the methyl-cyclohexane. The virtually low exchange, below the detection limits, in the other positions of the *trans*-1,2-dimethyl-cyclohexane may be associated with a higher energy barrier, compared with the methyl-cyclohexane, to achieve an eclipsed conformation between the equatorial hydrogens and the cationic center. Upon distorting the ring (twist-boat like conformation), steric repulsion between the two methyl groups in equatorial positions can be dominant, impairing elimination/protonation reactions. For the *cis*-1,2-dimethyl-cyclohexane this repulsion is significantly lower. The two adjacent methyl groups are in equatorial and axial positions and, thus, far from each other, allowing a more convenient distortion of the molecule and exchange in the ring. Besides exchange in the equatorial



SCHEME 5. Structural representation of the *cis*-1,2-dimethyl-cyclohexane, showing the dihedral angles between the two tertiary hydrogens and between the axial tertiary hydrogen and the adjacent equatorial secondary hydrogen.

position adjacent to the tertiary center, there was exchange in the axial position. Exchange was also observed in the tertiary position (axial and equatorial). In the *cis*-1,2-dimethyl-cyclohexane molecule there is one tertiary hydrogen in the axial position and another in the equatorial position. If the proton (deuteron) attacks the axial tertiary hydrogen, it is possible to eliminate the axial secondary hydrogen adjacent to the tertiary carbon or the equatorial tertiary hydrogen, as both have a dihedral angle of 60° with the axial tertiary hydrogen and, by consequence, with the adsorbed carbenium ion being formed (Scheme 5). On the other hand, if the proton attacks the tertiary equatorial hydrogen, besides elimination of the axial tertiary proton and the equatorial secondary hydrogen adjacent to the tertiary carbon, it is also possible to eliminate the axial secondary proton adjacent to the tertiary carbon. Both secondary hydrogens have a dihedral angle of 60° with the equatorial tertiary hydrogen and can be eliminated by a distortion of the ring to achieve eclipsed conformation (Scheme 6).

The results of competitive exchange between the *cis* and *trans* isomers of decalin and 1,2-dimethyl-cyclohexane showed that the *cis* isomers are significantly more reactive than the *trans* isomer. This difference in reactivity is probably associated with difficulties for distorting the structure to eclipse the eliminating proton and the cationic center. The structure of *trans*-decalin is rigid and distortion of the ring to achieve an eclipsed conformation would cost a significant amount of energy. On the other hand, the structure of the *cis*-decalin is considerably more flexible, and distortion to achieve an eclipsed conformation is easier, compared to the *trans* isomer. In the *trans*-1,2-dimethyl-cyclohexane the presence of two di-equatorial adjacent methyl groups impair the distortion of the structure due to steric repulsion between the methyls. This effect is less pronounced in the *cis* isomer, where the methyls are located in equatorial and axial adjacent positions and distortion to achieve an eclipsed conformation is easier. The same effect was found for cracking reactions, where the *cis*-decalin was found to be significantly more reactive than the *trans*-decalin (31). This result suggests that, like proton elimination, the β-scission, which conceptually can be viewed as a carbenium ion elimination, also requires an eclipsed conformation between the cationic center and the alkyl group to be cracked.



SCHEME 6. Structural representation of the *cis*-1,2-dimethyl-cyclohexane, showing the dihedral angles between the equatorial tertiary hydrogen and the adjacent secondary hydrogens (axial and equatorial).

CONCLUSIONS

The H–D exchange between zeolite Y and cycloalkanes was successfully used to study the role of the zeolite framework in proton transfer reactions. With methyl-cyclohexane and *trans*-decalin, the equatorial hydrogens adjacent to the tertiary center were significantly more exchanged than the correspondent axial ones. This result is in agreement with recent theoretical calculations of protonation/elimination reactions on zeolites, which point out an eclipsed conformation between the cationic center and the eliminating proton. The difference in reactivity between *cis* and *trans* isomers of decalin and 1,2-dimethyl-cyclohexane may be attributed, at least in part, to difficulties in achieving the eclipsed conformation in the *trans* isomer.

The *t*-butyl-cyclohexane exchanged almost exclusively at the methyl position, indicating a different mechanism, not involving olefins. To explain this result we suggest that a 1,3-proton elimination, with formation of a cyclopropane ring, is taking place. However, additional experiments are required in order to confirm this hypothesis.

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REFERENCES

1. Corma, A., "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), p. 49, Elsevier, Amsterdam, 1989.
2. Olah, G., *Angew. Chem. Internat. Ed. Engl.* **12**, 171 (1973).
3. Mota, C. J. A., and Martins, R. L., *J. Chem. Soc., Chem. Commun.*, 171 (1991).
4. Mota, C. J. A., Nogueira, L., Martins, R. L., and Kover, W. B., *J. Chem. Soc., Faraday Trans.* **90**, 2297 (1994).
5. Olah, G. A., and Schlosberg, R. H., *J. Am. Chem. Soc.* **90**, 2726 (1968).
6. Olah, G. A., and Schlosberg, R. H., *J. Am. Chem. Soc.* **91**, 3261 (1969).
7. Hogeveen, H., and Bickel, A. F., *Recl. Trav. Chim. Pays-Bas* **88**, 371 (1969).
8. Sommer, J., Bukala, J., Hachoumy, M., and Jost, R., *J. Am. Chem. Soc.* **119**, 5193 (1997).

9. Sommer, J., Bukala, J., and Hachoumy, M., *Res. Chem. Intermed.* **22**, 753 (1996).
10. Mota, C. J. A., Nogueira, L., and Kover, W. B., *J. Am. Chem. Soc.* **114**, 1121 (1992).
11. Mota, C. J. A., Nogueira, L., Menezes, S., Alekstich, V., Pereira, R. C. L., and Kover, W. B., *Stud. Surf. Sci. Catal.* **75**, 463 (1993).
12. Sommer, J., Hachoumy, M., Garin, F., and Barthomeuf, D., *J. Am. Chem. Soc.* **116**, 5491 (1995).
13. Sommer, J., Hachoumy, M., Garin, F., Barthomeuf, D., and Vedrine J., *J. Am. Chem. Soc.* **117**, 1135 (1995).
14. Otvos, J. W., Stevenson, D. P., Wagner, C. D., and Breek, O., *J. Am. Chem. Soc.* **73**, 5741 (1951).
15. Stevenson, D. P., Wagner, C. D., and Otvos, J. W., *J. Am. Chem. Soc.* **74**, 3269 (1952).
16. Engelhardt, J., and Hall, W. K., *J. Catal.* **151**, 1 (1995).
17. Mota, C. J. A., Menezes, S., Nogueira, L., and Kover, W. B., *Appl. Catal. A: General* **146**, 181 (1996).
18. Sommer, J., Habermacher, D., Hachoumy, M., Jost, R., and Reynaud, A., *Appl. Catal. A: General* **146**, 193 (1996).
19. Senchenya, I. N., and Kazansky, V. B., *Catal. Lett.* **8**, 317 (1991).
20. Kazansky, V. B., *Acc. Chem. Res.* **24**, 379 (1991).
21. Kazansky, V. B., and Senchenya, I. N., *J. Mol. Catal.* **74**, 257 (1992).
22. Viruela-Martín, P., Zicovich-Wilson, C., and Corma, A., *J. Phys. Chem.* **97**, 13713 (1993).
23. Evleth, E. M., Kassab, E., Jessri, H., Allavena, M., Montero, L., and Sierra, L. R., *J. Phys. Chem.* **100**, 11368 (1996).
24. Lowry, T. H., and Richardson, K. S., “Theory and Mechanism in Organic Chemistry,” 2nd ed., p. 178, Harper & Row, New York, 1981.
25. Sohn, J. R., DeCanio, S. J., O’Donnell, D. J., and Lunsford, J. H., *Zeolites* **6**, 225 (1986).
26. March, J., “Advanced Organic Chemistry,” 4th ed., Chap. 17, and references therein, Wiley, New York, 1992.
27. Mota, C. J. A., unpublished results.
28. Olah, G. A., Halpern, Y., Shen, J., and Mo, Y. K., *J. Am. Chem. Soc.* **95**, 4960 (1973).
29. Sommer, J., Bukala, J., Rouba, S., and Graff, R., *J. Am. Chem. Soc.* **114**, 5884 (1992).
30. Mota, C. J. A., Esteves, P. M., Solis, A. R., and Lamoneda, R. H., *J. Am. Chem. Soc.* **119**, 5193 (1997).
31. Sousa-Aguiar, E. F., Mota, C. J. A., Valle, M. L. M., Silva, M. P., and Silva, D. F., *J. Molec. Catal. A: Chemicals* **104**, 267 (1996).