

## Zeolite Y-Catalyzed versus Superacid-Catalyzed Protium-Deuterium Exchange in Alkanes

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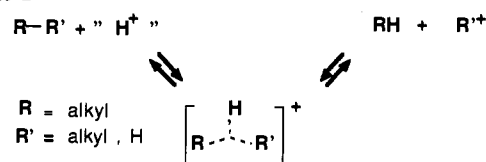
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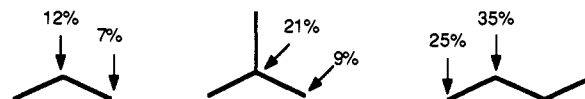
Since Olah's pioneering work in the late 1960s, it has been well-known that saturated hydrocarbons react with superacids under mild conditions of temperature and pressure.<sup>1,2</sup> The driving force of the reaction is the  $\sigma$ -basicity<sup>3</sup> of the alkane with regard to the extremely high acidity of the reagent.<sup>4</sup> The reaction takes place via protonation of the alkane and subsequent protolysis of the protonated C-H or C-C bond in the carbonium ion (R'H<sup>+</sup>) (Scheme 1). In contrast with these fundamental studies in liquid superacids, very little convincing material is available concerning the mechanistic aspect of C-H and C-C bond activation by the solid acidic catalysts used in the oil industry. The true nature of the "carbenium ions" adsorbed on the surface of the catalyst has been questioned,<sup>5</sup> and great effort has been devoted to observe directly the reaction intermediates on the solid by IR and NMR spectroscopy.<sup>6</sup> In relation with this problem, the report of the H/D exchange observed between branched alkanes and a Y zeolite, ascribed to carbonium ion formation and rearrangement,<sup>7</sup> prompts us to publish our results obtained (as well) in liquid superacids as on the D<sub>2</sub>O-exchanged Y-zeolite. The difference in behavior of linear and branched alkanes as well as the difference in isotope distribution observed in the products can only be rationalized by a completely different mechanism for each type of catalyst. We have thus investigated the exchange process in isobutane, *n*-butane, and propane as follows:

The mixture of alkane and carbon monoxide (1:2.6 molar ratio) was bubbled during 30 min at a rate of 4 mL/min through 1 mL of DF/SbF<sub>5</sub> (7:1 molar ratio) in a KelF reactor at -10 °C. (In order to inhibit reversible protide transfer, we have run all of our

### Scheme 1



### Scheme 2



experiments in the presence of carbon monoxide in order to trap the carbenium ions formed in the superacid via C-H or C-C bond protolysis.) The gaseous products were analyzed by GC and further collected at -78 °C for <sup>1</sup>H and <sup>2</sup>H NMR analysis after addition of an adequate amount of a CDCl<sub>3</sub>/CHCl<sub>3</sub> mixture used as internal standard for the H/D distribution measurement. The deuterium distribution observed for the three alkanes is shown in Scheme 2. As described earlier,<sup>8</sup> variable amounts of hydrogen, methane, and ethane can be found in the gas phase as products of C-H and C-C bond protolysis. The correspondingly formed carbenium ions are trapped as oxocarbenium ions, stable below 0 °C in the liquid superacid.

In the case of *n*-butane, we observed that, when a stronger superacid such as DF/SbF<sub>5</sub> (4:1) was used, the exchange was more extensive under the same experimental conditions: of the methylene hydrogens, up to 50 atom % were deuteriums, and in the methyl groups, up to 42 atom % were deuteriums. We noticed also that the H/D exchange rate decreased slowly with time on run in agreement with a decrease in acidity due to the competitive formation of oxocarbenium ions. No butane isomerization was detected.

These results are in agreement with the protonation (deuteration) process of the alkane following the concept of  $\sigma$ -basicity developed by Olah. The relative rates of exchange are in accord with the expected relative basicity of the  $\sigma$  bonds and increase when the superacidity is increased.

On the basis of these results, we have investigated the ability of the Y-zeolite to exchange hydrogens via the carbonium ion mechanism in a series of linear and branched alkanes.

As catalyst we used a D<sub>2</sub>O-exchanged acidic steam dealuminated zeolite USY (framework Si/Al = 4.5, residual Na<sub>2</sub>O = 0.5 wt %).<sup>9</sup> Five hundred milligrams of the zeolite was pretreated with dry nitrogen (38 mL/min) at 500 °C for 30 min and exchanged with D<sub>2</sub>O as described earlier.<sup>7</sup> The reaction was carried out in an all-glass, grease-free flow system.<sup>10</sup> The alkane (ca. 6 mol % in N<sub>2</sub>) was passed (20 mL/min) over the zeolite at 100 °C, collected in a dry ice acetone trap, and analyzed by <sup>1</sup>H and <sup>2</sup>H 400-MHz NMR as described above.

No H/D exchange could be detected in the linear alkanes we have tested (propane, *n*-butane, *n*-pentane, *n*-hexane). This confirms the previously published work on this subject.<sup>7</sup> The GC analysis of the reaction products showed that also isomerization did not take place.

When isobutane was used as starting material, the <sup>2</sup>H NMR spectrum of recovered isobutane showed only one line at 0.9 ppm corresponding to the methyl deuterons. By comparison the intensities with the internal standard in <sup>1</sup>H or <sup>2</sup>H spectra it could be estimated that 2.8 atom % of the original protons had exchanged for deuterons. When this partially exchanged isobutane was

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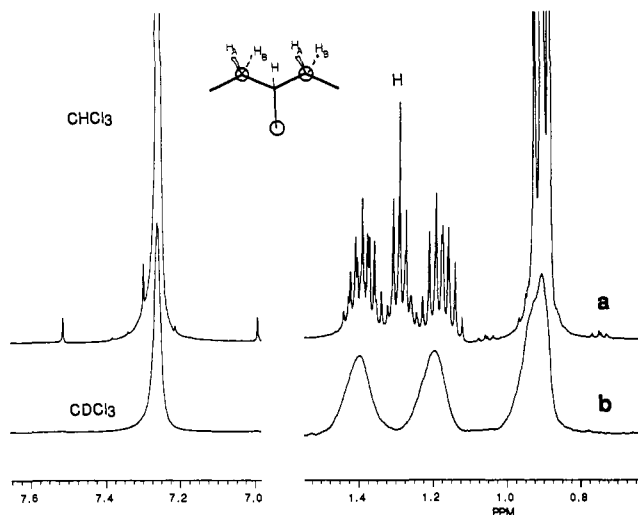
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**Figure 1.**  $^1\text{H}$  (a) and  $^2\text{H}$  (b) NMR spectra of 3-methylpentane as recovered after reaction at 100 °C with  $\text{D}_2\text{O}$ -exchanged zeolite USY.

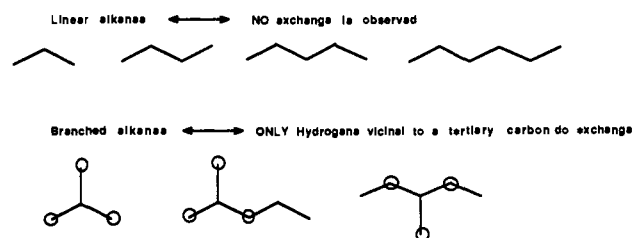
recycled in a second experiment on fresh deuterated zeolite, the exchange ratio increased to 5.4 atom % but *no exchange was detected on the methine proton*.

When 2-methylpentane was used as starting material, only two lines were observed in the  $^2\text{H}$  NMR spectrum (at 0.9 and 1.2 ppm). In comparison with the  $^1\text{H}$  spectrum these lines could be assigned to the methyl and methylene hydrogens vicinal to the tertiary carbon. The amount of exchange was 6 atom % and 8 atom %, respectively, for these groups, and *no exchange was detected on the methine proton*.

In the case of 3-methylpentane, three broad lines are observed by  $^2\text{H}$  NMR at 1.4, 1.2, and 0.9 ppm of relative intensity 1:1:1.6. By comparison with the original  $^1\text{H}$  spectrum, the low-field lines could be assigned to the nonequivalent (two by two) methylene protons which appear as an  $\text{ABMX}_3$  signal. *The methine hydron which appears at 1.3 ppm in the  $^1\text{H}$  spectrum does not appear in the  $^2\text{H}$  spectrum* (Figure 1). The broad line at 0.9 ppm was assigned to the methyl group  $\alpha$  to the tertiary carbon. The difference in interpretation by Mota and colleagues is mainly based on the difference in interpretation of the  $^2\text{H}$  spectrum of this compound. The same problem of nonequivalence of the

### Scheme 3

Catalyst :  $\text{D}_2\text{O}$ -exchanged Zeolite USY temperature : 100 °C  
GHSV : 3000 ( 6% alkane in nitrogen)



methylene protons is present in methylcyclohexane investigated by these authors.

The regioselectivity observed in the H/D exchange process on Y-zeolite is presented in Scheme 3. These results are very similar to those obtained by Otvos and Stevenson<sup>11</sup> using  $\text{D}_2\text{SO}_4$ . The H/D exchange was rationalized by a carbenium ion mechanism including successive deprotonation and re deuteration steps followed by a hydride (protide) transfer step.

In conclusion we notice that whereas alkanes are  $\sigma$ -bases in which all  $\sigma$ -bonds can be protonated (deuterated) with formation of a pentacoordinated carbonium ion, their basicity is very weak and superacids are needed for the protonation step.

It seems that the Y-zeolite, at least at 100 °C, cannot be considered as a superacid capable of protonating  $\sigma$ -bonds in alkanes; the behavior is comparable to that of sulfuric acid.<sup>12</sup> This conclusion is in good accord with the recent acidity estimation based on the in-situ  $^{13}\text{C}$  chemical shift measurements of mesityl oxide, which shows that the acidity of ZSM-5 is comparable to that of a solution of 70% sulfuric acid. The question which remains unfortunately unanswered is that of the origin of the olefin or of the initial carbenium ion. It does not surprise us, however, that no olefin could be detected in the reaction products as oligomerization is very fast.

This work will be extended on solid strong acids of varying types and acidity and at various temperatures to help elucidate the detailed nature of these effects.

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