

## Carbenium and carbonium ions in liquid- and solid-superacid-catalyzed activation of small alkanes\*

J. Sommer<sup>†</sup> and R. Jost

*Laboratoire de Physico-Chimie des Hydrocarbures, UMR 7513 CNRS Faculté de Chimie, Université Louis Pasteur, Strasbourg, France*

*Abstract:* Acid-catalyzed hydrocarbon reactions involve by far the largest amount of catalyst and the largest volume of transformation in oil refinery and chemical industry. However, despite the general agreement on the carbocationic nature of the reaction intermediates, the initial steps and the true nature of the cations on the surface are still open to debate. On these points our basic knowledge has gained enormously from landmark experiments in physical organic chemistry with spectroscopic observations using liquid superacids as solvents. As the range of superacidity covers over 11 logarithmic units of the Hammett acidity scale, the mechanistic behavior of small alkanes vary accordingly. This allows for comparison with strong solid acids such as zeolite or others used in industry. Isotopic labeling of the alkane and the acids is a powerful tool used to understand the nature of the intermediates, as well as the reaction mechanism in which carbenium and carbonium ions intervene.

### INTRODUCTION

Solid- and liquid-acid-catalyzed reactions involve by far the largest amount of catalysts and the largest economic efforts in oil refining and chemical industry [1,2]. Saturated hydrocarbons are the main compounds of natural gas and raw oil, which play a key role in world economy as the number one source of chemicals, but also of energy, useful for heating and transportation. In order to overcome their chemical inertness, the chemical industry relies on processes based on high-temperature, noble-metal or liquid- and solid-acid catalysts. Despite worldwide trends toward severe environmental legislation restricting the use of liquid acids such as HF and H<sub>2</sub>SO<sub>4</sub> these acids are still used due to their high activity at low temperature. Nevertheless, simultaneously a huge effort has been displayed to develop solid or supported acids which are easier to handle and to recycle. This trend is also reflected by the impressive number of patents, special issues, reviews, and books devoted to this subject [3,4]. The preparation of new solid acids, their characterization, mechanistic studies and theoretical approaches to understand the fundamental aspects of acid-catalyzed hydrocarbon conversion constitute an increasing number among the topics discussed in all journals related to catalysis and physical chemistry. However, in contrast with liquid acid-catalyzed alkane activation, and despite huge research efforts, many fundamental questions stay open concerning the nature of the initial step, the true nature of the reaction intermediates, and the real number of active sites on the solid-acid catalyst.

In the present paper, we will focus more on the similarities than on the differences between liquid- and solid-acid-catalyzed alkane activation on the basis of recent results obtained by using a variety of experimental techniques such as <sup>13</sup>C labeling of starting material, D-labeling of alkanes and acids, batch and flow systems in combination with GC-MS, UV, and multinuclei high-field liquid- and solid-state NMR.

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<sup>†</sup>Corresponding author

## ACIDITY AND SUPERACIDITY OF SOLID SUPERACIDS

Solid acids are generally inorganic oxides, mostly silicoaluminates, but including also frequently other elements such as phosphorus, gallium, zirconium, etc. The categories that are the most studied by far are crystalline aluminosilicates (zeolites), due to their large industrial potential, followed by heteropolyacids and sulfated metal oxides. Well-established, large-volume alkane conversion currently used in industry, based on zeolite catalysis [5], comprises processes such as catalytic cracking, hydrocracking, C<sub>5</sub>–C<sub>7</sub> isomerization, whereas heteropolyacids are used in alkane alkylation, and sulfated metal oxides are still under development. The main advantages of solid acids in comparison with liquids is the easier product separation after reaction and a larger temperature range (up to 600 °C). As a consequence, solids can be easily regenerated avoiding waste treatment. On the other hand they are less toxic and easier to handle. Finally, the 3D geometry of some solids can induce stereo- and regioselectivity, especially in the case of zeolites, for which the channels and cages can control reactant or product diffusion as well as the volume available for transition states [6].

The acidity of solid materials has, of course, received much attention, and hundreds of papers address yearly this topic. The measurement of the acidity needs a univocal definition of what is to be measured. The usual acidity functions pH or H<sub>0</sub> used for the determination of acidity in liquids are intrinsically inappropriate as the activity of the protons a<sub>H<sup>+</sup></sub> has no explicit physical meaning on the solid. Moreover, solids are heterogeneous and Brønsted acid sites may coexist of different strengths as well as Lewis acid sites. The accessibility of the sites plays also an important role, and it is not surprising that different methods will lead to discrepancies in results. Under these circumstances, relative acidities are generally determined. Some of the most frequently used techniques comprise Hammett indicators, <sup>1</sup>H and <sup>13</sup>C chemical measurements, temperature desorption of bases, microcalorimetry, and infrared shifts of OH groups among others. This explains why many experimental approaches continue to be used [7,8] and recently a special issue has been devoted to this topic [9].

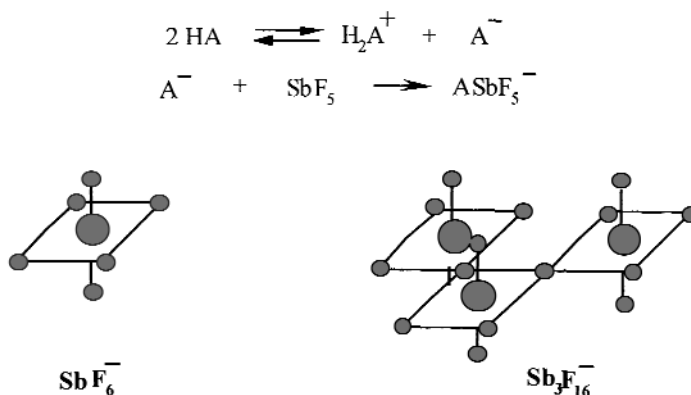
The superacid [10] character of some solids has also been addressed at various times and on the basis of different experimental techniques, but in the absence of an acceptable definition of superacidity in solids, we may consider these suggestions as presumption of superacidity. The most frequently quoted solid superacid is still sulfated zirconia (SZ) on the basis of its unique ability to isomerize *n*- to isobutane at temperatures below 200 °C. Nevertheless, the first step of *n*-butane activation is a subject of controversy as is the mechanism of its skeletal rearrangement. Since its discovery in the late 1970s [11], hundreds of papers have been devoted to this catalyst either genuine or modified by addition of transition metals, and several reviews have appeared on this subject [12,13]. On the basis of the initial product distribution, when 2-methylpentane was cracked on HZSM-5 at 500 °C [14], many zeolites have also been qualified as superacids, and this point is still a matter of discussion, especially given the important role of zeolites as cracking and isomerization catalysts in oil refining [15]. On the basis of other experimental results, heteropolyacids, chlorinated aluminas, and Nafion-H have also been presumed solid superacids.

## LIQUID ACIDS AND SUPERACIDS

For liquid acids, the limit of superacidity has been clearly defined by R. Gillespie and widely accepted now as H<sub>0</sub> = –12 in the Hammett acidity function, that is the acidity of concentrated sulfuric acid [16]. Superacid media are generally made by combining already strong fluorinated Brønsted acids such as HF, HSO<sub>3</sub>F, CF<sub>3</sub>SO<sub>3</sub>H with strong Lewis acids such as SbF<sub>5</sub>, TaF<sub>5</sub>, AsF<sub>5</sub>.

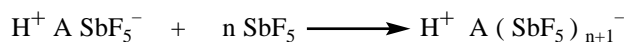
The role of the Lewis acid is to ionize further the Brønsted acid by adduct formation with the corresponding conjugate base. In this way, large anions are generated which are very weak bases and weak nucleophiles (Fig. 1).

A recent reinvestigation [17] of the anionic and cationic composition of the HF-SbF<sub>5</sub> system gives us an indication both of the difference in acidity and reactivity of this system in comparison with the



**Fig. 1** Liquid superacids. Anions and cations.

fluorosulfonic or triflic acid-based superacids. After the first ionization when more  $\text{SbF}_5$  is added to  $\text{HSO}_3\text{F-SbF}_5$  it continues to ionize the acid whereas when it is added to  $\text{HF-SbF}_5$  it prefers to add to the anion which leads to larger anions of the type  $(\text{SbF}_5)_n\text{F}^-$  and fewer protons.



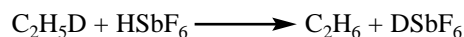
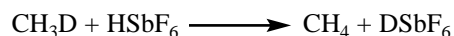
The highest acidity which could be estimated was reached by  $\text{HF-SbF}_5$  (90% molar  $\text{SbF}_5$ ) at  $H_0 = -23$  [18]. The superacidity scale extending over 11 orders of magnitude, it should not be surprising that the reaction mechanism as well as the reactivity of these acids toward hydrocarbons may also change depending on the acidity level and the composition of the superacid.

## ALKANES AND SUPERACIDS

### Methane and ethane

Methane and ethane are the weakest  $\sigma$ -bases [19] available and also the least reactive alkanes. Nevertheless, both compounds are known to undergo direct hydron exchange with superacids. Protonated alkane (methonium and ethonium ions) were suggested as reaction intermediates to rationalize the protium/deuterium exchange observed by Hogeveen and coworkers and Olah [20,21].

Quantitative studies on this type of reaction have been made by Hogeveen [22] with monodeutero-methane and -ethane in  $\text{HF-SbF}_5$  (11:1 molar ratio)



These reactions, which proceed in a very clean manner at room temperature and below, are the simplest examples of intermolecular electrophilic aliphatic substitution. The structure of protonated methane has been extensively studied by *ab initio* theoretical calculations. The conclusion of various groups [23–25] was that at the highest level of calculations there was practically no barrier between the three most stable structures  $\text{C}_s(1)$ ,  $\text{C}_s(2)$ , and  $\text{C}_{2v}$ . This was recently confirmed by the high-resolution IR spectra of  $\text{CH}_5^+$  observed by T. Oka and his group [26] showing that in this ion the five protons bound to the central carbon atom scramble freely.

Methane is slightly soluble in  $\text{HF-SbF}_5$  even at atmospheric pressure (0.005 M) which facilitates direct kinetic studies by NMR and the exchange rate constants for protium deuterium exchange reactions of the isotopologous methanes in the  $\text{DF-SbF}_5$  (6:1 molar ratio) have been recently measured [27].

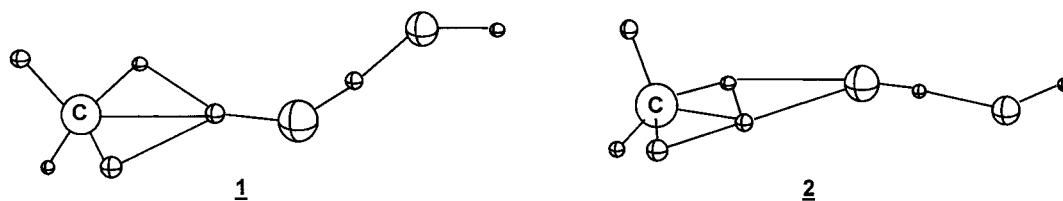


Fig. 2 Calculated geometries of  $\text{CH}_5^+$  solvated by HF.

The first-order rate constants, determined experimentally on the basis of  $^2\text{H}$  decoupled 600 MHz  $^1\text{H}$  NMR time-dependent spectra, are of the order of  $3.2 \times 10^{-4} \text{ s}^{-1}$  at  $-20^\circ\text{C}$  and show a secondary kinetic isotope effect (SKIE) of  $1 \pm 0.02$ .

Recent high-field  $^{19}\text{F}$  NMR experiments [18] have shown that the superacid system  $\text{HF-SbF}_5$  is composed of  $(\text{HF})_x$  polymers solvating  $\text{H}_2\text{F}^+$  ions. DFT and *ab initio* methods have been used by Ahlberg and coworkers [27] to calculate structures, energies of intermediates, activated complexes and SKIEs.

Figure 2 shows the strongly hydrogen-bonded  $\text{CH}_5^+$  ion **1** obtained when methane is protonated by  $\text{H}_3\text{F}_2^+$ . For H/D exchange, additional 4 kcal mol $^{-1}$  are needed to generate the activated complex **2**. For the  $\text{HF:SbF}_5$  system 6:1 molar ratio the suggested solvated ion is  $\text{H}_6\text{F}_5^+$ , but decreased solvation causes only small structural changes and the calculated barrier at 298 K using  $\text{H}_6\text{F}_5^+$  is 22.6 kcal mol $^{-1}$  very close to the experimentally determined values [28, 29]. These results show that  $\text{CH}_5^+$  is not an intermediate but rather a transition state in which the methonium ion is a part of an activated complex strongly solvated by HF as in **2**.

When weaker superacids are used such as the  $\text{HSO}_3\text{F-SbF}_5$  (1:1 molar, Magic Acid $^{\text{®}}$ ) the exchange rate is much slower, and substantial exchange can only be monitored above  $60^\circ\text{C}$ . The relationship between acidity and rate of exchange could be demonstrated as the rate decreases when the  $\text{SbF}_5:\text{FSO}_3\text{F}$  ratio is decreased, and no exchange is observed when pure  $\text{HSO}_3\text{F}$  is used.

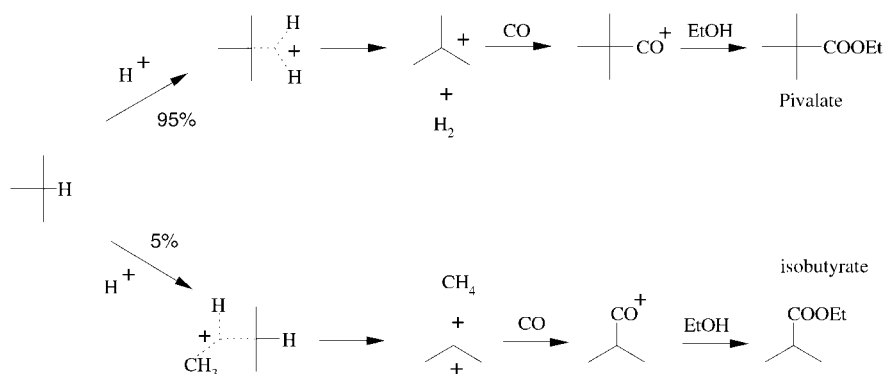
### Small alkanes with more than two carbon atoms in the strongest superacid

Whereas methane and ethane show a very similar behavior toward superacidic media, alkanes with more than 2 carbon atoms undergo a more complex reaction scheme in which C–H and C–C bond cleavage compete with reversible protonation. In order to follow the initial steps, it is very useful to run the reaction in presence of carbon monoxide which reacts rapidly with the initially formed carbenium ions yielding stable oxocarbenium ions unable to activate alkanes by hydride transfer [30].

When isobutane is contacted with  $\text{HF-SbF}_5$  at  $-10^\circ\text{C}$  in the presence of carbon monoxide, analysis of the reaction products both from the gas phase and from the liquid phase can be rationalized by the two pathways described in Scheme 1 [31].

The main pathway for ionization as expected is the protolytic cleavage of the tertiary C–H bond producing stoichiometric amounts of t-butyl cation and hydrogen. The t-butyl ion is converted in ethylpivalate after reaction with CO and neutralization of the superacid with ethanol-bicarbonate mixture. The fact that in earlier work the purely protolytic pathway was questioned [32] has now been explained on the basis of the composition of the  $\text{HF-SbF}_5$  system: when the concentration of  $\text{SbF}_5$  exceeds 20% HF a small and increasing amount of uncomplexed  $\text{SbF}_5$  is present, which participates in the activation by an oxidative process [33].

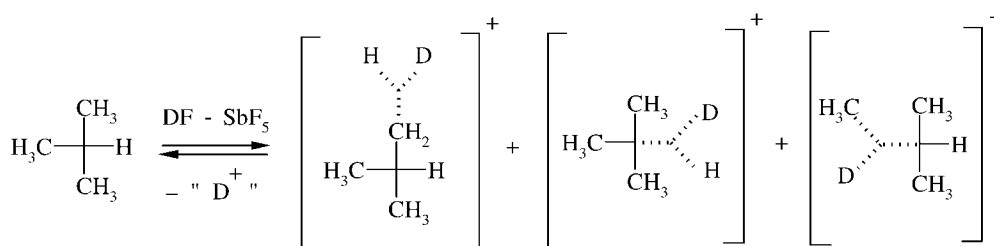
It was shown that the amount of hydrogen and ester obtained from isobutane are stoichiometric only as long as the  $\text{SbF}_5$  concentration is lower than 20%. For higher concentrations the ester production increases steadily, whereas hydrogen formation decreases. An increasing amount of esters is accompanied by a decreasing amount of  $\text{H}_2$  concomitant with reduction of  $\text{SbF}_5$  to  $\text{SbF}_3$ .



**Scheme 1** Isobutane conversion with HF-SbF<sub>5</sub>/CO at 0 °C (GHSV = 250).

The protolytic activation of the alkane is, however, only the apparent part of the reaction as long as the alkane or the acid are not isotopically labeled.

When HF is replaced by DF and the isobutane/CO mixture is bubbled through the DF-SbF<sub>5</sub> (6:1 molar ratio) at -10 °C, the apparent conversion based on ester or H<sub>2</sub> formation is only 4% but the <sup>1</sup>H/<sup>2</sup>H NMR analysis of the apparently unreacted isobutane (96%) shows extensive H/D exchange (18 atom % in the tertiary position and 9 atom % at each primary position). The most plausible rationalization of hydron exchange was via the formation of carbonium ions (here pentacoordinated transition states or intermediates) as described in Scheme 2.

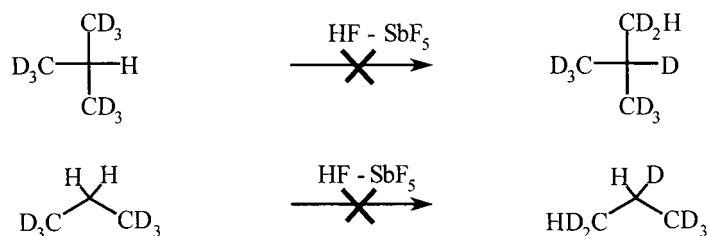


**Scheme 2** H/D exchange versus ionization of isobutane in DF/SbF<sub>5</sub>.

If we take into account a recent high level *ab initio* theoretical study [34] of the i-C<sub>4</sub>H<sub>11</sub><sup>+</sup> species, these cationic species are most probably transition states. The most stable structures are Van der Waals complexes formed by the interaction of the t-butyl cation with hydrogen and of the isopropyl cation with methane. Whereas, among the carbonium ions, the <sup>2</sup>H and <sup>1</sup>H isobutonium ions are at higher energy than the C-butonium cation.

By selective labeling experiments we could show that, in contrast with CH<sub>5</sub><sup>+</sup>, the proton scrambling does not occur in the i-C<sub>4</sub>H<sub>11</sub><sup>+</sup> species. The proton exchange takes place between the alkane and the acid and not between the isotopolog structures of the i-C<sub>4</sub>H<sub>11-x</sub>D<sub>x</sub><sup>+</sup> species (Scheme 3).

Under the same experimental conditions, propane is slightly ionized (2% conversion) but extensively deuterated when bubbled through DF-SbF<sub>5</sub> in the presence of CO (12 atom % in the primary position and 17 atom % in the secondary position). Skeletal rearrangement in protonated propane via carbonium ion type intermediates has been suggested several times based on results obtained with zeo-



**Scheme 3** Absence of scrambling in protonated alkanes.

lites. This type of rearrangement could be excluded as  $^{13}\text{C}$  labeled propane, extensively deuterated in  $\text{DF-SbF}_5$ , showed no  $^{13}\text{C}$  label scrambling [35].

Isopentane is the smallest alkane in the series, having primary, secondary, and tertiary hydrogens. Under similar conditions as propane and isobutane, isopentane was partly ionized in  $\text{DF-SbF}_5$  at  $-10^\circ\text{C}$  (conversion 10%), the recovered 90% of alkane showed extensive deuterium / protium exchange (12 at% of the primary, 16 at% of the secondary, 19 at% of the tertiary hydrogens were exchanged as expected in accord with their relative  $\sigma$ -basicity).

From these experiments some general conclusions can be drawn concerning the behavior of small alkanes in the strongest  $\text{HF-SbF}_5$  system:

- The *reversible protonation* of the alkane
  - is *fast* in comparison with the ionization step,
  - takes place on *all*  $\sigma$ -bonds independently of the subsequent reactivity of the alkane, and
  - involves *carbonium ions* (T.S.), which do not undergo molecular rearrangements.
- *Protonation* of an alkane is a typical acid-base reaction, and carbon monoxide has *no* effect on *this* step.

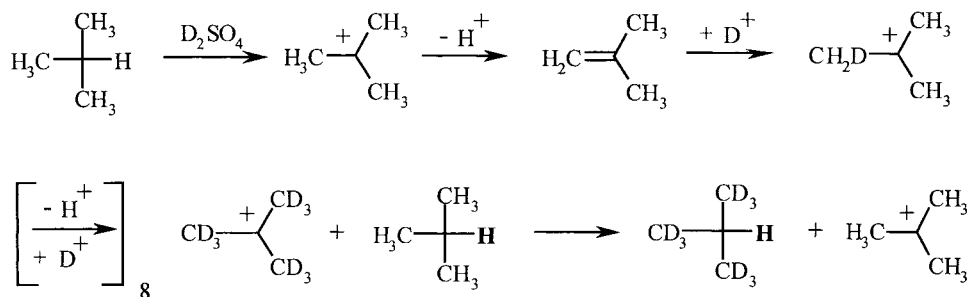
### Small alkanes with more than two carbon atoms in weaker superacid systems

As already observed for methane (*vide supra*), with decreasing acidity, it becomes less and less easy to protonate reversibly C–H bonds. Nevertheless, when alkanes with more than two carbon atoms are used as starting material, carbenium ions are generated by competitive protolytic and oxidative processes. Depending on the strength of the superacid system, protium exchange can take place by two competitive reactions: A) directly via reversible protonation and (B) via deprotonation of the carbenium ion and reprotonation of the alkane.

Whereas the importance of the exchange mechanism via route A is rapidly decreasing with decreasing acidity, route B is facilitated by the increasing basicity of the superacid counterion.

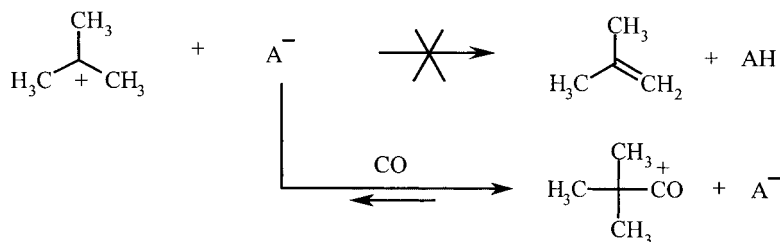
For this reason, when Magic Acid<sup>®</sup> ( $\text{HSO}_3\text{F-SbF}_5$  1:1 molar) is used under the same experimental conditions as above at room temperature isobutane undergoes very slow ionization and the formation of the t-butyl ion can be monitored. However, recovered isobutane shows no exchange as the reversible protonation via carbonium ion transition state does not take place and because the t-butyl ion, stable in this solution at room temperature, does not deprotonate.

When still weaker superacids are used, such as  $\text{HSO}_3\text{F}$  ( $H_0 = -15$ ) or  $\text{CF}_3\text{SO}_3\text{H}$ , ( $H_0 = -14$ ) linear alkanes do not react at room temperature, but branched alkanes are ionized via an oxidative process concerning the reactive tertiary C–H bond. The tertiary cations that are generated undergo reversible deprotonation to alkenes that are reprotonated. This process ends when hydride transfer occurs from unreacted isoalkane, and leads, when deuterated acids are used, to isoalkanes extensively and regioselectively deuterated on the carbons vicinal to the branching carbon. This exchange process is similar to the one observed by Otvos and coworkers [36] in the early 1950s as described in Scheme 4.



**Scheme 4** Deuteration of isobutane in  $\text{D}_2\text{SO}_4$ .

As the reaction is catalytic in t-butyl ion and the deprotonation/reprotonation steps are very fast, extensive regioselective deuteration of the isoalkane is observed at room temperature as shown by GC-MS analysis. The absence of mass 68 (isobutane  $\text{d}_{10}$ ) and the presence of mass 64 due to  $\text{SO}_2$  formation in the oxidative process are typical features in accord with the oxidative activation of the alkane and the Markovnikov-type addition of deuterons on the intermediate isobutene. However, the exchange process does not take place in the presence of carbon dioxide which traps the t-butyl ion and prevents deprotonation (Scheme 5).



**Scheme 5** Trapping of the reactive carbonium ion by carbon monoxide.

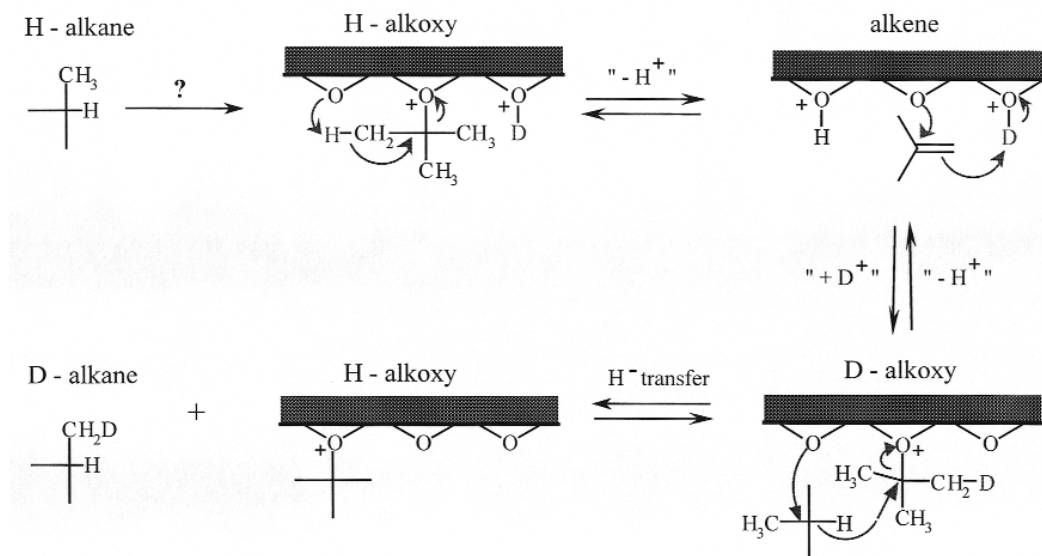
## ALKANES AND SOLID STRONG ACIDS

Since the early reports by Nenitzescu on alkane isomerization on wet aluminium chloride in 1933 [37] all mechanistic studies have led to a general agreement on the carbenium ion type nature of the reaction intermediates involved in acid-catalyzed hydrocarbon conversion. In contrast with this statement, the nature of the initial step is still under discussion, and a variety of suggestions can be found in the literature among which direct protolysis of C–H and C–C bonds, protonation of alkenes present as traces and oxidative activation are the most often quoted [38].

Solid acids are generally oxides containing various OH groups which may function as proton donors. The deuteration of these OH groups allows mechanistic isotope tracer studies. Monitoring the appearance and localization of the isotope in the alkane activated by the solid acids will provide interesting information on the reaction mechanism. H/D exchange of the OH groups occurs readily at moderate temperatures below 200 °C when the solid is exposed to  $\text{D}_2\text{O}$  or at higher temperatures (500 °C) in the presence of  $\text{D}_2$ .

When isoalkanes are contacted with  $\text{D}_2\text{O}$  exchanged solid acids such as zeolites, sulfated zirconias, or heteropolyacids, protium-deuterium exchange takes place slowly even at room temperature but above 100 °C the catalysts are rapidly depleted of their deuterons which are recovered in the alkane.

This exchange process is regioselective as only hydrogens vicinal to the branched carbon are exchanged in accord with a mechanism very similar to the one observed in  $\text{H}_2\text{SO}_4$  and in weak acids (Scheme 6).



**Scheme 6** Deuteration of isobutane on solid acids.

Linear alkanes, known to be less reactive, undergo also H/D exchange by the same mechanistic scheme at slower rates and above 150 °C. This exchange reaction occurs in a very clean way as no side products from cracking and isomerization are observed. The cations, which are adsorbed on the surface, are prone to deprotonation, but the alkenes, which are formed, are rapidly re-protonated before substantial oligomerization can take place.

The occurrence of carbenium ions as reaction intermediates is strongly supported by the observation that the isotopic exchange can be totally suppressed in the presence of carbon monoxide [39]. Furthermore, trapping of the intermediate carbenium ions by CO and water has been observed by *in situ* NMR spectroscopy when isobutane, water, and CO reacted on HZSM-5 zeolite to form pivalic acid [40]. Regarding the small conversion, only a limited number of acid sites are suggested to be strong enough for the initial protolytic activation to take place.

Methane does not react with D<sub>2</sub>O-exchanged solid acids at temperatures below 400 °C. The H/D exchange has, however, been observed on sulfated zirconia (SZ) at 400 °C [41]. When the stronger acid SZA<sub>3</sub> (sulfated zirconia doped with 3% Al<sub>2</sub>O<sub>3</sub>) [42] is used, the exchange rates are substantially higher [41]. In the presence of D<sub>2</sub>O-exchanged zeolites, the H/D process can only be measured at temperatures as high as 500 °C or higher [43,44].

## THEORETICAL APPROACHES

Computer modeling is an increasingly fruitful tool in catalysis, and several research groups have attempted to rationalize hydrocarbon conversion over zeolites from a theoretical point of view. The main problem to be solved is the choice of a model (generally a small cluster) representative of the zeolite framework [44].

Both the carbenium ion and carbonium ion transition states have been investigated. In the presence of the oxygen lone pairs, it is clear that the most stable reaction intermediates will not be free carbenium ion but surface alkoxy groups. The generation of these alkoxy species from alkenes has been



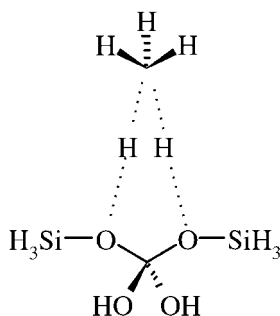


Fig. 3 Calculated transition-state geometry for H/D exchange between zeolite and methane.

demonstrated by Haw and coworkers [45]. The structure of the transition state of the H/D exchange process in methane has been calculated by Van Santen and coworkers [46] to be symmetrical with essentially covalent bond sharing character (Fig. 3).

By modifying the proton affinity, the authors could demonstrate the dependence of the exchange rate on the proton affinity of the zeolite cluster, relating the activity of the catalyst with its acidity. The activity of the catalyst was found to be determined by the acidity differences between the proton-donating and proton-accepting oxygen sites. The calculated energy of activation was close to the experimentally determined values of approximately  $140 \text{ kJ mol}^{-1}$ .

It is interesting to compare this transition state in the solid with the one calculated from the HF-SbF<sub>5</sub> system. In the liquid superacid, the ionic character is very strong, and it is easier to connect the reactivity with the unusual activity of the proton even when solvated by the HF solvent. In contrast, on the solid the theoretical calculated transition state is further away from the carbonium ion type and in line with the much higher temperatures needed to activate the alkane with weaker acids.

## CONCLUSION

Despite large differences in reaction conditions, experimental procedures, and experimental techniques for liquid superacid and strong solid-acid-catalyzed alkane activation, experimental and theoretical results with labelled acids and alkanes show a high degree of resemblance in reaction mechanisms for both systems. Alkanes with more than two carbon atoms generate carbenium ions which, in equilibrium with alkenes, are at the origin of coke formation and deactivation of the catalysts. Methane and ethane less reactive undergo at first a strongly acidity-dependent reversible proton exchange which may occur below room temperature in superacids but only at high temperature on zeolites.

## ACKNOWLEDGMENT

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## REFERENCES

1. H. Pines. *The Chemistry of Catalytic Hydrocarbon Conversion*, Academic Press, New York (1981).
2. G. A. Olah and A. Molnar. *Hydrocarbon Chemistry*, Wiley, New York (1995).
3. A. Corma. *Chem. Rev.* **95**, 559 (1995).
4. *Acid-base catalysis*, special issue of *Catalysis Today*. **38**, 255–390 (1997).
5. A. Dyer. *An Introduction to Zeolite Molecular Sieves*, Wiley, New York (1988).

6. J. A. Martens, W. Souverijns, P. Jacobs. In *Comprehensive Supramolecular Chemistry*, J. M. Lehn (Ed.), Pergamon Press (1996).
7. W. E. Farneth and R. J. Gorte. *Chem. Rev.* **95**, 615 (1995).
8. J. A. Martens, W. Souverijns, W. Van Rhijn, P. Jacobs. *Handbook of Heterogeneous Catalysis*, Vol. 3, p. 633, VCH Wiley (1997).
9. J. A. Dumesic and J. J. Fripiat (Eds). *Acidity in Aluminas, Amorphous and Crystalline Silico-Aluminas, Topics in Catalysis.* **4** (1997).
10. G. A. Olah, S. K. Prakash, J. Sommer. *Superacids*, Wiley, New York (1985).
11. M. Hino, S. Kobayashi, L. Arata. *J. Am. Chem. Soc.* **101**, 6439 (1979).
12. K. Song and A. Sayari. *Catal. Rev. Sci. Eng.* **38**, 329 (1996).
13. T. Yamaguchi. *Appl. Catal.* **61**, 1–25 (1990).
14. W. O. Haag, R. M. Dessau. *Proceedings 8<sup>th</sup> International Congress on Catalysis*, Vol. 2, p. 305, Berlin (1984).
15. A. Corma and A. V. Orchilles. *Microporous Mater.* **35–36**, 21 (2000).
16. R. J. Gillespie. *Adv. Phys. Org. Chem.* **9**, 1 (1972).
17. J. C. Culmann, M. Fauconet, R. Jost, J. Sommer. *New J. Chem.* **23**, 863–867 (1999).
18. R. Jost and J. Sommer. *Rev. Chem. Intermediates* **9**, 171 (1988).
19. G. A. Olah. *Angew. Chem. Int. Ed. Engl.* **12**, 171 (1973).
20. G. A. Olah, G. Klopman, R. H. Schlosberg. *J. Am. Chem. Soc.* **91**, 3261 (1969).
21. H. Hogeveen and A. F. Bickel. *Recl. Trav. Chim. Pays-Bas* **88**, 371–374 (1969).
22. G. A. Olah and J. A. Olah. *J. Am. Chem. Soc.* **93**, 1256 (1971).
23. P. R. Schreiner, S.-J. Kim, F. Schaefer III, P. von Ragué Schleyer. *J. Chem. Phys.* **99**, 3716 (1993).
24. H. Müller, W. Kutzelnigg, J. Noga, W. Klopper. *J. Chem. Phys.* **106**, 1863 (1997).
25. P. von Ragué Schleyer and J. N. D. M. Carneiro. *J. Comput. Chem.* **13**, 997 (1992).
26. T. White, J. Tang, T. Oka. *Science*, **284**, 135 (1999).
27. P. Ahlberg, A. Karlsson, A. Goepfert, S. Nilson, P. Diner, J. Sommer. *Europ. Chem. J.* Accepted November 2000.
28. H. Hogeveen and C. J. Gaasbeek. *Recl. Trav. Chim. Pays-Bas* **87**, 319 (1968).
29. D. M. Brouwer and H. Hogeveen. *Prog. Phys. Org. Chem. Ed. NY*, 180 (1972).
30. J. Sommer and J. Bukala. *Acc. Chem. Res.* **26**, 370 (1993).
31. J. Sommer, J. Bukala, M. Hachoumy, R. Jost. *J. Am. Chem. Soc.* **119**, 3274 (1997).
32. M. Herlem. *Pure Appl. Chem.* **49**, 107 (1977).
33. J.-C. Culmann and J. Sommer. *J. Am. Chem. Soc.* **112**, 4057 (1990).
34. C. J. A. Mota, P. M. Esteves, A. R. Solis, R. H. Lamonedá. *J. Am. Chem. Soc.* **119**, 5193 (1997).
35. A. Goepfert, A. Sassi, J. Sommer, P. M. Esteves, C. J. A. Mota, A. Karlsson, P. Ahlberg. *J. Am. Chem. Soc.* **121**, 10628 (1999).
36. J. W. Otvos, D. P. Stevenson, C. D. Wagner, O. Beeck. *J. Am. Chem. Soc.* **73**, 5741 (1951).
37. C. D. Nenitzescu and A. Dragan. *Chem. Ber.* **66**, 1892 (1933).
38. J. Sommer, M. Hachoumy, R. Jost. *Catal. Today* **38**, 309 (1997).
39. J. Sommer, D. Habermacher, R. Jost, A. Sassi, A. Stepanov, M. Luzgin, D. Freude, H. Ernst. *J. Catal.* **191**, 265 (1999).
40. A. Stepanov, M. Luzgin, A. Sassi, J. Sommer. *Chem. Eur. J.* **6**, 2368 (2000).
41. W. Hua, A. Goepfert, J. Sommer. *J. Catal.* Accepted December 2000.
42. Y. D. Xia, W. M. Hua, Y. Tong, Z. Gao. *J. Chem. Soc., Chem. Comm.* 1899 (1999).
43. B. Schoofs, J. A. Martens, P. A. Jacobs, R. Schoonheydt. *J. Catal.* **183**, 355 (1999).
44. R. A. Van Santen and G. M. Kramer. *Chem. Rev.* **35**, 637 (1995).
45. J. F. Haw, J. B. Nicholas, T. Xu, L. W. Beck, D. B. Ferguson. *Acc. Chem. Res.* **29**, 259 (1996).
46. G. M. Kramer, R. A. Van Santen, C. A. Eneis, A. K. Nowak. *Nature* **363**, 529 (1993).