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Activation of small alkanes on strong solid acids: mechanistic approaches

Jean Sommer*, Roland Jost, Mohammed Hachoumy

Laboratoire de Physico-Chimie des Hydrocarbures, Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg, France

Abstract

Various mechanistic aspects of small-alkane transformations on strong solid acids or superacids are developed in light of recent experiments involving isotope distribution patterns in ^{13}C-labelled alkanes and protium/deuterium exchange between alkanes and D_2O-exchanged catalysts. In comparison with experiments using liquid superacids, similarities and differences in hydrocarbon chemistry between the two types of catalysts are discussed as well as the initial steps leading to catalyst deactivation.

Keywords: Small-alkane transformation; Superacidity; H/D exchange

1. Introduction

Saturated hydrocarbons play a key role in world economy as the main components of raw oil and, as such, are the number one source of energy. Despite their chemical inertness, they also constitute the main feedstock for production of ethylene, propylene and benzene, these being the building blocks of industrial organic chemistry. In order to overcome the poor reactivity of the starting material, the chemical industry relies on processes based on high temperature, noble metal catalysts and/or liquid or solid strong acid catalysts [1,2]. Due to the worldwide trend towards more severe environmental legislation, the strongest and most common acids, such as HF and H_2SO_4, need to be progressively replaced by solid or supported acids, that are easier to handle and that can be recycled following regeneration. This trend is simultaneously reflected by an immense research effort in the field of solid acid and superacid [3] catalysts, focused on the preparation and characterization of new materials and on theoretical and experimental studies aimed at an understanding of the mechanistic aspects of solid acid-catalysed hydrocarbon conversion. In the last decade an impressive number of reviews, special issues and books have been devoted to this subject [4–9].

In the present paper, we will focus on the more recent progress achieved in understanding the mechanism(s) of small alkane activation and conversion of strong solid acids or superacids (sulfated zirconias, heteropolyacids, acidic zeolites) in comparison with the latest observations made with liquid superacids or sulfuric acid. The variety of experimental techniques, such as ^{13}C-labelling of alkanes, D-labelling of catalyst, used in combination with multinuclei high-field NMR spectroscopy, GC-MS spectroscopy and UV spectroscopy, reflect the diversity of research groups working on this subject.

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*Corresponding author.

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2. Strong solid acids or solid superacids (?)

The concept of superacidity is based on an arbitrary but clear definition proposed by Gillespie [10] in the late sixties which consists of defining a superacid as being any acid stronger than 100% sulfuric acid ($H_0 = -12$ on the Hammett acidity scale). Only a few liquid acids such as HF (100%), HSO_3F, CF_3SO_3H and perfluoroalkanesulfonic acids [3], are natural superacids in the $H_0 = -13$ to -15 range. Stronger superacids, up to $H_0 = -24$ [11], can be obtained by associating the Broensted acid with a Lewis acid that displaces the autoprotonation equilibrium and generates large anions.

The extremely low nucleophilicity of those anions, being associated with the availability of protons, lies at the origin of the development of the research area associated with superacidity, ever since the early papers by Olah et al. [12] in 1964 and extending beyond the recent consecration by the Nobel Prize award in 1994. Scheme 1 shows the composition and equilibria of liquid superacids.

Can solid acids be compared with superacids? Are solids, such as sulfated zirconias (SZ) [13] or modified SZ [14] at temperatures below 200°C, or acidic zeolites [15,16] at higher temperature, to be considered as solid superacids? At the present stage, we feel that these questions cannot be answered as long as no clear definition of a solid superacid exists. Gillespie's definition relies on the use of Hammett [17] indicators dissolved in homogeneous liquid acids, assuming a fast acid–base equilibrium between the base and its conjugate acid:

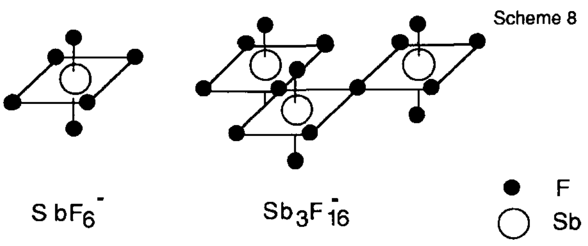
$$H_0 = pK_{BH^+} - \frac{(BH^+)}{(B)}$$

Broensted Acids : HF, HSO_3F, CF_3SO_3H, R_FSO_3H

Lewis Acids :. : SbF_5, AsF_5, TaF_5, BF_3

$$n\,HF \rightleftharpoons H(HF)_n^+ + F^- \qquad n = 1,2$$

$$F^- + n\,SbF_5 \rightleftharpoons (SbF_5)_nF^- \qquad n = 1\text{-}4$$



Scheme 1. Liquid superacids. Composition and equilibria.

However, on the solid, anisotropy of the surface, heterogeneity of the acidic and basic sites, interaction of the catalyst with the solvent and strong adsorption of the indicator are the handicaps in determining acidity by Hammett's technique. Similarly, results based on visual colour changes have raised increasing criticism related with experimental difficulties. The UV spectroscopic investigations by Hall et al. [18] seem to indicate that the acid strength of SZ is comparable to 100% sulfuric acid but somewhat lower than that of H-mordenite. The same conclusion was drawn by other authors on the basis of theoretical calculations, [19] in situ NMR experiments, [20,21] and H/D exchange studies [22].

On the other hand, whether associated with the Hammett technique or not, the superacid character was essentially based on the ability of SZ, and related catalysts, to isomerize *n*-butane at temperatures below 200°C. This method of quantifying the efficacy of solid acids as superacids has the advantage of practicality. As a consequence, the catalytic activity for *n*-butane conversion has been widely used for comparison and correlation with data obtained by various other techniques. In turn, such information can be used to characterize superacidity, such as temperature-programmed desorption (TPD) of various bases, electron paramagnetic resonance (EPR) and NMR chemical-shift measurements.

Nevertheless, using as a test reaction, a reaction for which the mechanism of the first step is unknown, and the nature of the second step is still under discussion, does not seem to be a sound basis for a definition widely applicable to various solids on which these steps might be of a different nature.

The most convincing evidence of the superacidic character of a solid would be its ability to reversibly protonate an alkane, taking advantage of the σ-basicity of a C–H or C–C bond [23,24]. As this point is related directly to the activation step, we will briefly review the present knowledge on this subject.

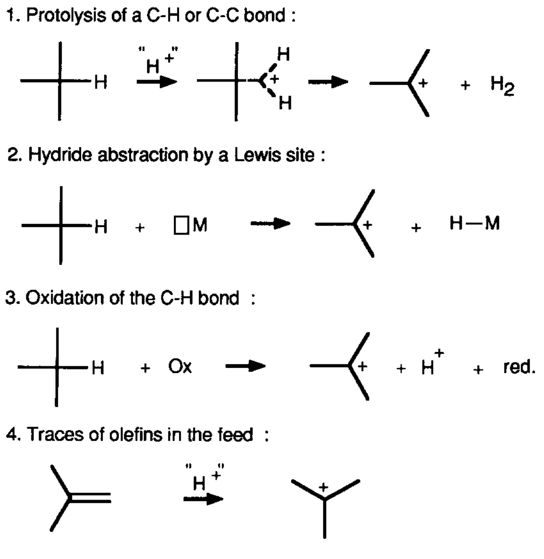
3. Alkane activation – the first step – some tracks

Since the early reports by Nenitzescu on alkane isomerization on wet aluminum chloride in 1933 [25,26], all mechanistic studies have led to general agreement on the carbenium-type nature of the reaction intermediates in acid-catalysed hydrocarbon conversion. In contrast to this consistency, and in the absence of a convincing experimental proof, the nature of the initial step is still under discussion. Here, we examine the four most often quoted suggestions for carbenium ion formation from alkane (Scheme 2).

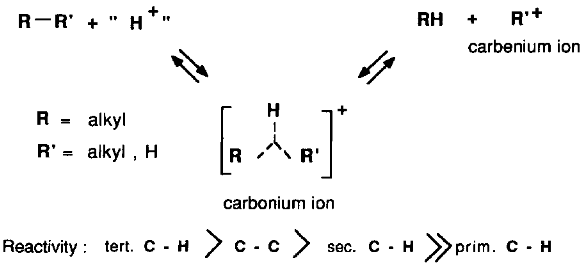
3.1. Protolysis of a C–H or C–C bond

This activation step relies on the concept of σ-basicity (shown in Scheme 3) as proposed by Olah in 1972 [23] on the basis of the reactions observed between alkanes and liquid superacids.

The ability of solids to protolyse non-activated C–H and C–C bonds was first suggested by Haag and Dessau in 1984 on the basis of methane and hydrogen formation in the initial stages of 2-methylpentane cracking at 500°C on H-ZSM5 zeolite [16]. Later, the same group at Mobil presented more data in accord with protolysis of alkanes [27,28]. More recently, Gates reported results on ethane conversion at 200°C on a modified SZ which were rationalized by protolytic activation of the alkane [29]. The reversible formation of carbonium ions, however, was not demonstrated and the ionic nature of the initial step remains unproven.



Scheme 2. The first step of carbenium ion formation from alkanes (here isobutane) on solid acids.



Scheme 3. The concept of σ-basicity of alkanes.

3.2. Hydride abstraction by a Lewis acid site on the solid

Hydride abstraction by alkyl carbenium ions acting as strong Lewis acids is well known in hydrocarbon chemistry as a chain propagation step and also as the last step (desorption) leading to the converted alkane [30]. Hydride abstraction at a Lewis acid site on the solid has also been mentioned several times as the initial step in alkane activation [31,32]. However, till now, no convincing experimental proof has been presented to support this hypothesis, which was also criticized on the basis that formation of a weak metal-hydride bond, under acidic conditions, from 100 kcal mol^{-1} strong C–H bond was not very favourable thermodynamically. It is generally admitted that the Lewis acid sites on the solid play an important role in enhancing the acidity of neighbouring Broensted acid sites [33] and it has been shown, for example, that SZ becomes inactive when the Lewis sites are blocked by carbon monoxide [34].

3.3. Direct oxidation of the alkane

This mode of activation is, of course, limited to systems containing strong oxidants such as SbF_5 in liquid superacids [35], SO_3 in sulfuric acid [36] or on sulfated oxides. The oxidative power of SZ at higher temperatures towards various organic compounds, including alkanes, has been reported recently [37–39] and initiation through one-electron oxidation of the alkane by sulfate groups was suggested [39]. The concomitant formation of SO_2, at the working temperature of the catalyst, has not been reported.

3.4. Protonation of traces of alkenes present in the feed

The presence of hypothetical traces of olefins, initially present in the feed or generated by thermal cracking, was the simplest hypothesis presented decades ago [40]. With improving analytical tools, the absence of traces of alkenes can be monitored and we have shown the influence of the addition of small amounts of isobutene on the rate of H/D exchange between isobutane and D_2O exchanged SZ [41]. However, formation of alkenes from alkanes at low temperature on solid acids has been reported by several authors on the basis of indirect experimental support and will be discussed below.

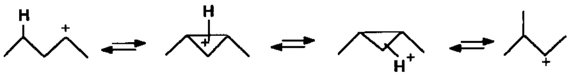
4. n-Butane isomerization: The second step: Mono- or bimolecular?

Conversion of linear-to-branched alkanes is of high economic importance because the latter have a much higher octane rating. Low temperature favours the branched isomers at thermodynamic equilibrium. On the other hand, isobutane is an essential intermediate in the production of alkylates and oxygenates for gasoline.

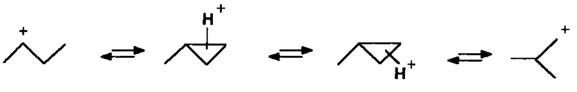
For *n*-pentane and heavier linear-alkanes, intramolecular rearrangement of the secondary ions with branching of the carbon chain can proceed via protonated cyclopropane intermediates without the necessity for forming highly-energetic primary carbenium ions (Scheme 4)

For *n*-butane, however, the branching step necessitates formation of the primary isobutyl cation (Scheme 5).

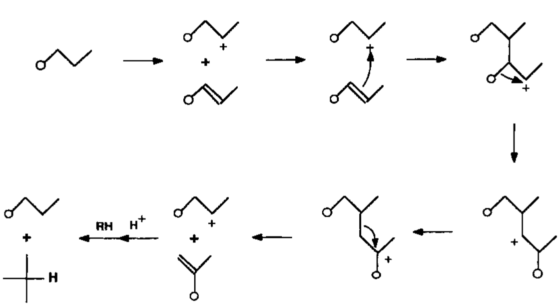
For this reason, and also because of the presence of C_3 and C_5 alkanes, often observed as side-products, a less energy demanding bimolecular pathway has been suggested in which butene, either present in the feed or generated from the butyl cation, is alkylated and in which isobutane is formed by isomerization and cracking of the C_8 intermediate (Scheme 6).



Scheme 4. Isomerization of 2-pentylium ion.



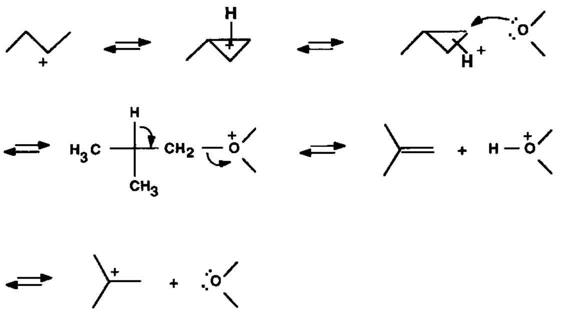
Scheme 5. Isomerization of 2-butylium ion.



Scheme 6. Dimerisation-cracking scheme for *n*-butane isomerization.

The bimolecular nature of *n*-to-isobutane conversion at 400°C on H-Mordenite was noticed more than a decade ago on the basis of kinetic and ^{13}C-labelling experiments [42,43]. However, after the report by Arata et al. [13] on the isomerization of *n*-butane on SZ at much lower temperatures, and the use of this reaction as a test for superacidity, a revival of interest in the mechanistic aspects of butane conversion could be noticed [44–50].

Several groups have reinvestigated the molecularity of *n*-to-isobutane conversion at temperatures below 200°C on sulfated oxides. Analysis of the isotope distribution in the products of mono-^{13}C-labelled *n*-butane reaction on SZ in the presence of hydrogen seemed to support the monomolecular mechanism associated with the superacid character of the solid [44]. In contrast, the binomial distribution of the ^{13}C-label was observed when 1,4-di ^{13}C-labelled *n*-butane was converted on FMSZ which was in accord with the involvement of oligomerization and disproportionation steps [46]. Also in favour of a bimolecular process was comparison of the rates of isomerization on Pt/SZ and Pt/mordenite: the isomerization of *n*-butane did not occur when the one-dimensional microporous



Scheme 7. Nucleophilic assistance in monomolecular 2-butylium ion isomerization on solid oxides.

catalyst was used [49]. It was thus suggested that the two mechanisms may compete:

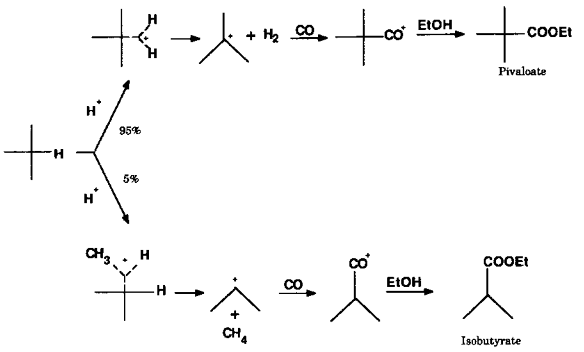
In the absence of hydrogen, the predominant mechanism for *n*-butane isomerization is the bimolecular one which necessitates the formation of butene. In the presence of hydrogen, the concentration of alkenes is kept very low and monomolecular rearrangement having a higher activation energy will prevail.

Here, we would also like to suggest that, on the solid, the *n*-to-isobutane monomolecular conversion could be much less energy demanding than in liquid superacids since the branching step does not necessitate a free isobutyl cation if nucleophilic assistance is involved (Scheme 7).

As formation of these alkenes on the solid acid can be considered as the first step leading to oligomerization, and thus to coke formation and deactivation of the catalyst, this mechanism explains the protective role played by hydrogen against catalyst deactivation; [51,52].

5. H/D exchange studies which underline the fundamental difference between solid and liquid superacids (formation of alkenes from alkanes at low temperature on solid acid catalysts)

The suggestion that electrophilic substitution on alkanes might be possible with strong acids was made as early as 1936 by Ingold, on the basis of H/D isotope exchange studies between D_2SO_4 and isoalkanes [53]. However, it is only thirty years later that both Olah [54] and Hogeveen [55] observed deuterium-protium exchange on deuterated methane in superacid medium under mild conditions of temperature and pressure.



Scheme 8. Isobutane conversion with HF-SbF_5/CO at 0°C (GHSV = 250).

In order to clarify the difference between liquid superacids and solid 'superacids or strong acids', here, we will first recall our results on H/D exchange, occurring between isobutane (or other small alkanes) and a liquid deuterated superacid, such as DF-SbF_5 at 0°C.

5.1. *H/D exchange between alkanes and deuterated liquid superacids*

When a mixture of isobutane and carbon monoxide (1 : 2 : 6 molar ratio) was bubbled during 30 min at 0°C at a rate of 4 ml/min through 1 ml of HF-SbF_5 (8 : 1) molar ratio (Scheme 8) the gaseous products were collected, and the superacid neutralized with ethanol bicarbonate at the end of the experiment. Analysis of the product distribution showed that only 4% of isobutane was converted, mainly by C–H bond cleavage (95%), with the formation of a stoichiometric amount of H_2 and pivalic ester. A small amount of methane and isobutyril ester was also detected in accord with the selectivity rating outlined by Olah for alkane protolysis [56].

When HF was replaced with DF in the same experiment under otherwise identical conditions, the ^{1}H- and ^{2}H-NMR spectra of the unreacted isobutane showed extensive deuteration of the alkane (Fig. 1). Comparison with an internal standard mixture of $CDCl_3/CHCl_3$ indicated that 18 at% of the tertiary and 8 at% of the primary hydrons had been exchanged for deuterium. This gives a total of 0.9 atom D ($0.18 + 9 \times 0.08$) per mole of isobutane which, in comparison with the apparent conversion (0.04),

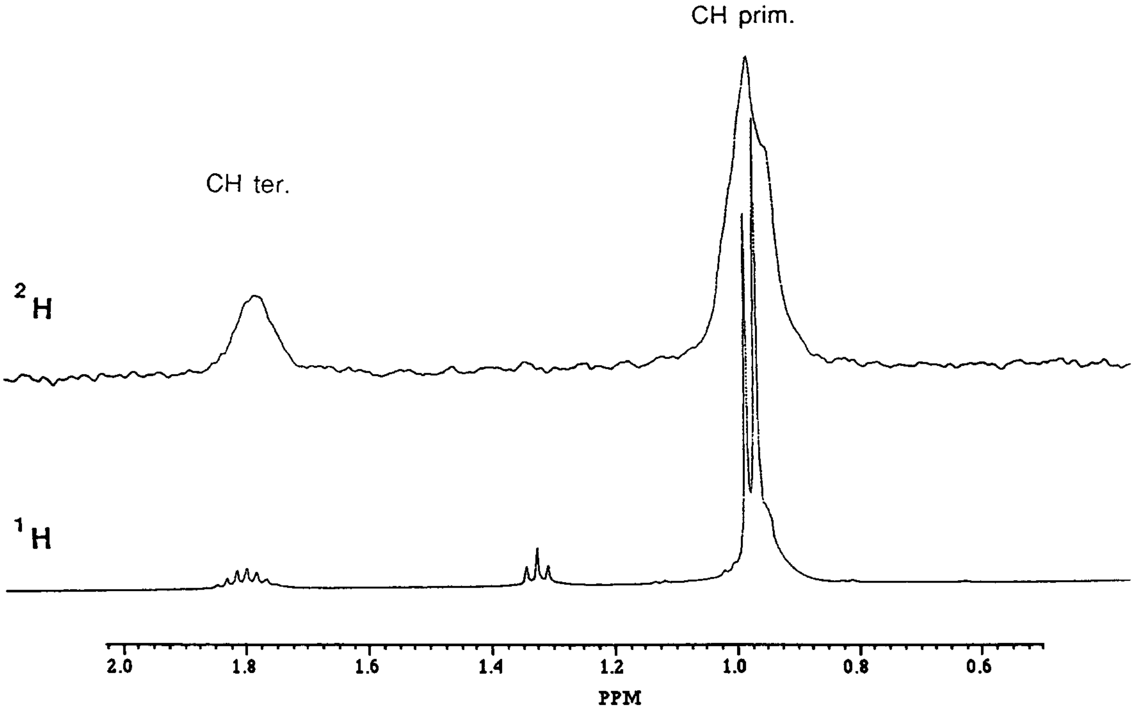
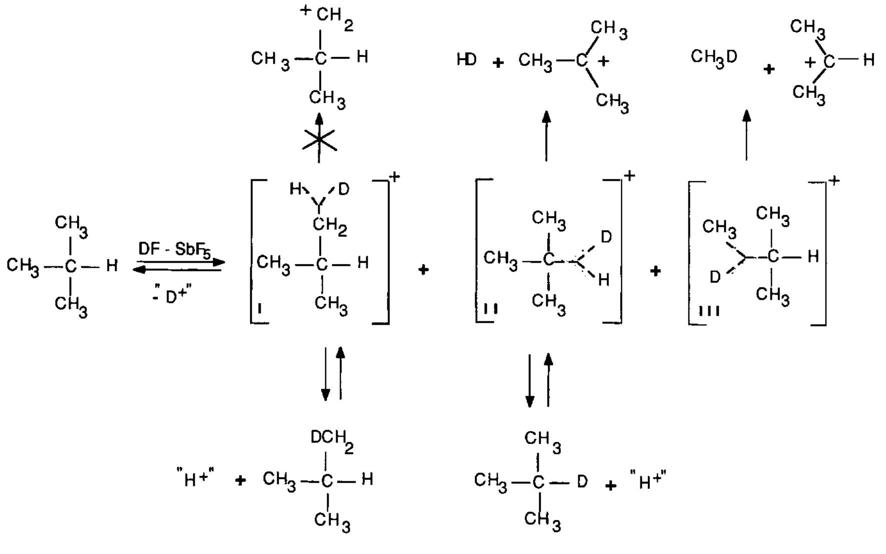


Fig. 1. ^{1}H- and ^{2}H-NMR spectra of isobutane after H/D exchange with DF/SbF$_5$ at 0°C.



Scheme 9. Exchange and protolysis equilibria of isobutane in DF-SbF$_5$.

shows that the reversible protonation of the alkane is very fast relative to protolysis. This regioselectivity is also more in accord with the relative basicities [57] of the two sigma bonds than with their relative reactivity. Scheme 9 describes the activation and isotope exchange mechanism.

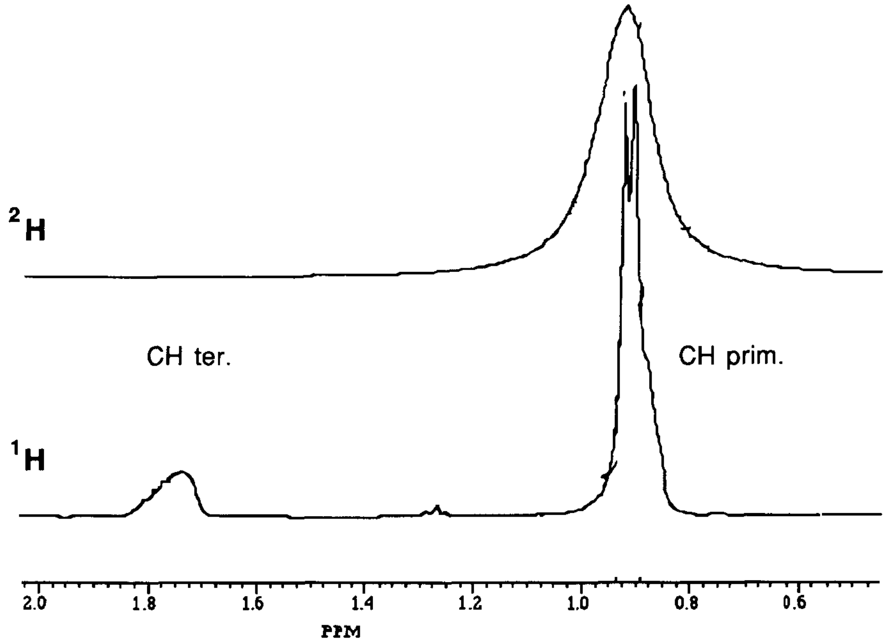


Fig. 2. ^1H and ^2H NMR spectra of isobutane after H/D exchange with D_2O-exchanged USY Zeolite at 200°C.

The conclusion to be drawn from these results, as well as those obtained on *n*-butane [58] and propane [59], is as follows:

In liquid superacids, alkanes behave like σ-bases as suggested earlier by Olah [23]

1. reversible protonation is very fast on all bonds in comparison with ionisation
2. regioselectivity of the protonation step is related to the relative basicities of these bonds, independent of the subsequent chemical reactivity of the protonated alkane.

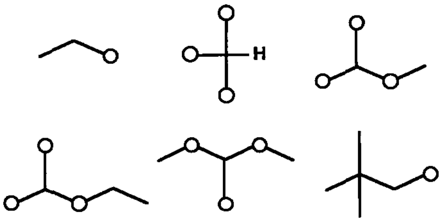
5.2. *H/D exchange between alkanes and D_2O-exchanged solid acids*

In contrast with the preceding results, when isobutane (2 mMol, 6% in N_2) was passed at a rate of 20 ml/min over 500 mg (of any of the D_2O-exchanged solid acids such as SZ, various H-zeolites or heteropolyacids) in the 25 to 200°C temperature range, [22,41,60,61] the ^1H and ^2H NMR analysis of the recovered isobutane showed (in the absence of isomerization and cracking) a truly regiospecific isotope exchange pattern in which only primary hydrons were replaced by deuterons (Fig. 2).

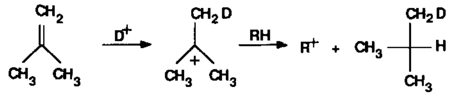
This regiospecificity was observed as a general phenomenon on various small alkanes on different solid acids (Scheme 10).

The extent of isotope exchange is, of course, dependent on the number of acid sites available on 500 mg of catalyst and the time dependence observed at 200°C showed that the catalyst was rapidly depleted of its deuterons [60].

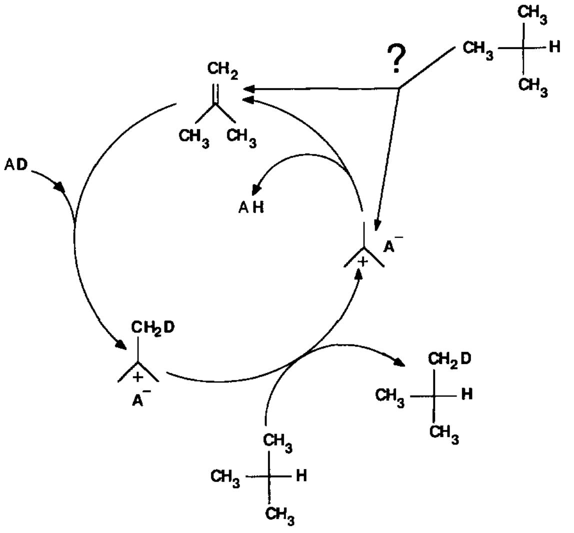
At lower temperature, an induction period was generally observed which could be suppressed by



Scheme 10. Regiospecific H/D exchange between alkanes and D_2O exchanged solid acids. O: site where HD exchange takes place.



Scheme 11. Markovnikov addition.



Scheme 12. Catalytic cycle of H/D exchange on solid acids (AH).

addition of small amounts of isobutene before reaction [41].

These results can be best rationalized by the intermediate protonation (here deuteronation) of the corresponding alkene generated on the solid as a reaction intermediate. This scheme was proposed in the early fifties by Stevenson to explain the H/D exchange pattern observed in isoalkanes contacted with D_2SO_4 [62]. It is based on the rule (adapted from Markovnikov's observations [63]) which states that protonation of an alkene should always lead to the most stable trivalent carbenium ion (Scheme 11).

Thus the regiospecific deuteration can be rationalized in the form of a catalytic cycle (Scheme 12).

As already pointed out, the nature of the activation step of the alkane has not been unambiguously demonstrated on solid acids and is intriguing, especially when the reaction takes place at temperatures as low as room temperature [60].

In protic superacids, such as HF-SbF_5, the stoichiometric production of hydrogen and *t*-butyl ion from isobutane is a clear indication for protolytic cleavage of the tertiary C–H bond. In the absence of protic acid, SbF_5 itself has been shown to oxidize isobutane with formation of SbF_3, HF and the *t*-butyl cation [35]. In sulfuric acid, the formation of SO_2, during ionization of isobutane, is also in accord with an oxidative process involving SO_3 [53].

On the solid acido-basic catalyst, where the alkene and the cation are in equilibrium, mechanistic conclusions, as to which one is first, cannot be drawn from product analysis alone. Protonation of isobutene by the deuterated solid acid gives the α-deuterated carbenium ion which, in turn, gives a new carbenium ion and 1-deutero 2-methyl propane via hydride transfer from incoming isobutane. The high deuterium content in isobutane collected during the first few minutes of the experiment shows, in fact, that deprotonation and re-deuteronation can occur several times over the catalytic cycle before desorption of the isoalkane [60]. Formation of alkenes from alkanes, or from the carbenium ion intermediates, gives the opportunity to underline the fundamental difference between liquid superacids in which neither nucleophile nor proton acceptor is present and solid acids or superacids based on oxides in which the lone pairs of each oxygen represent as many basic sites.

To sum up, whatever the acid-strength of the Broensted sites, associated or not with Lewis sites, the carbenium ions formed on the solid will have the possibility (besides rearrangement, hydride transfer and β scission) to return a proton to the surface, thus generating an alkene.

If this alkene is not immediately reprotonated, alkylation and oligomerization processes will progress, giving higher molecular weight material and finally leading to the formation of coke and deactivation of the catalyst. It is interesting to note that whereas during the previous decades the idea of alkene formation from small alkanes on solid acids was rejected, it has been rapidly progressing in the recent literature [45–50] mainly in relation with the *n*-to-isobutane isomerization mechanism.

Directly relevant to this point is the recent UV-visible diffuse reflectance study, (DRS) by Knözinger et al. [52] of the deactivation and regeneration of SZ on which *n*-butane was isomerized. In the presence of hydrogen, the catalyst was stable. Under helium, however, at temperatures 120–200°C, during the deactivation period formation of allylic and polyenylic cations from the *n*-butane precursor could be monitored spectroscopically as well as the disappearance of the corresponding bands when the catalyst was reactivated.

The stability of enylic ions in concentrated sulfuric acid is well known. The generation of these ions from various precursors and their UV and NMR spectroscopic properties have been reviewed by Deno [64] and Sorensen [65]. Recently, Haw has reported the direct observation of stable cyclopentenyl cations in H-Beta zeolite by solid-state NMR [66]. Formation of polyenylic cations from isobutane in concentrated sulfuric acid has also been observed [67].

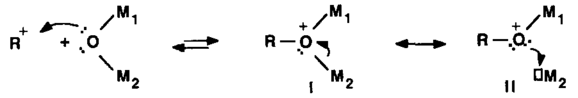
All these results emphasise the similarity between concentrated sulfuric acid and strong solid acids. At this stage we would like to address the question of the 'true' nature of carbenium ions as reaction intermediates on the solid. A couple of years ago this question was raised on the basis of theoretical calculations [68] supporting the idea that carbenium ions were not intermediates but only high-energy transition states in solid acid catalysed reactions. It is well known, however, from solution chemistry that carbocationic intermediates should not be considered as free ions. Since the pioneering work of Hughes and Ingold [69] in the thirties up to the first NMR observations of alkyl carbenium ions by Olah et al. [70] in the sixties, the interaction of solvent with these reaction intermediates has been thoroughly studied:

The lifetime of carbocations, that is their existence as transient reaction intermediates at a given temperature, depends only on two factors:

1. the ability of the ion to delocalize its positive charge over its own molecular framework by inductive and resonance effects; and
2. the nucleophilicity, or basicity, of its environment.

For this reason, taking two extreme cases as examples, the primary ethyl cation could never be observed in the condensed phase even in the strongest superacid media whereas trityl (triphenyl methyl cation) derivatives are stable salts, commercially available or may be directly synthesized and observed inside large-pore zeolites [71].

The nature of the carbenium ions on the solid should not be an exception. Due to the nucleophilicity of the oxygens present in the solid, alkylcarbenium ions are stabilized in the form of alkoxy species **I** which can also be considered as oxonium ions **II** (Scheme 13). Such species have been directly observed by solid-state NMR spectroscopy [72–77].



Scheme 13. Secondary and tertiary alkyl carbenium ions on the surface of solid acids.

The equilibrium can, however, be shifted towards the carbenium ion when the positive charge is delocalized, as in allylic ions or aromatic ions. In this case, carbocations can be observed by solid-state NMR spectroscopy as persistent species in the presence of the solid acid catalyst [77].

6. Outlook and conclusion

Despite the economic importance of acid-catalysed alkane conversion and the intense research effort devoted to clarifying the mechanism of formation of the reaction intermediates, the question of the mechanism of the C–H bond activation step at low temperature stays open: Why does the addition of manganese and iron oxide to SZ dramatically increase the reactivity of this solid acid? How are alkenes formed from alkanes at low temperature on all these solid acids? Can the initial carbenium ion be formed as smoothly, and in a similar manner on the surface, as it has recently been reported with a metal-free enzyme on the basis of steric constraints in the acid–base interaction [78] or does the reaction start as redox (monoelectronic) process as suggested by Rabo [79] in the early eighties? Obtaining answers to these questions presents a formidable challenge, especially as the activation step of alkane and the deactivation processes of the catalyst have an intimate relationship.

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