Reaction mechanisms on liquid and solid acid catalysts. Correlation with acidity *

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The probe bases used for measurement of strength of acid catalysts need to be structurally similar to the catalytic substrates. Traditional acidity measurements are inapplicable when the hydron transfer forms a tight ion pair, as on solid acids. Also, solid acids are much weaker than liquid acids of similar structure. Alkane activation by C–H and C–C cleavage, evidenced in strong superacids, does not occur in less strongly acidic media. The reactivity patterns and structure–reactivity relationships are the same for the cationoidic species (weakly coordinated carbocations) occurring in the less strong acids as for the full-fledged carbocations intervening in superacids. Even in trifluoromethanesulfonic acid, a weak superacid, the first step in alkane activation is an oxidation, forming unsaturated carbocations. On sulfated zirconia, the first step of alkane reactions is a one-electron oxidation. Mechanistic features incompatible with standard (or "traditional") carbocationic processes, are observed in the reaction of 3-methylpentane on the zeolite HZSM-5.

KEY WORDS: acid strength; acidity measurements; bifunctional catalysts; carbocations; cationoidic intermediates; oxidation; superacid catalysts

1. Significance of catalyst acid strength and its measurement

In the acid-catalyzed conversion of an organic compound, the acid strength of the catalyst must be appropriately matched with the basic strength of the substrate. Thus, carbocationic reactions of alkenes occur in trifluoroacetic acid (H_0 -3), as shown in the formation of trifluoroacetates [1], or on slightly acidic solids, conditions under which alkanes are inert. Even among alkenes, ethylene adds sulfuric acid of at least 94% concentration (H_0 ca. -9.6) at 80 °C, whereas isobutene reacts with 60% H_2SO_4 (H_0 -4.5) at 0 °C [2]. On the other hand, if the olefin is reacted with an acid stronger than the optimum, the carbocation does not find a nucleophile in solution and the unwanted reaction of the carbocation with the olefin excess can occur.

The matching of strength requires an understanding of acid strength of the catalysts, which has been hindered by the fact that the acidity evaluation methods could not be applied to the catalysts in the conditions of their use [3]. We have developed a method of acidity measurement by NMR spectroscopy, described elsewhere [4], in which unsaturated ketones are used as indicators. The acidity-sensitive parameter is the difference between the chemical shifts of the two carbon atoms of the double bond, α and β to the carbonyl: $\Delta\delta = \delta(\mathrm{C}\beta) - \delta(\mathrm{C}\alpha)$. The value of $\Delta\delta$ at infinite dilution ($\Delta\delta^0$) was correlated with H_0 [4,5]. The method was successfully applied to molecular acids, as well as to complex and composite acids and to real-life catalysts from industrial installations [3b,4].

For the measurement, the basic strength of the probe base must also be matched with the strength of the investigated acid, a point obvious for NMR studies [3], but not always understood in calorimetric measurements. Yet, as pyridine is completely converted to pyridinium ions in 2 N HCl, dissolving it in a much stronger acid will not give a higher heat of *neutralization* than that measured in 2 N HCl. Any extra heat evolved and measured comes from other interactions. In a favorable case, it might be a measure of the increase of anion stabilization (see below) in the stronger acid and thus reflect the difference in acid strength, but not necessarily in a simple way.

We have also stressed that for correlation of hydrocarbon reactivities, it is important to use probe bases in which the positive charge acquired upon hydronation (hydrogen cations: "hydron" (natural isotopic distribution), "proton", "deuteron", and "triton" [6]) is found in the hydrocarbon skeleton and not in the immediate vicinity of a polar group [3,4]. (This is why *saturated* ketones are not suitable. In the unsaturated ketones, employed as probe bases in our studies, the positive charge acquired upon hydronation and reflected in a change in the NMR chemical shift is found mostly at $\mathrm{C}\beta$.) There are, nonetheless, a number of reports in which water was proposed as a probe base for assessing the strength of solid acids, particularly zeolites [7]. There is no agreement, however, among the authors as to whether water is hydronated or not in these media [7]. The unusual properties of the water–hydronium ion acid–base pair are also manifested in the ^{17}O NMR chemical shift, which varies nonmonotonically between water and hydronium ion, thus pre-

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cluding the determination of the degree of hydronation by interpolation [8].

Another difficulty is encountered when the hydron transfer produces a tight ion pair. In such a case, Hammett-type measurements cannot be used at all. Again, water offers a good example here. Its basicity was evaluated by the measurement of the acid strength of the hydronium ion, which was found to vary greatly with the anion. Thus, a $1:10^3:10^5$ acid strength ratio was found for the hydronium trifluoromethanesulfonate (triflate), fluoroborate, and phosphotungstate [9]. Therefore, there is a very large change in water basicity toward different acids in stoichiometric ratio, which stems most likely from the variation of the activity coefficient of ions in the ion pair. Moreover, after the completion of the first version of this paper, a computational study has shown that even for sites of equal acid strength the degree of hydronation of water changes dramatically with the relative position of sites and diameter of pores [10]. The practical consequence of these findings is that water is useless as an indicator of strength of sites in solid acids. On the other hand, any base forms a tight ion pair upon hydron transfer from a solid acid site, so the application of Hammett measurements to solids [11] is *in principle* incorrect [3b,4]. The derived H_0 values do not correlate with catalytic activity [12]. Solid acids belong to a group of acids for which no acidity function can be defined; these species were named non-Hammett acids [4,5].

Ion pairing also influences profoundly the structure, whence also the reactivity, of the carbocation intermediates, as demonstrated by the high-level *ab initio* MO calculations conducted on the 2-propyl [13a] and *tert*-butyl cations [13b] in ion pairs [13].

For non-Hammett acids, only empirical and more limited evaluations of acid strength are possible. Comparison of acids by a relative hydronating ability parameter was proposed [3a,4]. The probe bases employed need to be as much as possible similar to the bases or catalytic substrates with which the acid is intended to react. Thus, a calibration with a nitrogen probe base cannot be expected to have a high predictive value for the strength of the acid toward carbon bases.

A practical approach for comparing the strength of two non-Hammett acids was provided by the $\Delta\delta$ parameter measured at stoichiometric ratio of acid to probe base ($\Delta\delta^1$) [14]. It was shown that the hydron transfer to bases devoid of polar groups, like the hydrocarbons, requires the cooperation of at least two molecules of acid for each hydron transferred [14c]. It was also established that the effect of solvents upon the strength of acids is determined by their basicity (strength-reducing), polarity (enhancing), and hydrogen bonding, or *anion-stabilizing*, ability (also enhancing), which is more important than polarity [14]. The results are shown in table 1. It can also be seen in the table that silica gel, shown earlier to be a strong hydrogen bond donor [15], also has an acidity enhancing effect.

An alternative approach, applied to comparing acidities in the strong acid and superacid ranges, has used aromatic hydrocarbons as probe bases. Because the charge in the cation is distributed only among carbon and hydrogen atoms, the results are relevant for the evaluation of catalysts used in hydrocarbon conversions [3a,4,14,16]. We found that the strength ratio of the acid systems CF_3SO_3H (TFMSA), 30 : 1 HF–TaF_5, 4 : 1 HF–TaF_5, and 4 : 1 HBr–$AlBr_3$ is $1:10^{11}:2\times10^{11}:10^{12}$ [3]. As it is well known, TFMSA is about hundred times stronger than 100% H_2SO_4, the conventional beginning of the superacid range of acidities.

Table 1
Effect of the solvent on the hydronation of mesityl oxide (**1**) by 95.8% sulfuric acid[a], evaluated by the $\Delta\delta^1$ parameter.

No.	Solvent	$\Delta\delta^1$	$\Delta\delta$(B)[b]	$\Delta\delta^1 - \Delta\delta$(B)
1	–[c]	55.00	29.70	25.30
2	SO_2	58.40	32.42	25.98
3	Sulfolane	38.26	30.15	8.11
4	HFIP[d]	71.35	39.13	32.22
5	Silica gel	60.00	30.70	29.30

[a] Concentration ca. 0.5 M, equal to that of mesityl oxide (interpolated values).
[b] The $\Delta\delta$ value at the same concentration in the absence of acid; see [12].
[c] Neat acid.
[d] HFIP = hexafluoroisopropanol.

Table 2
Values of the $\Delta\delta^1$ parameter for **1** dissolved in liquid acids or adsorbed on solid acid surfaces.[a]

No.	Acid	H_0	$\Delta\delta^1$
1	Nafion-H	–	50–51[b]
2	Amberlyst 15	–	32.4
3	100% MSA[c]	−7.60	41.0
4	80.52% MSA	−4.35	38.0
5	89.80% H_2SO_4	−9.00	53.0
6	86.35% H_2SO_4	−8.50	51.0
7	80.03% H_2SO_4	−7.50	48.3
8	60.21% H_2SO_4	−4.50	39.5

[a] For a more comprehensive collection of data, see [18].
[b] Broad signal.
[c] MSA = methanesulfonic acid.

It is noteworthy that the $AlBr_3$ and $AlCl_3$ composites had been considered “borderline” between strong acids and superacids [17a] and their catalytic chemistry was not recognized as superacid chemistry. Following our reports [16], that evaluation was modified [17b].

In order to relate the acidity of solids to that of acids in solution, we have assessed the relative hydronating ability of pairs of liquid and solid materials that have very similar structures, with the $\Delta\delta^1$ parameter [14b]. The results are shown in table 2. A more comprehensive collection of data is also available [18]. If the nature and way of manifestation of acidity in solution and on the solid surface were the same, the degree of hydronation of the probe base should be similar within each pair. Instead, Amberlyst 15 gave a $\Delta\delta^1$ value for mesityl oxide (**1**) much lower than 100% methanesulfonic acid (MSA), its liquid analog, and even lower than 80.5% MSA. Likewise, the perfluorinated polymersulfonic acid, Nafion-H, had been referred to as a solid superacid [19], by analogy with TFMSA (H_0 −14.2). Yet, the $\Delta\delta^1$ value of **1** placed Nafion-H close to 85% H_2SO_4.

Our results have demonstrated that solid acids are consistently much weaker than liquid acids of similar structure. This is understandable, because hydrogen bonding is more important than polarity in promoting the acid–base reaction [14c,20], which can occur in non-polar solvents only if it leads to strongly hydrogen-bonded tight ion pairs [20], in equilibrium with hydrogen-bonded neutrals (equation (1)). For hydrocarbon bases, the conjugate acids (carbocations) do not normally form strong hydrogen bonds. A specific interaction with the solvent would be based on the solvent nucleophilicity, which destroys the carbocation. Formation of a free or weakly coordinated carbocation, necessary for catalysis, is possible only through the strong stabilization of the anion by interaction with a Lewis acid (as in the composite superacids [17,21]) or with an excess of acid, by hydrogen bonding (equation (2)) [14,20].

$$\mathrm{AH}\cdots\mathrm{B} \rightleftharpoons \mathrm{A}^- \cdots \mathrm{H{-}B}^+ \qquad (1)$$

$$n\mathrm{AH} + \mathrm{A}^- \rightleftharpoons (\mathrm{AH})_n\mathrm{A}^- \qquad (2)$$

$$n\mathrm{SOH} + \mathrm{A}^- \rightleftharpoons (\mathrm{SOH})_n\mathrm{A}^- \qquad (3)$$

Because of the rigidity of the lattice or backbone, the *cooperative effect* [14] of equation (2), by which non-reacting acid sites assist the hydron transfer from the reacting site to a base or catalytic substrate, cannot be manifested by solid acids. As it is manifested toward very weak, nonhydrogen-bonding bases, superacidity requires very strong anion stabilization. The consequence of this observation is that solids can hardly, if at all, manifest Brønsted superacidity [22]. The “mounted” superacids like $\mathrm{AlCl_3}$ on sulfonic resins, $\mathrm{SbF_5}$ on metal oxides or graphite, etc. [17d], most likely have a superacid liquid layer at the surface of the solid, equivalent to the “lower layer” [21b] or “sludge” [23] on the catalyst in the reactions catalyzed by aluminum halides [16]. The molecules of acid in the complex anion of equation (2) can, however, be replaced by molecules of a strongly hydrogen-bonding solvent (*anion stabilizing solvent*) (equation (3)) [14]. Indeed, Nafion-H exhibits superacidic strength when its surface is covered by such a solvent [14b]. This observation was exploited in catalytic applications [24].

2. Mechanism of hydrocarbon conversions and its connection to acidity

In the carbocationic reactions [25] of an alkane, there are four essential steps: formation of a carbocation from the reactant (“initiation,” equation (4)), conversion of the carbocation of the reactant to that of the product (equation (5)), hydride abstraction by the latter from a molecule of starting material (equation (6) [26]), and loss of cationic state (equation (7)):

$$\mathrm{R{-}H} \rightleftharpoons \mathrm{R}^+ \qquad (4)$$

$$\mathrm{R}^+ \rightleftharpoons \mathrm{R}'^+ \qquad (5)$$

$$\mathrm{R{-}H} + \mathrm{R}'^+ \rightleftharpoons \mathrm{R}'{-}\mathrm{H} + \mathrm{R}^+ \qquad (6)$$

$$\mathrm{R}^+, \mathrm{R}'^+ \rightleftharpoons \mathrm{R{-}H}, \mathrm{R}'{-}\mathrm{H} \qquad (7)$$

In a catalytic process, the repetition of the steps of equations (5) and (6) leads to a chain reaction. The catalyst intervenes in an essential manner in the step of equation (4) and it provides the counterion for the cations, in equations (5) and (6). It is possible and even likely, however, that the reaction can sometimes occur in “cationoidic species,” in which the carbocations are not fully formed (weakly coordinated carbocations) [27]. It appears that the reactivity pattern and structure–reactivity relationships are the same for the cationoidic species as for the full-fledged carbocations. The step of equation (7) occurs when the catalyst is deactivated (“dies”) or the reaction is quenched.

Equation (5) includes isomerization [25,28] and cracking to a smaller carbocation and an alkene. If the acid is strong enough, the alkene is hydronated and forms also a cation, as shown in equation (8) for the cracking of the trimethylpentyl cation, $\mathrm{C_8H_{17}^+}$, in HF–$\mathrm{SbF_5}$ [29]. The number of carbocations doubles and chain branching occurs. The reverse of the cracking reaction, alkane–alkene alkylation, is faster than hydronation in HF–$\mathrm{SbF_5}$, because in the presence of 2-propyl cations the $\mathrm{C_8H_{17}^+}$ cations formed $\mathrm{C_7H_{15}^+}$ cations (equation (9)) at a lower temperature than they had formed $\mathrm{C_4H_9^+}$ cations in the previous experiment [29].

$$\begin{aligned}&\mathrm{Me_2CH{-}CHMe{-}C^+Me_2}\\ &\quad \rightleftharpoons \mathrm{Me_3C{-}CH_2{-}C^+Me_2} \rightarrow 2\mathrm{Me_3C^+} \qquad (-85\,^\circ\mathrm{C}) \quad (8)\\ &\mathrm{Me_3C{-}CH_2{-}C^+Me_2} + \mathrm{Me_2CH^+}\\ &\quad \rightarrow \mathrm{Me_3C^+} + \mathrm{Me_2CH{-}CH_2{-}C^+Me_2} \qquad (-95\,^\circ\mathrm{C}) \quad (9)\end{aligned}$$

At lower acidities, the alkene formed by cracking or hydron loss from the product cation polymerizes (at low temperature) or is evolved as gas (at high temperatures). Carbocationic pentane cracking was shown to require elimination and alkylation before C–C bond cleavage [30]. Dimeric cations were also proven as intermediates in the isomerization of small alkanes [31].

Brønsted acids form carbocations from alkanes by cleavage of C–H or C–C bonds. Indeed, alkane isomerization by $\mathrm{AlCl_3}$ [21a] required the addition of 0.5–1.0 equivalents of water [32], to form the Brønsted acid; hydrogen gas was evolved as a by-product, demonstrating the intervention of equation (10) [21b]. The cleavage proceeded cleanly and reversibly at 0 °C with HF–$\mathrm{SbF_5}$ ($\mathrm{A} = \mathrm{Sb}_x\mathrm{F}_{5x+1}$) [21c,d]:

$$\mathrm{AH} + \mathrm{R_3C{-}H} \rightleftharpoons \mathrm{A}^- + \mathrm{R_3C^+} + \mathrm{H_2} \qquad (10)$$

$$\mathrm{AH} + \mathrm{R_3C{-}R'} \rightleftharpoons \mathrm{A}^- + \mathrm{R_3C^+} + \mathrm{R'H} \qquad (11)$$

The cleavage of C–C bonds, equation (11), first demonstrated by Oelderik [21c], was then studied by Hogeveen [21d,33] and Olah [34]. Isohexanes had been seen in the methylcyclopentane (MCP) isomerization with $\mathrm{AlCl_3{\cdot}H_2O}$, but they were rationalized by a β-cleavage of $\mathrm{MCP^+}$ [21b], a reaction shown later not to occur in the long-lived $\mathrm{MCP^+}$, even at 110 °C [35].

Alkane reactions involved also condensations to heavier ions in $1:1$ $\mathrm{FSO_3H{-}SbF_5}$ [34], but not in $\geqslant 15:1$ HF–$\mathrm{SbF_5}$ [33]. This condensation was said to prove that hypervalent structures, "carbonium ions" intervened as *intermediates* in the cleavage of C–H and C–C bonds (equation (12)) [17,36].

$$AH + R_3C\text{–}H \rightleftharpoons A^- + R_3CH_2^+ \rightarrow \text{products} \qquad (12)$$

It was pointed out, however [21e], that the special features of the alkane reaction in 1 : 1 FSO_3H–SbF_5 are not in line with a hydron transfer mechanism (equation (12)), because HF–SbF_5 is the stronger acid [37]. The results in FSO_3H–SbF_5 were not compatible with hydronation [38], but indicated an oxidation superimposed over the acid–base reaction [39]. The counter argument [17c] that the Sb–H bond is too weak to justify a hydride abstraction by SbF_5 from the hydrocarbon [40] is not convincing, because the oxidation should involve a one-electron transfer, rather than a hydride transfer; this point will be discussed below. We can also mention that no hypervalent intermediate with the formula $(C_nH_{2n+3})^+$ was evidenced as a persistent [14c] ion in superacid; all equilibrium species claimed to contain pentacoordinated carbons have been hydronated cyclopropanes [21e]. There is agreement, however, that $(C_nH_{2n+3})^+$ ions are transition structures for alkane reactions in superacids, such as H/D exchange, which is faster than acidolysis (equation (10)) and in which tertiary C–H bonds are ten times more reactive than primary C–H bonds [21e]. It is also unquestionable that all the acids proven to activate alkanes by hydron attack as in equations (10) and (11) possess superacidic strength, including $AlCl_3{\cdot}H_2O$ and $AlCl_4^-{\cdot}H_3O^+$ [4,9].

3. Acid strength and mechanism in catalysis by solid acids

The theoretical representations of carbocations in superacids have also permeated the discussion on hydrocarbon reactions with solid acid catalysts. Thus, the high catalytic activity of some H-zeolites was ascribed to sites of superacidic strength present on these materials [41]. A partially exchanged (51% H) NaHY was said to have an H_0 value of -14.52, which would make it stronger than TFMSA [41b]. Alkyl cations [42] and the unsubstituted allyl cation [43] were claimed to be formed as "stable" (persistent [14c]) entities from alcohols or alkenes, whereas toluene was said to be converted to the arenium ion on HZSM-5 [44]. For comparison, we can note that TFMSA did not hydronate toluene to any measurable extent at equilibrium [45]. A speculative model of zeolites as "pseudoliquids" was offered to explain their superacidity [46].

The representation of zeolite acid sites as superacidic was certainly involved in the proposal of a mechanism involving pentacoordinated ("carbonium") ion *intermediates* in alkane cracking [47]. It was argued that on HZSM-5 at low temperature, the reaction is controlled by the hydride transfer and the cation R'^+ in equation (6) would be formed from an olefin ("*Ol*", equation (13)), whereas at high temperature equation (12) should operate [47]. It was not noticed that "*Ol*" was a cracking product and, therefore, the "initiation" step *in which the catalyst participates* need not be different for the two cases. The difference between the two cases then should be that olefin hydronation (equation (13)) produce secondary cracking at low temperature, which the authors indicated to be unimportant.

$$\text{“}Ol\text{”} + AH \rightleftharpoons R'^+ + A^- \qquad (13)$$

Also, hydrogen loss from the pentacoordinated ion would give (equation (10)) the carbocation which was the intermediate in the other mechanism ("carbenium" route). Thus, when *more* hydrogen was formed, the product distribution on the "carbonium" route should differ *less* from that on the "carbenium" route, opposite to what was claimed [47]. Nevertheless, this mechanism was accepted and extended to other reactions and catalysts [48].

At about the same time with the studies cited above, our own investigations led us to challenge the superacidity of solid acids [22]. Subsequently, the ideas on zeolite acidity started to shift gradually. Thus, MO calculations indicated that carbocations should bond covalently to the anion of the acid site [49]. ^{13}C NMR spectra then showed that adsorption of propene on HY [50] and of *t*-BuOH on HZSM-5 [51] form, indeed, surface alkoxides (thus correcting the earlier reports [42]). It was also shown [52] that persistent allyl cations had not been formed on HZSM-5 as claimed [43d]; the earlier identification of the actual product, propanal [53a], was then confirmed [53b]. Furthermore, it was proved that the level of hydronation of toluene is very much lower on HZSM-5 than in TFMSA (also correcting an earlier claim [44]), thus showing that the zeolite sites are several orders of magnitude below the superacidic range [52]. The measurement of the acidity of some zeolites with mesityl oxide as probe base (the $\Delta\delta$ method [4]) has also shown that HZSM-5 is not a superacid, but it is roughly similar in strength to 70–75% H_2SO_4, whereas HY is even weaker [54].

It follows immediately that hypervalent $(C_nH_{2n+3})^+$ ions are not intermediates in reactions on solid acids in general and zeolites in particular. Putting aside the controversy on the intervention of these intermediates in HF–SbF_5 and 1 : 1 FSO_3H–SbF_5 [17c,21e,38,39], we still can see that the solids cannot provide a medium in which such species would be energy minima. The intervention of such ions as transition structures in the formation of carbocationic, or more correctly cationoidic, short-lived reaction intermediates from alkanes by equation (3) is not "forbidden" in principle. At the level of acid strength of the solid acids, however, this reaction pathway can be expected to have such a high energy barrier that an alternative, easier mechanism is normally available and followed.

An intriguing class of solid acids was discovered (or rather invented) by Holm and Bailey, in the sulfated metal oxides (SMOs) [55a]. These catalysts are so active for alkane conversions, that subsequent workers have considered them solid superacids [55b]. Among them, sulfated zirconia (SZ) has the highest catalytic activity and was assigned the highest acidity expressed as H_0 [55b]. It was shown, however, that the measurements on which the conclusion of superacidity was based did not measure acid strength [56] and the catalytic activity *did not* correlate with the H_0 values [12]. Examination of the interaction of SZ with benzene by IR [57] and with acetonitrile by IR and NMR [58] indicated that this material has sites of strength between HY and HZSM-5, that is, not superacidic.

4. Conversion of alkanes at less than superacidic strength. Bifunctional catalysts

Acid-catalyzed reactions can be initiated by addition of small amounts of materials that can generate carbocations (or cationoidic intermediates) at lower acidity than the alkanes themselves. Thus, alkyl halides promote the reaction of alkanes on anhydrous $AlCl_3$ [59], as does 0.01% of an alkene, which can form alkyl chloride by reaction with HCl [60], or can react directly with the Brønsted acid sites.

A larger amount of alkene poisons the catalyst by formation of alkenyl cations [50,61] or even polymers, so a dehydrogenation catalyst which generates reversibly minute amounts of alkene from the alkane is added to the acid catalyst. Because the basicity of alkenes is much higher than that of alkanes, a much lower level of acidity is required of the catalyst. Such bifunctional catalysts have acquired wide industrial application [62].

As discussed above, the exceptional catalytic activity of sulfated zirconia (SZ) is not justified by its acid strength [57, 58]. Moreover, we observed that the reaction of methylcyclopentane (MCP) on SZ gave no ring-opened (C_6H_{14}) byproducts [12]. It had been shown that acidolysis (Brønsted acid attack) of MCP occurs exclusively by the breaking of a C–C bond [21e,63]. This reaction is hundred times faster for MCP than for neopentane, even though the latter forms a tertiary carbocation and the former a secondary carbocation upon bond cleavage [21e]. Therefore, the reaction on SZ cannot involve the reaction of MCP with a Brønsted superacid site as the initiation step (equation (4)) [12].

We studied the nature of the initiation step in catalysis by SZ, by identifying the first formed intermediates. This approach is difficult to use in heterogeneous catalysis, because the very large excess of feed masks the transient intermediates and the use of the catalyst in stoichiometric ratio to the feed leads normally to intractable products. We selected as probe molecule adamantane (AdH), which combines the reactivity of normal C–H bonds with an enormous thermodynamic stability of the skeleton. Two types of products obtained at 65–150 °C were most revealing, mechanistically. The first group, shown in equation (14), showed that an oxidation took place and the sulfate of the catalyst was reduced. Another product, diadamantyl (equation (15)) demonstrated the intervention of free-radical intermediates in the reaction [12]:

$$\mathrm{AdH} \rightarrow \text{1-Ad–OH, 2-Ad–OH,} \quad [C_9H_{14}] > C{=}O \text{ (ketone), Ad–SH} \qquad (14)$$

$$\text{Ad–H} \rightarrow \text{1-Ad–Ad-1} \qquad (15)$$

Thus, the initiation consists of a one-electron oxidation of the hydrocarbon by SZ, with the formation of a radical-cation, which then donates to the radical-anion site on the solid either a hydron to form a free radical, or a hydrogen atom to form a carbocation. In another study, the recombination of the radical pair or ion pair leading to a surface ester was shown to occur [64]. The surface ester ionizes by the reaction pattern of carbocationic solvolyses, forming the cationic or cationoidic intermediate, which reacts by equations (5) and (6). Alternatively, elimination can occur from the surface ester or even at an earlier point in the initiation reaction. Both the olefin and the surface ester can react at the acid strength level of the sulfated metal oxide, which is much below the superacidic range [64]. It is seen that SZ has a bifunctional character, combining oxidation in the initiation step with acid-catalyzed reaction of the intermediates formed. The oxidation is normally achieved on the account of the reduction of the sulfate, or of added redox promoters, which increase the catalytic activity [65] but not the acid strength [58]. At high temperatures, extensive oxidation of the organic materials takes place, with both the sulfate and the metal oxide lattice providing oxygen [56b].

The related view that SMOs are not superacidic but provide an alternative, lower energy pathway for the reaction of alkanes was expressed by Adeeva et al. [58]. Data fitting better our mechanistic description than the superacid catalysis were also obtained by other investigators [66].

Intervention of oxidation in reactions of alkanes, particularly cracking, in sulfuric acid, has been indicated before [67]. Even the superacids have oxidizing properties toward hydrocarbons [39], in some cases suggesting one-electron transfers [16a,b]. Moreover, anodic oxidation accelerated isobutane isomerization in TFMSA and also led to condensation products [68], reminiscent of the products assigned to “carbonium” intermediates in 1 : 1 FSO_3H–SbF_5 [36]. One-electron acceptor properties of aluminosilicates were also evidenced [69] and their possible relevance for catalysis was discussed [70]. More recently, we showed that chemically generated radical-cations of a large alkane undergo typical carbocationic reactions (isomerization, cracking) around 0 °C [71].

The bifunctional nature of SMO catalysts should have the following consequences:

(1) The one-electron acceptor ability should also be manifested toward donors other than saturated hydrocarbons. This prediction was verified by ESR in the reaction of benzene on SZ [72].

(2) The observed catalytic activity should be high (higher than the acid strength would warrant).

(3) Alkane reaction in early stages should give free-radical-derived products, just like AdH does.

(4) The reactions of alkanes should exhibit an induction period.

(5) The number of cationoidic chains initiated until deactivation occurs, should be determined by the num-

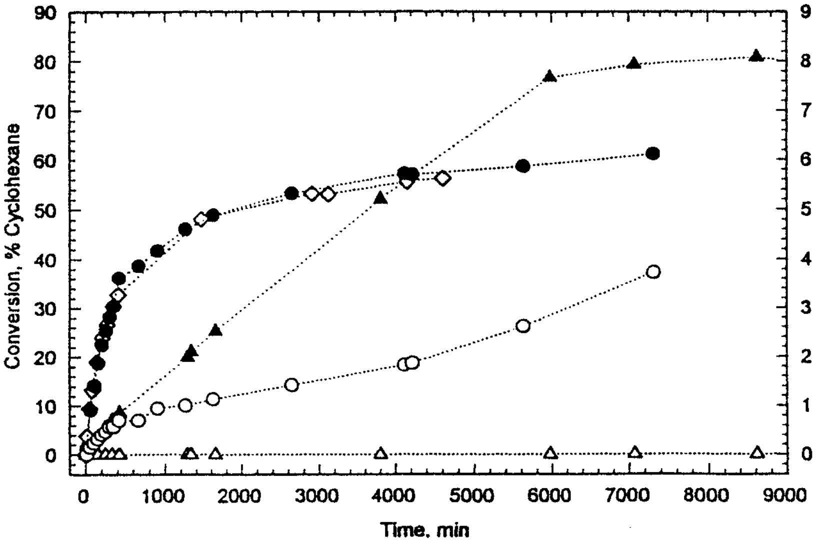

Figure 1. Conversion and formation of dimers in the isomerization of MCP on SZCH-3.0 and on $AlCl_3$. (MCP/cat. = 4.0, 65 °C). (●) SZCH conversion, (○) SZCH dimer formation, (▲) $AlCl_3$ conversion, (△) $AlCl_3$ dimer formation, and (◇) SZCH conversion, run one month after catalyst activation [75].

ber of oxidizing centers (stoichiometric); the length of cationoidic chains should be determined by the acid strength (non-stoichiometric). This type of behavior was substantiated experimentally [73,74].

(6) Rapid deactivation should occur, because of multiplicity of available pathways (acid-induced coking, free-radical polymerization, loss of oxidizing ability).

The behavior predicted in the statements (2), (3), and (6), was observed in a comparison of the reactions of MCP catalyzed by SZ and by $AlCl_3$ (figure 1) [75]. Thus, the initial reaction rate is much higher for SZ than for $AlCl_3$, but the former reaction never reaches equilibrium, because of catalyst deactivation. Free-radical products (dimers) are formed throughout the reaction on SZ, faster in the early stages, whereas no dimers are formed on $AlCl_3$ until the equilibrium is reached. As for prediction number (4), an induction period was evidenced for SZ catalysis in both batch [76] and flow experiments [77].

5. Reactions of 3-methylpentane (3MP) with TFMSA and HZSM-5

A difficulty in any attempt to compare alkane reactions catalyzed by liquid and solid acids is the large difference between the temperatures at which the two classes of catalysts operate. We found out that the interconversion of 3-methylpentane (3MP) and 2-methylpentane (2MP) (equation (16)) can be conducted at temperatures as low as 120 °C on HZSM-5, which is close to the range in which TFMSA catalyzes this reaction

$$\underset{\text{3MP}}{CH_3\text{–}CH(CH_2\text{–}CH_3)_2} \rightleftharpoons \underset{\text{2MP}}{(CH_3)_2CH\text{–}(CH_2)_2\text{–}CH_3} \tag{16}$$

For TFMSA, it was observed that the acid layer near the interface colored gradually yellow. To observe clean isomerization, the yellow-colored material had to be periodically dispersed into the bulk of the acid by shaking or stirring. The activation parameters, $\Delta H^\ddagger = 19$ kcal/mol, $\Delta S^\ddagger \approx -16$ cal/mol deg, were quite different from the reported $E_a = 5.4$ kcal/mol for the HF–SbF_5 catalyst [78]; the specific features of the latter experiment made the reaction 3MP $\rightleftharpoons$ 2MP transport-limited [78]. (More recent investigations have identified the colored species as alkenyl cations, thus showing that the initial reaction of the alkane with the catalyst is an oxidation [79a–c].)

The activation parameters can also be compared with the values reported for the mechanistic steps. Thus, interconversion of the tertiary cations, $3MP^+ \rightleftharpoons 2MP^+$ (equation (5)), had $\Delta H^\ddagger = 13.4$ kcal/mol, $\Delta S^\ddagger = -3$ cal/mol deg [21e]. The thermoneutral intermolecular hydride transfer $2MP^+ + 3MP \rightleftharpoons 2MP + 3MP^+$ (equation (6)) can be modeled after the *t*-butyl cation–isobutane pair ($\Delta H^\ddagger = 3$ kcal/mol, $\Delta S^\ddagger = -27$ cal/mol deg in SO_2–CH_2Cl_2 with AsF_5 as catalyst [80a], or $E_a \leqslant 1$ kcal/mol in 1,2,4-trichlorobenzene with $AlBr_3$ as catalyst [80b]). Hence, neither of these steps appears a good candidate for the rate-determining step of the process. It is then possible that the initiation step controls the kinetics of the reaction. Indeed, the activation parameters are of the size observed for carbocationic solvolyses of tertiary substrates [76]; if this similarity was not coincidental, the generation of an alkyl trifluoromethanesulfonate in the initial stage of the alkane reaction in TFMSA would be indicated. No intermediate was evidenced, however, by ^{13}C NMR in the acid layer. At long reaction times, the typical spectrum of polysubstituted cycloalkenyl cations was observed [50,61]. The alkenyl cations identified by UV/visible spectroscopy in the earliest stages of the reaction [79a–c] must, however, have a simpler structure. (No alkenes were observed in the reaction product, but more recent work indicated that the formation of all the alkane products involves alkenes as intermediates [79c].)

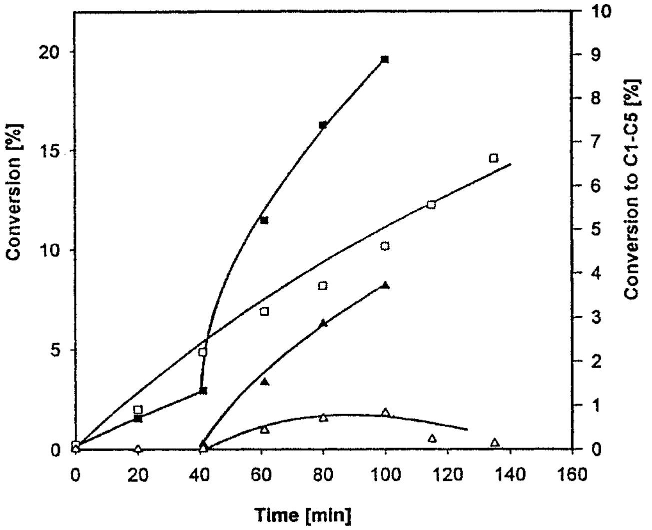

Figure 2. The reaction of 3MP with TFMSA at 26 °C. (a) With shaking: (□) conversion to 2MP and (△) cracking; (b) without shaking: (■) conversion to 2MP and (▲) cracking.

When the acid layer was not mixed, the reaction showed an induction period, after which it was faster than in the "homogenized" runs. Also, significant amounts of cracking products (C_1–C_5) were formed. The two reaction modes of 3MP with TFMSA (isomerization and cracking) are shown in figure 2.

The batch reaction of liquid 3MP on HZSM-5 at 120 °C also had an induction period, after which conversion to 2MP was the main pathway. Unexpectedly, however, a sizable amount of *n*-hexane (H) was formed. In the early stages of the reaction, the ratio 2MP/H was about 3, a result incompatible with the cationic isomerization mechanism, for which the rates of formation of 2MP and H from 3MP differ by a factor of more than 1000 and, therefore, H appears in measurable amounts long after the mixture of 3MP and 2MP is at equilibrium [21e,78]. The rate relationship 3MP/H about 1000 was also observed for the reaction with TFMSA in the "clean" isomerization mode (with homogenization of the acid layer), but not for the reaction in the cracking mode. Thus, the reaction on HZSM-5 is similar to the reaction on TFMSA in the cracking mode, rather than in the isomerization mode.

Also similar to the reaction on TFMSA, no olefinic products were observed on HZSM-5 at these low temperatures (up to 170 °C). (A more recent study, with hexane as reactant, has shown that the alkane products are formed from alkene as intermediates on HZSM-5 as well [79d].) Therefore, hexane is formed on HZSM-5 by another mechanism than the one described by the traditional carbocationic scheme.

The reaction of 3MP on HZSM-5 in the gas phase in a flow reactor in the same low temperature range, 120–142 °C, was also intriguing, because at short reaction times the combined amount of C_3 and C_4 products was greater than that of 2MP which was formed. Afterwards, the relative amount of 2MP in the product increased and that of the cracking products decreased, such that the amount of 2MP passed through a maximum. Such a behavior suggests that the cracking products are primary products from 3MP on HZSM-5 at these low temperatures, but 2MP is not.

The interconversion between the isomers prevented us from evaluating their relative reactivity by following the changes in their ratio during the reaction of their mixture. The comparison was made by the evaluation of their rates of consumption on HZSM-5 in separate experiments run under the same conditions. It was found that the linear isomer, H, was about ten times more reactive than the monobranched isomer 3MP in the reaction at 142 °C in the gas phase. Unexpectedly, the reverse was true for the reaction at the same temperature of the liquid hydrocarbons in sealed tubes, under which conditions H was the less reactive of the two, by a factor of about 10.

The nature of the species formed on the catalyst surface from 3MP on HZSM-5 at 120 °C in the liquid phase was examined by ^{13}C NMR, after 65 h of reaction, when the catalyst was still active, albeit at a reduced level. No peaks attributable to allylic ions were observed, but several strong resonances were recorded in the aliphatic region (14–40 ppm). Some weak signals around 130 ppm might indicate aromatic species or coke, whereas another weak resonance, at 65–70 ppm was consistent with a carbon (other than tertiary) bonded to oxygen. It is tempting to assign the latter signal to a surface ester (as noted above, alkoxy species had been evidenced before from alkenes [50] and alcohols [51,81] on zeolites), but the rigidity of the species containing the C–O bond was not tested by varying the spinning rate.

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