The kinetics of isomerization of 3-methylpentane catalyzed by trifluoromethanesulfonic acid[1]

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Reaction of 3-methylpentane (3MP) was conducted in a two-phase liquid phase system, with the weak superacid trifluoromethanesulfonic acid (TFMSA) as catalyst, below 40 °C. The reaction pattern depended upon the way in which the process was conducted. If the acid layer was homogenized periodically, isomerization to 2-methylpentane occurred, with very little cracking. If the acid layer was left undisturbed, a yellow zone (indicating unsaturated organic species) at the interface with the hydrocarbon layer was formed, the reaction showed an induction period after which the overall conversion was greater than for the other reaction mode, and the extent of cracking (direct or following alkylation) increased significantly. For the same quantities of TFMSA and 3MP, increasing the diameter of the reaction tube increased the reaction rate, indicating that the reaction takes place at the interface. The reaction kinetics for the clean isomerization mode (dispersion of the unsaturated organic species formed in the acid layer from the interface) were analyzed by the rate equations reported previously, allowing for catalyst deactivation. Rate measurements at five temperatures between 14 and 32 °C gave the activation parameters $\Delta H^{\ddagger} = 19\ \mathrm{kcal\ mol^{-1}}$ and $\Delta S^{\ddagger} \approx -16\ \mathrm{cal\ mol^{-1}\ deg^{-1}}$, which did not change when the ratio of catalyst to substrate was varied by a factor of two. These values are not compatible with a mass-transfer controlled reaction as found for the HF–SbF_5 catalyst. Instead, the ionization of an alkyl trifluoromethanesulfonate intermediate or a methyl group shift in the cation could be rate-determining. No intermediate could be evidenced by NMR in either layer, but the ^{13}C NMR spectrum of the acid layer at the end of the reaction showed the presence of several alkenyl cations (polyalkylcyclopentenyl and possibly even some polyalkylcyclohexenyl cations).

1. Introduction

The interconversion of C_6H_{14} isomers has been considered for a long time a standard reaction for the definition of a carbocationic mechanism in an alkane conversion.[2] A mixture of all five isomers, *n*-hexane (H), 2-methylpentane (2MP), 3-methylpentane (3MP), 2,3-dimethylbutane (2,3DMB), and 2,2-dimethylbutane (2,2DMB) is ultimately obtained from either of them. Starting from *n*-hexane (H), four isomerization steps are identified (eqns. (1)–(4)). Two of them (eqns. (1) and (3)) involve a change in the degree of chain branching and the other two (eqns. (2) and (4)) do not. The reactions of hexane to 2MP and 3MP (eqns. (1a) and (1b)) are not treated separately.

$$\underset{\text{H}}{CH_3\text{–}(CH_2)_4\text{–}CH_3} \rightleftharpoons \underset{\text{2MP}}{(CH_3)_2CH\text{–}(CH_2)_2\text{–}CH_3} \qquad (1a)$$

$$\underset{\text{H}}{CH_3\text{–}(CH_2)_4\text{–}CH_3} \rightleftharpoons \underset{\text{3MP}}{CH_3\text{–}CH(CH_2\text{–}CH_3)_2} \qquad (1b)$$

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

$$\underset{\text{2MP}}{(CH_3)_2CH\text{–}(CH_2)_2\text{–}CH_3} \rightleftharpoons \underset{\text{2,3DMB}}{(CH_3)_2CH\text{–}CH(CH_3)_2} \qquad (3)$$

$$\underset{\text{2,3DMB}}{(CH_3)_2CH\text{–}CH(CH_3)_2} \rightleftharpoons \underset{\text{2,2DMB}}{(CH_3)_3C\text{–}CH_2CH_3} \qquad (4)$$

The first study of hexane isomerization employed an aluminum chloride–water (1 : 0.22 molar ratio) catalyst.[3] In later work, aluminum chloride under hydrogen chloride pressure was used in an attempt to determine the equilibrium isomer distribution.[4] Traces of water must have been the actual co-catalyst in that study as well.[5] A remarkably accurate determination of the ratios of the five isomers at equilibrium was achieved in 1944 by the room temperature catalytic isomerization of *n*-hexane, but the authors did not reveal the composition of the catalyst.[6]

An estimation of the rates of these reactions was first obtained with $AlCl_3$ as catalyst, at 100 °C.[7] The reaction on silica–alumina at 150 °C was also reported, but only interconversion of 2MP and 3MP (eqn. (2)) and a slower conversion of the monobranched isomers to 2,3DMB were observed.[8] The same observations were made in a liquid phase study, with 99.8% sulfuric acid as catalyst, at room temperature.[9] Rates for all the reactions (eqns. (1)–(4)) were determined with an HF–BF_3 catalyst system in which the BF_3 content was changed from zero for the reactions of eqn. (2) to 10% molar for the reactions of eqn. (1) and eqn. (4), whereas eqn. (3) was studied at both acidity levels. It was then assumed that the increase in acidity changes all rates by the same factor.[10] Because the reaction of eqn. (2) exhibited rates roughly proportional to the amount of HF used, it was concluded that the reaction occurred in the acid layer.[10]

A complete kinetic study of the isomerization of the C_6H_{14} hydrocarbons used a 38 : 1 composite of HF–SbF_5 as catalyst.[11] Reaction with methylcyclopentane prior to the reaction gave a mixture of tertiary cations in the acid layer, which was thus the locus of the isomerization reaction. Rates, activation parameters, and the rate-determining step for each isomerization (eqn. (1)–(4)) were determined.[11] The non-branching rearrangement of eqn. (2) was the fastest, followed by the branching rearrangement of eqn. (3). The non-branching rearrangement of eqn. (4) and the branching rearrangements of eqn. (1) were much slower. This important work was much cited by workers in the field and the conclusions about rate-determining steps were adopted as general for the respective reactions.[12]

We were interested in a reaction of a saturated hydrocarbon which can be conducted with strong liquid acids and typical solid acids at temperatures not very far apart.[13] The isomerization of eqn. (2), found to occur relatively fast over sulfated zirconia at ambient temperature, seemed the best candidate.[14] We report here our studies of the interconversion of 3MP and 2MP catalyzed by trifluoromethanesulfonic acid (TFMSA).

2. Experimental

2.1. General

The hydrocarbons 3-methylpentane (3MP) and 2-methylpentane (2MP) were reagent grade materials and were used as purchased, as was 99%+ TFMSA. The composition of isomerization products was determined by GLC both on a packed column[15] and on a 50 m × 0.25 mm HP-5 capillary column, held at 40 °C for 8 min, then heated to 170 °C at a rate of 10 °C min^{-1}, as well as by GC-MS[15] on a 50 m × 0.2 mm HP-1 capillary column, held at 40 °C for 8 min, then heated to 180 °C at a rate of 10 °C min^{-1} and kept at 180 °C for 10 min. The mass spectra were obtained in the EI mode, at 70 eV. The NMR spectra were acquired at room temperature, on a Bruker DMX-300 spectrometer (^{13}C frequency 75.468 MHz), as described before, with a WALTZ decoupling pulse sequence and a 30 KHz spectral width.[16]

2.2. Reaction of 3-MP

For each run, TFMSA (typically 0.5 g or 1 g) and 3MP (typically 2.5 g) were introduced into a 10 cm × 12 mm ID glass tube, which was capped with a rubber septum. These operations were conducted under nitrogen. The tube was then placed in a thermostatted bath. Samples (0.5 µl) were withdrawn with a syringe through the septum from the upper layer and analyzed by GLC to measure the conversion. A few samples were also analyzed by GC-MS. Two modes of operation were followed. In one of them, the tube was left undisturbed in the bath, in the other, the tube was shaken right after adding the acid and feed and before each sample was withdrawn. Care was taken that the liquid did not touch the septum during shaking.

2.3. Treatment of data

Plotting of data with the equations shown in the text was accomplished with the program SigmaPlot, developed by Jandel Scientific. The activation parameters and rate constants at different temperatures were calculated with the program C2Plus.[17]

3. Results and discussion

It is apparent that a comparison of the results of Brouwer and Oelderik[11] with data gathered for media or catalysts where the carbocations are no more than unstable reaction intermediates is by no means straightforward. Indeed, their experiments were conducted under unusual circumstances, because the reaction medium was an HF solution (1.5 M) of the tertiary hexyl cations: 3-methyl-3-pentyl (**1**), 2-methyl-2-pentyl (**2**), and 2,3-dimethyl-2-butyl (**3**) at equilibrium (eqn. (5)).[11,18] The rate constant under those conditions for the slowest of the steps in eqn. (5), **2**$\rightleftharpoons$**3** was estimated as about 0.1 s^{-1} at 0 °C.[18]

$$\underset{\mathbf{1}}{\mathrm{CH_3{-}C^+(CH_2{-}CH_3)_2}} \rightleftharpoons \underset{\mathbf{2}}{\mathrm{(CH_3)_2C^+{-}(CH_2)_2{-}CH_3}} \rightleftharpoons \underset{\mathbf{3}}{\mathrm{(CH_3)_2C^+{-}CH(CH_3)_2}} \quad (5)$$

Trifluoromethanesulfonic acid (TFMSA) was more appropriate for our purpose. As a pure compound, it is a weak superacid[19] (H_o −14.2,[20] −14.1[21]). Even the commercially available 99–99.5% acid is superacidic. From the published diagram,[22] a 97.8% acid is equal in strength with 100% sulfuric acid (H_o −12.2). The 99+% TFMSA has been used as catalyst, first for the isomerization of polycyclic hydrocarbons[23] and then also for that of alkanes.[21] At its level of acidity, no significant concentrations of carbocations exist at equilibrium in TFMSA, which makes it a better term of comparison for solid acids than the HF–$\mathrm{SbF_5}$ superacid. It has a lower oxidizing ability than sulfuric acid, although acceleration by polycyclic aromatics of some reactions catalyzed by TFMSA indicates promotion of acid catalysis by a one-electron oxidation.[24]

Table 1 Effect of dispersion of unsturated organic species formed in the acid layer, on the conversion and extent of cracking in the reaction of 3MP with TFMSA (4.4:1 molar ratio 3MP/TFMSA) at 26 °C

	Without dispersion		With dispersion[a]	
Time/ min	conversion to C1–C5	conversion to 2MP	conversion to C1–C5	conversion to 2MP
20	0.0	0.0155	0.0	0.020
41	0.0011	0.0294	0.0	0.0486
61	0.0152	0.1149	0.0043	0.0691
80	0.0286	0.1626	0.0070	0.0819
100	0.0371	0.1956	0.0082	0.1016
115			0.0022	0.1226
135			0.0012	0.1456

[a] Occasional shaking.

The reactions of alkanes with TFMSA are conducted in the liquid phase, but not in a homogeneous system. Instead, the reaction is based on the contact between two phases, being thus similar to the reaction on solid catalysts. An important concern, not existing for the solid catalysts, is that the contact area between the acid and the hydrocarbon stay constant throughout the experiment. Stirring the mixture produces droplets and increases the contact area, accelerating the reaction. This approach was convenient for catalyst comparisons.[25] It is not appropriate for kinetic experiments, however, because the properties of the acid layer, particularly the viscosity and surface tension, change during the reaction, as small amounts of soluble organic materials, like polyalkylcyclopentenyl cations, are formed. The result is that the contact area does not stay constant throughout the run. We conducted the experiments with 3MP and this catalyst as we had done for isomerizations catalyzed by solid acids: in the batch mode, in a glass tube capped with a rubber septum, without stirring.[15,26]

Two modes of operation were followed in our experiments. In the first, the content of the tube was shaken just after mixing and before taking each sample for analysis. (During the mixing, the contact area obviously increased, but compared to the time elapsed between taking samples the 1–2 seconds of shaking is negligible.) A rather clean isomerization (eqn. (2)) was observed, with very little cracking. The same behavior was observed with magnetic stirring of the acid layer conducted carefully such as to avoid the disturbance of the interface. For the kinetic runs, we preferred shaking, which homogenized the hydrocarbon layer before the samples were taken.

In the alternative approach, no stirring or shaking was performed and the samples were taken carefully, to avoid disturbing the system. In the experiments conducted in this mode, the acid layer colored at the interface with the hydrocarbon layer, an induction period was observed after which the conversion of 3MP was significantly faster than in the experiments in which the acid layer was periodically homogenized, and the formation of the cracking products ($\mathrm{C_1}$–$\mathrm{C_5}$ alkanes) increased several times. These observations are illustrated in Table 1 and Fig. 1. Homogenization after the cracking mode had started did not restore the isomerization mode. From the latter experiments it was determined that the lack of homogenization of the hydrocarbon layer did not alter much the compositions

Table 2 Rate constants and activation parameters for the isomerization of 3MP to 2MP catalyzed by TFMSA (4.4 : 1 molar ratio 3MP/TFMSA) at various temperatures, calculated with eqn. (6)

Temperature/ °C	K^a	$k/10^{-5}$ s^{-1}	$k_d/10^{-5}$ s^{-1}	k(av)$^b/10^{-5}$ s^{-1}	k_d(av)$/10^{-5}$ s^{-1}
		0.543	0.92		
14.0	2.904			0.626	1.40
		0.690	1.88		
		1.052	12.33		
19.0	2.858			1.097	12.62
		1.141	12.90		
		1.910	7.32		
24.0	2.813			1.946	8.63
		1.982	9.94		
27.5	2.783	2.155	13.20	2.155	13.20
28.5	2.775	2.952	13.90	2.952	13.90
		4.775	5.33		
32.0	2.746			5.544	10.44
		6.312	15.54		

[a] Calculated from ΔH_f^o and ΔG_f^o values at 25 °C, taken from: *Perry's Chemical Engineering Handbook*, ed. D. W. Green, McGraw Hill, New York, 1984, pp. 3–148. [b] $\Delta H^{\ddagger} = 18.88 \pm 0.06$ kcal mol^{-1}, $\Delta S^{\ddagger} = -16.59 \pm 0.20$ cal mol^{-1} deg^{-1}, correlation coefficient $r = 0.979$.

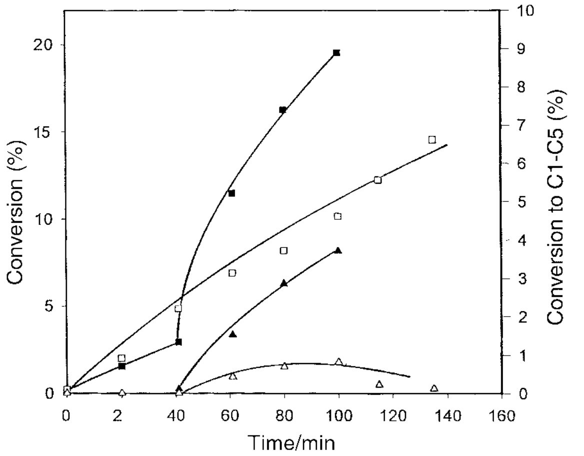

Fig. 1 Effect of dispersion of unsaturated organic species formed in the acid layer on the conversion and extent of cracking in the reaction of 3MP with TFMSA at 26 °C. Reaction without occasional shaking: ■ conversion to 2MP; ▲ cracking. Reaction with occasional shaking: □ conversion to 2MP; △ cracking.

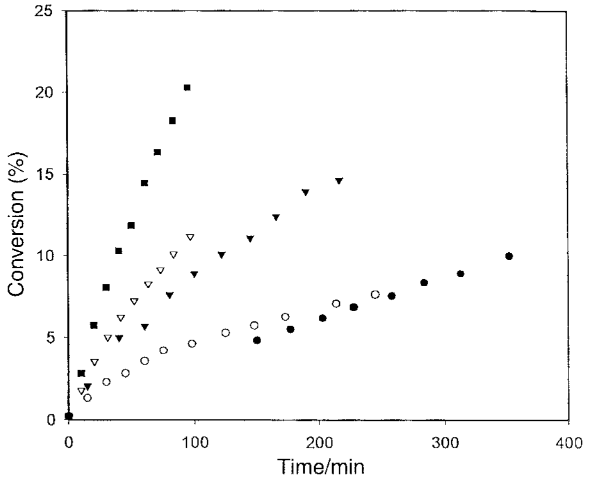

Fig. 2 Isomerization of 3MP to 2MP catalyzed by TFMSA at different temperatures. ● 14 °C; ○ 19 °C; ▼ 24 °C; ▽ 28.5 °C; ■ 32 °C.

measured by taking samples in a given point. Nonetheless, it was felt that the data could not be used for accurate kinetic measurements.

It is possible that disproportionation is responsible for at least a part of the cracking products, if the products with larger molecules are unstable. It was reported that 2,2,4-trimethylpentane added in small amounts to butane in contact with TFMSA is immediately consumed and promotes the isomerization to isobutane, together with the formation of C_5–C_6 products.[21] We found earlier that the reaction of methylcyclopentane with $AlCl_3$ forms dimers only in the late stages, after the equilibrium has been reached, but the oxidatively initiated isomerization on sulfated zirconia forms dimers fastest in the early reaction stages.[27] When the reactant 3MP was shaken with water in a separating funnel before reaction, the rate decreased but no increase in the cracking products was observed. By contrast, addition of a very small amount of propan-2-ol to the reacting mixture led to a jump in the amount of cracking products, demonstrating that the latter process is stimulated by the organic materials of increased basicity.

Examples of conversion to 2MP in the isomerization mode (with occasional shaking) conducted at several temperatures are presented in Fig. 2. The rates of reaction were analyzed in two ways. The first was based on the application of eqn. (6), developed for reactions with a constant quantity of catalyst, which are first order in reactant and affected by deactivation.[26]

$$x = \frac{1}{M} - \frac{1 - Mx_o}{M} \exp[(M\frac{k}{k_d}[\exp(-k_d t) - 1]] \qquad (6)$$

In eqn. (6), $M = (K + 1)/K$. The limits of integration have been changed from the previous application,[26] because the procedure with catalyst homogenization removed or masked any induction period (*i.e.*, $t_o = 0$) and the starting material contained a small amount of product (x_o). The results of determinations for a 4.4 : 1 molar ratio reactant to catalyst at several temperatures between 14 and 32 °C are listed in Table 2, together with the calculated activation parameters.

The last two columns of Table 2 show deactivation to be very important. As acidolysis of *tert*-C–H bonds does not occur in TFMSA,[28] activation must involve an oxidation.[14a,15,27,29] Deactivation results from the decrease in acid strength and accumulation of alkylcyclopentenyl cations in the catalyst phase.

The alternative kinetic treatment consisted of the calculation of average values for pseudo-first order rate constants with neglect of deactivation, between consecutive sampling times (eqn. (7)) and extrapolation to time zero.[26] The results are

$$(k_r)_{i,i+1} = [M/(t_{i+1} - t_i)] \ln[(1 - Mx_i)/(1 - Mx_{i+1})] \qquad (7)$$

shown in Table 3. The rate constants are slightly greater than the values determined by eqn. (6), but the activation parameters are about the same as those in Table 2.

Table 3 Rate constants and activation parameters for the isomerization of 3MP to 2MP catalyzed by TFMSA (4.4:1 molar ratio 3MP/TFMSA) at various temperatures, calculated by eqn. (7)

Temperature/°C	$k^a/10^{-5}$ s^{-1}
14.0	0.70
19.0	1.30
24.0	2.60
27.5	2.70
28.5	3.50
32.0	6.20

[a] $\Delta H^‡ = 19.06 \pm 0.06$ kcal mol^{-1}, $\Delta S^‡ = -15.66 \pm 0.19$ cal mol^{-1} deg^{-1}, correlation coefficient $r = 0.983$.

When the same quantities of 3MP and TFMSA were placed in contact in tubes of various sizes, the reaction rate increased with the increase in diameter, suggesting that the reaction takes place at the interface. On the other hand, when the tube was kept the same but the quantity of acid was reduced (molar ratio 3MP–TFMSA 8.7:1), the isomerization was slower and the deactivation faster, as expected, but the activation parameters, $\Delta H^‡ = 19.0$ kcal mol^{-1} and $\Delta S^‡ = -16.7$ cal mol^{-1} deg^{-1}, were not significantly different from those shown in Tables 2 and 3. The average values of these three sets of data, $\Delta H^‡ = 19$ kcal mol^{-1} and $\Delta S^‡ \approx -16$ cal mol^{-1} deg^{-1}, are very different from the values for the diffusion-limited reaction catalyzed by HF–SbF$_5$ ($E_a = 5.4$ kcal mol^{-1}).[11]

The analysis of eqn. (2) in terms of its mechanistic steps, eqns. (8)–(12), is more complicated for TFMSA than for HF–SbF$_5$. As discussed for other catalysts where oxidative activation is involved, the first intermediate is most likely trapped as an alkyl ester of the catalyst (eqn. (8)),[14a,15,27,29] whereas in the acidolysis mechanism (superacid catalysis) initiation is a one-time generation of carbocationic intermediates, either in a sludge on the surface of a catalyst[30] or in the HF solution as in the experiments of Brouwer and Oelderik,[11] and thus it is a separate operation, conducted before the actual conversion of the feed.

$$\text{3MP} \longrightarrow [..] \longrightarrow \text{3MP–TFMS} \tag{8}$$

$$\text{3MP–TFMS} \rightleftharpoons \text{3MP}^+\cdot\text{TFMS}^- \tag{9}$$

$$\text{3MP}^+\cdot\text{TFMS}^- \rightleftharpoons \text{2MP}^+\cdot\text{TFMS}^- \tag{10}$$

$$\text{2MP}^+\cdot\text{TFMS}^- \rightleftharpoons \text{2MP–TFMS} \tag{11}$$

$$\text{2MP}^+\cdot\text{TFMS}^- + \text{3MP} \rightleftharpoons \text{3MP}^+\cdot\text{TFMS}^- + \text{2MP} \tag{12}$$

The thermoneutral intermolecular hydride transfer $\text{2MP}^+ + \text{3MP} \rightleftharpoons \text{2MP} + \text{3MP}^+$ can be modeled by the corresponding reaction of the *tert*-butyl cation–isobutane pair: $\Delta H^‡ = 3$ kcal mol^{-1}, $\Delta S^‡ = -27$ cal mol^{-1} deg^{-1} in SO$_2$–CH$_2$Cl$_2$ with AsF$_5$ as catalyst,[31] or $E_a \leq 1$ kcal mol^{-1} in 1,2,4-trichlorobenzene with AlBr$_3$ as catalyst.[32] At least in the last solvent the cations should be ion-paired, making the reaction a good model for eqn. (12). Therefore, the latter cannot be the rate-determining step of our process.

Information also exists about the energy barriers for the isomerization step (eqn. (10)). The corresponding reaction in HF–SbF$_5$ (**1**$\rightleftharpoons$**2**, eqn. (5)) had $\Delta H^‡ = 13.4$ kcal mol^{-1}, $\Delta S^‡ = -3$ cal mol^{-1} deg^{-1}.[33] These values are much lower than those measured by us, but it is possible that ion pairing, important in our case but not in HF–SbF$_5$, alters the barriers significantly. On the other hand, the activation parameters are compatible with the ionization (solvolysis) (eqn. (9)) as rate-determining step. Because the hexyl trifluoroacetates are nonpolar compounds, they should be present in the hydrocarbon layer. Their solvolysis, however, requires a polar medium and should thus take place in the acid layer or at the interface. Examination of the organic phase by ^{19}F NMR showed a very small signal which did not change in time, indicative of extracted acid, rather than an ester. The total amount of ester is limited, however, to the amount formed in the initial oxidation by the catalyst.

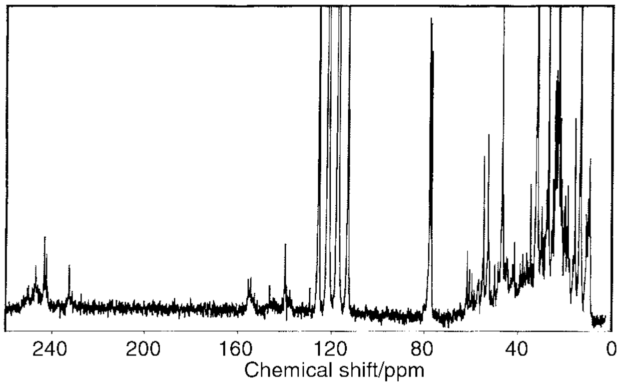

Fig. 3 ^{13}C NMR spectrum of TFMSA after the reaction of 3MP at 26 °C (144 hours). The quartet centered at 126 ppm is the resonance of TFMSA.

Our search for reaction intermediates in the acid layer by ^{13}C NMR, was also unsuccessful, which indicates that the concentration of the intermediates must be very small. As the catalyst deactivates, however, the ^{13}C NMR spectrum (Fig. 3) reveals increasing concentrations of alkenyl cations, most likely stable polyalkylcyclopentenyl cations.[34] The number of signals in the regions around 150 and around 250 ppm indicate the presence of several such species (the existence of some polyalkylcyclohexenyl cations in that mixture cannot be precluded). These carbocations were evidenced even in media of rather low acidity, like zeolite HY.[35]

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