The two modes of reaction of hexane catalyzed by trifluoromethanesulfonic acid[1]

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The initial reaction observed on reacting hexane (H) with trifluoromethanesulfonic acid (TFMSA) under mild conditions was a dehydrogenation with the formation of alkenyl cations, identified by UV-visible spectroscopy. When these ions were dispersed from the liquid/liquid interface, isomerization to methylpentanes (2MP and 3MP) occurred. The reaction rates were measured at low conversions and gave $\Delta H^\ddagger = 15$ kcal mol^{-1} and $\Delta S^\ddagger \approx -40$ cal mol^{-1} deg^{-1}. When the acid layer was not homogenized, a much faster reaction, mostly cracking and disproportionation, was observed, after an induction period needed to achieve a critical concentration of initiators at the interface. The homogenized acid initiated the cracking mode after a much longer time, when the alkenyl ions reached the critical concentration throughout the acid phase. The induction period was reduced by the addition of small amounts of one-electron oxidizers, such as ferric ions. The relative reactivity 3MP/H, which in the isomerization mode was about the same as for HF-based catalysts (1000), was reduced to about 10 in the cracking mode. Some key reaction features of the cracking mode are reminiscent of zeolite catalysis. These are: the dramatic acceleration of the reaction of *n*-hexane relative to the reaction of 3-methylpentane, a large excess of the branched isomers in the C_4 and C_5 fractions above the equilibrium ratio, the absence of unsaturated cracking products (the unsaturated products are retained by the catalyst in both cases), and formation of dibranched C_6H_{14} isomers, particularly 2,2-dimethylbutane (2,2DMB) as primary products. Neither steric control in cages or channels, nor intermediacy of pentacoordinated carbocations, invoked as explanations for the reactions in zeolites, can apply to the reaction with TFMSA as catalyst.

1. Introduction

A difficulty in any attempt to compare alkane reactions catalyzed by liquid and solid acids is the large difference between the temperatures at which reactions catalyzed by these two types of catalysts are usually conducted. Our group has been examining conversions of saturated hydrocarbons which can be induced by solid and liquid acids at temperatures not too far apart.[2] Thus, interconversion of 3-methylpentane (3MP) and 2-methylpentane (2MP) can be conducted at 120–160 °C with zeolite HZSM-5[1,3] and at room temperature with sulfated zirconia (SZ)[4] or trifluoromethanesulfonic acid (TFMSA)[5] as catalysts.

A similarity between TFMSA and the solid acids is that in both cases the catalyst and the reacting alkane are in different phases and the reaction is based on the contact between the two phases. The difference, however, is that the contact area is well determined for the solids, but it varies with the type and intensity of mixing for the liquid acid and its actual value is unknown. In addition, the properties of the acid layer, particularly the viscosity and surface tension, change during the reaction, as small amounts of acid-soluble organic species are formed, such that the contact area (determined by the size and number of droplets) does not stay constant throughout the run, even if stirring is rigorously constant. We decided, therefore, to conduct the experiments without stirring. Under these circumstances the contact area is well determined and can be varied by changing the diameter of the reaction tube.[5] The same experimental approach (batch reaction in a capped tube, without stirring) was successfully applied to the solid catalysts.[6]

Upon studying the reaction of 3MP with TFMSA under these conditions, we observed that clean isomerization kinetics (3MP$\rightleftarrows$2MP) could be achieved only if the acid layer was periodically homogenized. Otherwise, a significantly faster reaction was observed, after an induction period, during which some organic species, yellow in color, were formed in the acid layer at the interface with the reactant and significant cracking and disproportionation accompanied the isomerization.[5] To understand better this type of reaction, we studied in more detail the reaction of *n*-hexane and we report our findings here.

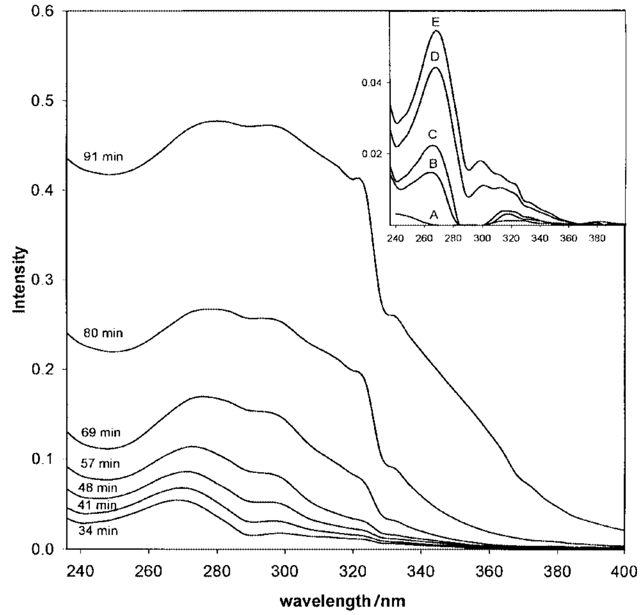


Fig. 1 UV spectra of the acid layer in the early stages of reaction at room temperature. The first spectra recorded are shown at higher amplification in the insert. A: 3 min, B: 13 min, C: 17 min, D: 28 min, E: 34 min.

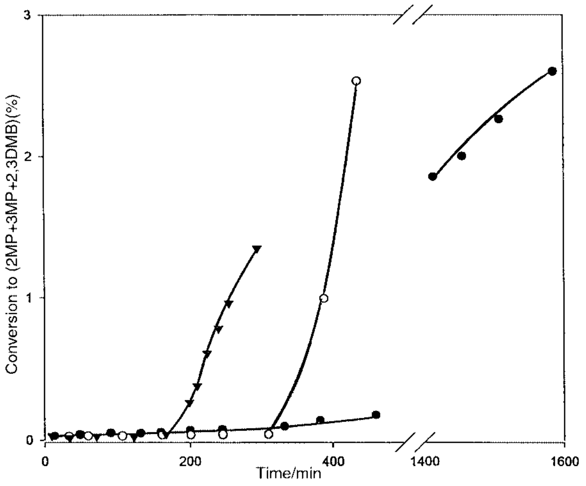


Fig. 2 Conversion of hexane to isomeric products as a function of time for the two modes of operation (see text). ▼ Sample undisturbed. ○ Samples shaken at intervals for 300 min, then left undisturbed. ● Samples shaken at intervals for 500 min, then left overnight undisturbed.

2. Experimental

2.1. General

Hexane was obtained from Fluka (*puriss*, absolute, ≥99.5%, actual purity 99.7–99.8%, containing 0.2–0.3% methylcyclopentane, MCP, by GLC). TFMSA (≥99%) and TFMSA anhydride were procured from Aldrich. For comparison, some experiments were run with TFMSA from Acros. To make 100% TFMSA, a slight excess of its anhydride (calculated for 1% water in the acid) was added to the acid in a volumetric flask, which was then stoppered and stirred for 48 hours at 50–60 °C.

The GLC (packed column, 48 °C) and GC-MS analyses were conducted as described in the references cited.[5]

The construction of curves from the experimental points in Fig. 2 was accomplished with the program SigmaPlot, developed by Jandel Scientific.[7]

2.2. Reactions of hexane

Hexane (2.5 g) and TFMSA (1 g, molar ratio 4.36:1) were maintained at a constant temperature between 24 and 42 °C in an 11 mm ID glass tube, capped with a rubber septum. Experiments with 0.75 g H and 0.3 g TFMSA in a 6 mm tube were conducted only at two temperatures. The reaction tube was shaken briefly (*ca.* 1 s) every 25–30 min for the homogenization of the acid layer, making sure that the liquid did not touch the septum,[5] and samples were withdrawn through the septum and analyzed by GLC and GC-MS. Alternatively, the acid layer was magnetically stirred, carefully so as not to disturb the interface and vary the contact area. In the other mode, the homogenization operation was not done. To test the effect of MCP on rates, the reaction was conducted in the isomerization mode on a synthetic mixture of H and MCP (92:8) at 36 °C. No significant change in rates was found.

3. Results and discussion

The initial observation for the reaction of H with TFMSA under mild conditions was the same as for the reaction of 3MP described previously,[5] that is, the acid layer became yellow in the immediate vicinity of the interface. In order to observe a clean isomerization reaction, the acid layer had to be homogenized, either by quick shaking every 25–30 min, or by slow magnetic stirring (such as not to alter the catalyst/reactant contact area). The former approach was preferred for the kinetic study, because it homogenized the hydrocarbon layer as well. If the acid was not homogenized, a different reaction pattern was observed after an induction period, again in the same manner as for 3MP (the cracking mode).[5] For the isomerization mode (reaction mode A), the products were a mixture of 2MP and 3MP in their equilibrium ratio, as expected.[5,8] The reaction rates were determined at three temperatures and are given in Table 1, together with the calculated activation parameters. Because the reaction could be followed only to low conversions, the values are less accurate than those reported for 3MP, but it can be seen that the reaction of H is about 1000 times slower than that of 3MP. This reactivity ratio is similar to the one observed with HF-based catalysts.[8] The activation parameters were calculated from the rates at four temperatures between 33 and 50 °C in a 11 mm tube (see Experimental section), as $\Delta H^\ddagger = 14.9$ kcal mol^{-1} and $\Delta S^\ddagger \approx -42.5$ cal mol^{-1} deg^{-1}. Rates in a narrower tube were measured at only two temperatures, 24.5 and 42 °C. The rate constant found at the higher temperature was in agreement with the value obtained in the other setup, but the activation parameters obtained, ($\Delta H^\ddagger = 16.4$ kcal mol^{-1}, $\Delta S^\ddagger \approx -38$ cal mol^{-1} deg^{-1}) have to be considered as less accurate. Because of the errors normally expected for reactions followed only at low conversions, particularly for the slowest reaction, at 24.5 °C, we take the agreement between the values as satisfactory and retain the values $\Delta H^\ddagger = 15$ kcal mol^{-1} and $\Delta S^\ddagger \approx -40$ cal mol^{-1} deg^{-1}. In any event, the activation enthalpy of isomerization is lower for H than for 3MP (19 kcal mol^{-1}).[5] There are few examples of carbocationic solvolysis of tertiary and secondary substrates with the same leaving group, but there is at least one such example, showing that the activation enthalpy is similar to, or rather, somewhat lower for the tertiary substrate.[9] Thus, ionization of a trifluoromethanesulfonate ester intermediate is not the likely rate-determining step in the reaction of H. We cannot choose, however, between the other mechanistic steps, hydride transfer and rearrangement of the cationic or cationoidic (incompletely ionized)[6] intermediate as rate-determining.

Table 1 Reaction rates and activation parameters for the conversion of hexane by TFMSA in the isomerization mode[a]

No.	Temperature/°C	$10^8\,k$/s^{-1}	
1	33	7.75	
2	36	9.43	$\Delta H^\ddagger = 14.9$ kcal mol^{-1}
3	41	13.9	$\Delta S^\ddagger \approx -42.5$ cal mol^{-1} deg^{-1}
4	50	29.3	

[a] Reaction in an 11 mm diameter tube (see Experimental Part). Reactions in a 6 mm diameter tube were conducted at 24.5 °C ($k = 2.3 \times 10^8$) and 42 °C ($k = 11.4 \times 10^8$) and gave $\Delta H^\ddagger = 16.4$ kcal mol^{-1}, $\Delta S^\ddagger \approx -38$ cal mol^{-1} deg^{-1} (see text).

The much slower reaction of H than of 3MP allowed us to examine the undisturbed acid layer in the initial stages (during the induction period). The ^{13}C NMR spectrum failed to reveal any organic species, other than TFMSA itself. The examination of the acid layer by UV spectroscopy (Fig. 1) showed, however, at the shortest time (3 min) a very weak absorption centered at 320 nm. At somewhat longer times (13–31 min) an absorption at 270 nm grew faster and a 300 nm band also overtook the 320 nm band. At even longer reaction times (40–90 min) the 300 nm band grew the fastest, such that after 91 min it was as strong as the 270 nm band and gave a broad absorption from 260 to 330 nm (Fig. 1). These wavelengths correspond to absorption bands recorded for alkenyl cations of various degrees of substitution, acyclic and cyclic.[10] Thus, the reaction consists of an oxidative dehydrogenation of the alkane by TFMSA, with an alkene as the most probable earliest product. As we have already reported, polysubstituted cycloalkenyl cations can be observed by ^{13}C NMR at the end of the reaction, whether the acid had been homogenized or not.

When the tube was left undisturbed, the concentration of alkenyl cations (yellow color) in the acid layer near the interface

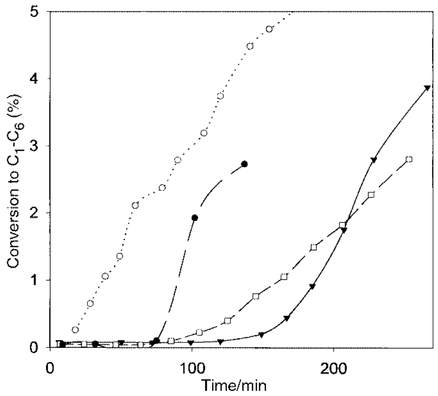


Fig. 3 Effect of additives on the conversion of hexane to isomeric products. ▼ Same as in Fig. 2. ○ With $FeCl_3$. □ With $CuCl_2$ ●. With anthracene.

Table 2 Distribution of products from the reaction of hexane with TFMSA in the cracking mode, at different temperatures and levels of conversion[a]

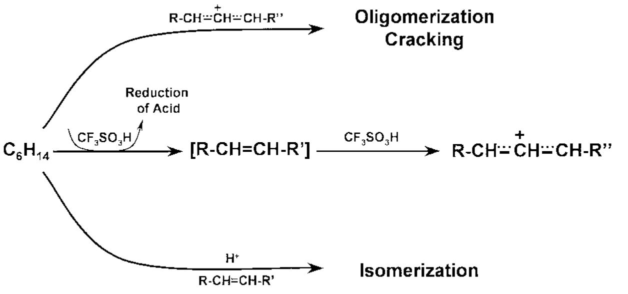
Temperature	24.5 °C		42 °C	
Total conversion[b]	2.8%	6.3%	2.8%	6.3%
propane	1.45	1.33	1.86	1.94
i-butane	36.15	31.61	32.53	30.87
n-butane	4.06	3.79	4.13	4.44
i-pentane	26.69	25.65	25.52	25.34
n-pentane	2.97	2.59	3.44	3.08
2,2DMB	5.22	5.26	4.30	5.07
2,3DMB + 2MP	15.95	18.38	16.33	16.45
3MP	3.44	5.28	4.61	4.88
C_7^+	4.06	6.15	7.29	7.93

[a] Methane and ethane might be lost in the gas phase. [b] Cracking and isomerization.

increased in intensity and the isomerization reaction seemed to slow down. Because the conversions were very small at that stage, the latter point is only tentative. After this induction period, the conversion rate increased dramatically and cracking and disproportionation products ($\leq C_5$ and $\geq C_7$) were observed, with the lighter products predominating heavily. This reaction pattern is identified as reaction Mode B (cracking mode). Differing from the reaction of 3MP,[5] where the amount of cracking was no greater than 20%, the amounts of cracking-disproportionation products formed from H in the reaction Mode B were 75-80% of the total reaction products. Also, the conversion of H in the reaction Mode B was more than 100 times faster than in the isomerization mode (A), whereas for 3MP the acceleration was about threefold. The two patterns of hexane reaction are shown in Fig. 2, in which only the C_6H_{14} products, common to the two reaction modes, are plotted. Therefore, the figure underrepresents the acceleration observed in the cracking mode. The transition from the "clean" isomerization mode to the cracking mode can be achieved at any moment during the reaction, simply by discontinuing the periodic homogenization. This finding is also illustrated in Fig. 2. On the other hand, after the cracking mode has been initiated, shaking of the tube does not restore the system to the isomerization mode.

The length of the induction period is related to the concentration of the acid. Thus, when the acid concentration was increased by reaction with a slight excess of TFMSA anhydride for 24 hours at 40 °C to convert the existing water to TFMSA,[11] the rate of formation of the alkenyl cations (development of the yellow color at the interface) was reduced and the length of the induction period was increased. On the other hand, addition of water to the acid by saturation of the hydrocarbon with water reduced the reactivity of the hydrocarbon in both modes A and B.[5] The induction period for the cracking mode evidenced in Fig. 2 represents the time needed for the formation of initiators in the acid layer, which are concentrated at the interface with the organic phase. Indeed, a linear dependence of $\ln(t_{\text{induction}})$ upon $1/T$ was observed (three temperatures). A possibility considered at first was water, that is, the reduction in acid strength, but at concentrations higher than 89.3% of TFMSA water is entirely converted to hydronium ions.[12] The diffusion of hydronium ions within the acid should be fast in comparison with the length of the induction period (at least 2.5–3 h at 42 °C) and, therefore, the periodic homogenization of the acid should have no effect.[13] The alkenyl cations remain the only alternative for the initiator of the disproportionation/cracking reaction mode.

An oxidative nature for the initiation of disproportionation was indicated by the observation that the addition of a small amount of a one-electron oxidizing material, like ferric chloride and, to a smaller extent, cupric chloride, reduced the induction period, as shown in Fig. 3. Addition of a similar amount of sodium chloride had no effect on the length of the induction period, indicating that the effect of the other salts was not related to the increase in the ionic strength. The participation of the unsaturated cations in the initiation process is in line with the observation that addition of small amounts of anthracene (1%), which is extracted and hydronated in the acid layer, also reduces the induction period, as seen in Fig. 3. It is also seen that the additives do not affect the rate of conversion after the cracking mode is initiated. It was reported that polycyclic aromatics (*e.g.* naphthalene or anthracene) accelerate transalkylation of alkylbenzenes[14a] and isomerization of tetrahydronaphthol,[14b] both catalyzed by TFMSA. In other studies, a very slow isomerization of butane catalyzed by TFMSA was accelerated by precursors of free-radicals[15] and polyenylic cations were indicated to intervene in the H/D exchange occurring between isobutane and deuterated zeolites, sulfated zirconia, or sulfuric acid.[16] An illustrative description of the reaction pathways of H and TFMSA is shown in Scheme 1.



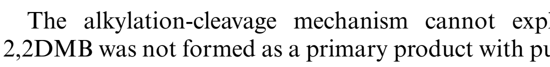
Scheme 1

It is interesting to point out that the relative reactivity of hexane and 3MP in the reaction Mode B is *ca.* 1 : 10. The increase in reactivity of H relative to 3MP in the reaction Mode B from the ratio observed under well-established carbocationic conditions (1 : 1000),[8] which is the same as in our isomerization mode (A), is remarkable. A change in the same direction was observed for the reaction catalyzed by medium-pore zeolites, such as HZSM-5, and was rationalized exclusively by steric factors.[17] That rationalization is now open for questioning. It is noteworthy that the relative reactivity, H : 3MP on HZSM-5 at 120–160 °C is close to 10 : 1 for the reaction in the gas phase but it is about 1 : 10 (the same as for the cracking mode in this work) for the liquid phase reaction.[3]

The product distribution found for the cracking mode at two levels of conversion and at two temperatures is presented in Table 2. An interesting observation is that the *iso*/*normal* ratio was much higher than the equilibrium value for both C_4H_{10} and C_5H_{12} isomers. This feature was recorded before cracking reactions catalyzed by zeolites[18] and indicates that the cracking products were not affected by subsequent isomerization. The large excess of isopentane over *n*-pentane is the most significant in this respect, because the pentyl cations, if formed as intermediates, should isomerize much more easily than the butyl cations.[19] Also similar with cracking on zeolites was the excess of alkanes over alkenes in the product.[20] As a matter of fact, no alkenes were formed in TFMSA, in the sense that there were no alkenes in the hydrocarbon phase. The missing components can in both cases be found in the catalyst, however, as coke precursors on solid catalysts and unsaturated carbocations in the TFMSA phase.

The composition of the C_6H_{14} isomers in Table 2 is also unexpected in that dimethylbutanes appear as primary products. Even 2,2-dimethylbutane (2,2DMB) is found in the mixture in higher concentration than 3-MP at a hexane conversion level as low as 2.8%. This result indicates that the hexane isomers are also formed mainly by a pathway different from normal carbocationic isomerization, for which the sequential conversion: H→(2MP, 3MP)→(2,3DMB, 2,2DMB) applies and the rate constant for the 2,2DMB formation is much lower than the rate constants of the preceding steps.[8] Significantly, in the isomerization of hexane on Pt/mazzite and Pt/mordenite under high pressure, 2,3-dimethylbutane and small amounts of 2,2-dimethylbutane were also formed as primary products.[21] The explanation offered in that case, the unidirectional pore structure of those zeolites,[21] cannot be invoked for TFMSA.

In the carbocationic mechanism, isomerization and cracking are controlled by the interplay of hydrogen and alkyl shifts and β cleavage.[22] The relative rates of these steps and of the intermolecular hydride transfers determine the selectivities for the two pathways. In superacidic media, the formation of carbocations is the result of C–H,[19,23] or C–C bond cleavage[23*c*,*d*,24,25] by a hydron from the acid. A mechanism originally proposed for the strongest superacids,[26] in which the competitive pathways include hypercoordinated carbocations as intermediates has also been extended to solids,[20,27] but the solid acids, particularly zeolites, have long been shown to be too weakly acidic to produce such cations.[2,28] The standard carbocationic mechanism does not account, however, for the products in the reaction Mode B. We have mentioned already that 2,2DMB cannot result as a primary product in the isomerization of H (hydrogen and alkyl shifts in hexyl cations). The alternative involving alkyation to dimeric cations followed by cracking, requires the intervention of dimeric or oligomeric structures like **1** (eqn. (1)) and **2** (eqn. (2)), as intermediates.



$$\mathrm{Me_3C\text{-}CHMe\text{-}C\text{-}C^{+}\text{-}R} \longrightarrow \mathrm{Me_3CCH^{+}\text{-}Me} + \mathrm{>C{=}C\text{-}R} \qquad (1)$$

1

$$\mathrm{Me_3C\text{-}CH^{+}\text{-}CH_2\text{-}CRR'R''} \longrightarrow \mathrm{Me_3CCH{=}CH_2} + \mathrm{RR'R''C^{+}} \qquad (2)$$

2

The alkylation-cleavage mechanism cannot explain why 2,2DMB was not formed as a primary product with pure HF as catalyst, which is in the same range of acid strength with TFMSA,[29] nor the existence of the induction period and the effect of additives. A pathway involving odd-electron intermediates would account for these findings.

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References

1 Presentations in part: (*a*) D. Fărcaşiu, P. Lukinskas and W. Vargas, 36th Annual Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Pittsburgh, 14 May 1998; (*b*) D. Fărcaşiu and P. Lukinskas, 37th Annual Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, Pittsburgh, 3 May 1999; (*c*) P. Lukinskas, W. Vargas and D. Fărcaşiu, 16th North American Catalysis Society Meeting, Boston, MA, 3 June 1999, Abstract C041.

2 (*a*) D. Fărcaşiu, *Top. Catal.*, 1999, in print; (*b*) D. Fărcaşiu and P. Lukinskas, *Rev. Roumaine Chim.*, 1999, in print.

3 D. Fărcaşiu, W. Vargas and K.-H. Lee, *J. Catal.*, submitted for publication.

4 (*a*) D. Fărcaşiu, presented at the 15th Meeting of the North American Catalysis Society, Chicago, IL, 20 May 1997; (*b*) J. Q. Li, unpublished results from our laboratory.

5 D. Fărcaşiu and P. Lukinskas, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 1609.

6 (*a*) D. Fărcaşiu, A. Ghenciu and J. Q. Li, *J. Catal.*, 1996, **158**, 116; (*b*) A. Ghenciu and D. Fărcaşiu, *Catal. Lett.*, 1997, **44**, 29; (*c*) D. Fărcaşiu, J. Q. Li and A. Kogelbauer, *J. Mol. Catal.*, 1997, **124**, 67.

7 Currently part of SPSS, Inc., http://www.spss.com/software/science/SigmaPlot/

8 (*a*) D. A. McCaulay, *J. Am. Chem. Soc.*, 1959, **81**, 6437; (*b*) D. M. Brouwer and J. M. Oelderik, *Recl. Trav. Chim. Pays Bas*, 1968, **87**, 721.

9 R. E. Robertson, *Prog. Phys. Org. Chem.*, 1967, **4**, 213.

10 N. C. Deno, in *Carbonium Ions*, vol. 2, eds. G. A. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, 1970, chapter 18.

11 (*a*) D. Fărcaşiu, G. Marino, G. Miller and R. V. Kastrup, *J. Am. Chem. Soc.*, 1989, **111**, 7210; (*b*) D. Fărcaşiu, A. Ghenciu, G. Marino and R. V. Kastrup, *J. Mol. Catal.*, 1997, **126**, 141.

12 D. Fărcaşiu and D. Hâncu, *J. Chem. Soc.*, *Faraday Trans.*, 1997, **93**, 2161.

13 M. Eigen, *Angew. Chem.*, *Int. Ed.*, 1964, **3**, 1.

14 (*a*) M. Farcasiu and T. R. Forbus, US Patent 4454364, 1984; (*b*) M. Farcasiu and C. Smith, *Energy Fuels*, 1989, **3**, 562.

15 H. Choukroun, A. Germain and A. Commeyras, *Nouv. J. Chim.* 1981, **5**, 39.

16 J. Sommer, A. Sassi, M. Hachoumy, R. Jost, A. Karlsson and P. Ahlberg, *J. Catal.*, 1997, **171**, 391.

17 (*a*) V. J. Frilette, W. O. Haag and R. M. Lago, *J. Catal.*, 1981, **67**, 218; (*b*) W. O. Haag, R. M. Lago and P. B. Weisz, *Faraday Soc. Discuss.*, 1982, **72**, 317; (*c*) J. A. Martens, M. Tielen, P. A. Jacobs and J. Weitkamp, *Zeolites*, 1984, **4**, 98; (*d*) J. Weitkamp, *Stud. Surf. Sci. Catal.*, 1990, **65**, 21.

18 For example: P. V. Shertukde, G. Marcelin, G. A. Sill and W. K. Hall, *J. Catal.*, 1992, **136**, 446.

19 D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.*, 1972, **9**, 179.

20 K. A. Cumming and B. W. Wojciechowski, *Catal. Rev.-Sci. Eng.*, 1996, **38**, 101.

21 J. F. Allain, P. Magnoux, Ph. Schulz and M. Guisnet, *Appl. Catal.*, 1997, **152**, 221.

22 H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversions*, Academic Press, New York, 1981.

23 (*a*) H. S. Bloch, H. Pines and L. Schmerling, *J. Am. Chem. Soc.*, 1946, **68**, 153; (*b*) C. D. Nenitzescu, M. Avram and E. Sliam, *Bull. Soc. Chim. Fr.*, 1955, 1266; (*c*) J. M. Oelderik, cited in: D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc.*, 1964, 147; (*d*) J. M. Oelderik, E. L. Mackor, J. C. Platteeuw and A. van der Wiel, Brit. Patent 981311, appl. 1962; see also US Patent 3201494, 1965.

24 (*a*) H. Hogeveen and A. F. Bickel, *Chem. Commun.*, 1967, 635; (*b*) G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, 1967, **89**, 2227, 4739.

25 D. Fărcaşiu, M. Siskin and R. P. Rhodes, *J. Am. Chem. Soc.*, 1979, **101**, 7671.

26 (*a*) G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, 1968, **90**, 2726; (*b*) G. A. Olah, G. K. S. Prakash and J. Sommer, *Science*, 1979, **206**, 13; (*c*) G. A. Olah, G. K. S. Prakash and J. Sommer, *Superacids*, Wiley-Interscience, 1985, Chapter 5.

27 W. O. Haag and R. M Dessau, *Proc. Intl. Congr. Catal.*, *9th 1984*, Dechema, Frankfurt-am Main, 1984, Vol. 2, p. 305.

28 (*a*) D. Fărcaşiu, G. M. Marino, R. V. Kastrup and K. D. Rose, *185th Natl. ACS Mtg.*, Seattle, WA, March 23, 1983; Abstr. ORGN160; (*b*) V. B. Kazansky, *Acc. Chem. Res.*, 1991, **24**, 379; (*c*) T. Xu, E. J. Munson and J. F. Haw, *J. Am. Chem. Soc.*, 1994, **116**, 1962; (*d*) D. Fărcaşiu, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1801.

29 R. J. Gillespie and J. Liang, *J. Am. Chem. Soc.*, 1988, **110**, 6053.

Paper 9/06133I