

The effect of cycloalkanes on the reaction of hexane with trifluoromethanesulfonic acid

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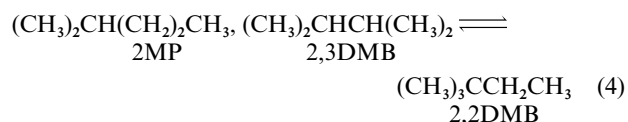
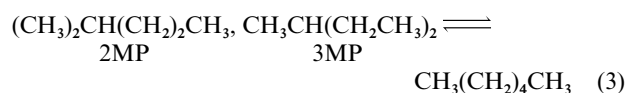
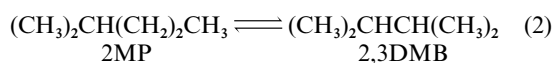
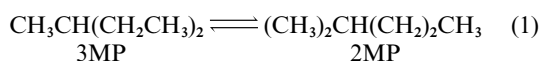
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The chain reaction of hexane catalyzed by trifluoromethanesulfonic acid (TFMSA) under mild conditions (disproportionation and cracking) was suppressed by small amounts (1–5%) of cycloalkanes, namely methylcyclopentane (MCP), cyclohexane (CH) and cyclopentane (CP). The reaction then proceeded in the isomerization mode. The addition of ferric ions to the acid overcomes the stabilizing effect of cycloalkanes. The formation of substituted allyl cations during the induction period for cracking was also inhibited by very small amounts of MCP. Addition of MCP or 3-methylhexane had the same effect on reduction of the induction period and (minor) on the increase in rate of the reaction stabilized against cracking by CP addition. Incorporation of deuterium into the products from hexane and MCP-*1-d* shows that MCP acts as a hydride relay in the reaction. Hydride transfer catalysis by the reaction product is disproved for any catalyst. Both the reaction of hexane with MCP-*1-d* and of uniformly labeled hexane-U-*d*_{4,3} with MCP showed H/D scrambling which is extensive among all products (2- and 3-methylpentane, cracking products and CH) and the acid catalyst, smaller in MCP, and is virtually zero in hexane. Thus, the main features of the reaction are the initiation by oxidation and the formation and hydration of alkenes.

1. Introduction

With the required reduction of aromatics in liquid fuels, paraffin isomerization and cracking remain, together with paraffin–olefin alkylation, the processes of choice for production of high-octane hydrocarbon mixtures.¹ As a model of isomerization, the interconversion of C₆H₁₄ isomers² has been considered for a long time to be the standard reaction for defining carbocationic mechanism in alkane conversion.³ A mixture of all five isomers, *n*-hexane, 2-methylpentane (2MP), 3-methylpentane (3MP), 2,3-dimethylbutane (2,3DMB), and 2,2-dimethylbutane (2,2DMB), is ultimately obtained from any of them (eqns. (1)–(4)). Characteristic rate relationships



for the isomerization steps, $k(1) > k(2) \gg k(3), k(4)$, were found and they are diagnostic for the carbocationic isomerization mechanism.

The kinetics and mechanism of these reactions with HF–BF₃ and HF–SbF₅ as catalyst have been studied,⁴ but neither of these systems is employed in industrial installations. The mechanism was, however, applied *in toto* to the solid acids of interest for that purpose, like silica–alumina and zeolites,¹ and also sulfated metal oxides.⁵ A comparison between the two types of

catalysts is difficult because of the large difference between the temperatures at which they catalyze the reactions. We have, therefore, initiated a study of saturated hydrocarbon conversions that can be induced by solid and liquid acid catalysts at similar temperatures.⁶ The liquid catalyst chosen for this comparison was trifluoromethanesulfonic acid (TFMSA), a weak superacid,^{7b} used previously for the isomerization of polycyclic hydrocarbons^{8a} and of butane.^{8b}

We have previously reported on the reactions of liquid alkanes hexane and 3-methylpentane (3MP) with (TFMSA).⁷ An unexpected feature was the existence of two reaction pathways, one of normal carbocationic isomerization, another of disproportionation–cracking, induced by the alkenyl cations (substituted allyl cations) formed in the acid layer near the interface. The *isomerization mode* was observed as an induction period for the *cracking mode*, which exhibited features of a free-radical chain superimposed over the carbocationic mechanism. When we maintained the concentration of alkenyl cations at the interface below a critical value by stirring the acid layer or periodically shaking the entire mixture, the transition to the cracking mode occurred only after long periods and kinetic studies of the isomerization were possible. The addition of one-electron oxidizers (*e.g.*, ferric ions) or of anthracene^{7b} shortened the induction period. This highly unusual type of reaction deserved further investigation, the results of which are reported here.

2. Experimental

2.1. General

The same commercial hexane ($\geq 99.5\%$ pure, analyzed as 99.7%, with 0.2–0.3% MCP) as in the earlier work^{7b} was used in most experiments in which MCP was added. The reagent-grade MCP contained about 2% hexane. Cyclopentane (CP), 99.5%, contained $\leq 0.5\%$ 2,2DMB and $< 0.05\%$ MCP. Cyclohexane (CH), 99.8%, contained 0.07% hexane, 0.06% branched hexanes, and 0.02% MCP. Hexa-1,5-diene (Aldrich) was of 97% purity. The TFMSA catalyst⁷ and its anhydride were also from

Aldrich. Deuterium gas of 99.8% isotopic purity was procured from Cambridge Isotope Laboratories and Pd on activated carbon (10%), from Acros. The GLC (packed column, 48 °C) and GC-MS analyses were conducted as described in ref. 7. ²H-NMR analyses were run at 46.073 MHz. The diagrams shown in the figures were constructed from the experimental points using the SigmaPlot program, developed by Jandel Scientific.⁹

2.2. Hexane¹⁰

A Grignard reagent was prepared from 82.5 g (0.5 mol) of 1-bromohexane and 12.3 g (0.525 equiv.) of magnesium in 100 mL of ether and was then decomposed with ammonium chloride (27 g) in water (80 ml). The solid was dissolved in 10% hydrochloric acid, the layers were separated and the organic layer was washed twice with 10% HCl and three times with water (pH of the final washing was 5–6). Drying (MgSO₄) and distillation through a 20 cm annular column gave 80 ml of a mixture of ether (70%) and hexane (30%) and a residue that upon straight distillation gave a 97:3 mixture of hexane and ether. The latter mixture was cooled in ice, then extracted twice with cooled concentrated sulfuric acid and twice with distilled water. Drying (MgSO₄) and distillation yielded 16 g of hexane (37% yield). The GLC analysis indicated a purity greater than 99.9%, with 3MP (<0.02%) as an impurity. The distillation forerun was used in a subsequent batch, roughly doubling the yield.

2.3. Deuterated hexane

Hexa-1,5-diene (4 g) and 10% Pd/C (0.04 g) were placed in a 10 mL round-bottomed flask containing a magnetic stirring bar and provided with a gas-inlet-and-vacuum adapter, with stoppers on both tubes and the inlet tube cut slightly shorter than the ground joint and drawn to an inner diameter of 2 mm to provide a hydrogen jet to hit the liquid surface upon filling. The adapter was connected with Tygon tubing to the top of a gas-buret, with silicon oil as leveling liquid. The alternative connection at the top of the buret, also through Tygon tubing, was to a stainless steel swagelock unit with a vacuum/pressure gauge and connections to the deuterium lecture bottle through a needle valve and to a vacuum pump through another needle valve. The Tygon tubes were heated with a hot air blower before being forced onto the glass or metal tubes. The oil was brought to the top of the buret, the deuterium admission part was evacuated with a roughing pump, then filled with deuterium, then the buret was also filled with gas. The reaction flask and its connection to the buret were then evacuated, after chilling the flask in liquid nitrogen. Deuterium was admitted from the buret and the flask was brought to room temperature, then stirring was started. Deuterium was introduced into the buret as the reaction progressed. When the absorption stopped (a stoichiometric amount of D₂ was consumed), the flask was removed from the installation and the product (3 g, 75% yield) was recovered by bulb-to-bulb distillation on a short vacuum line. Purification as described for the unlabeled synthetic hexane and another bulb-to-bulb distillation gave the product used in the reaction with TFMSA.

The deuterated hexane contained an average of 4.3 deuterium atoms per molecule and was a mixture of all isotopomers, from *d*₀ to *d*₁₄, with the distribution: 5.3, 9.8, 13.1, 14.8, 14.3, 12.8, 10.0, 7.4, 5.0, 3.2, 2.0, 1.2, 0.7, 0.3, and 0.2%, respectively (GC-MS). ²H-NMR analysis showed that the isotope was statistically distributed among all methyl and methylene groups. Therefore, by the rules of nomenclature of labeled compounds it is described as hexane-U-d_{4,3}.

2.4. Methylcyclopentane-1-d₁

The synthesis of this material has been recently described.¹¹

2.5. Deuterated TFMSA

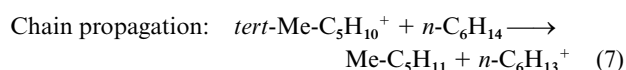
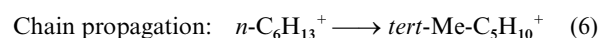
Deuterated TFMSA was prepared by the reaction of its anhydride with D₂O at 50–60 °C for 24 h.

2.6. Catalytic reactions

The TFMSA-catalyzed reactions of hexane and mixtures of it with other hydrocarbons (catalyst to reactant molar ratios 1:4 to 1:5) were conducted in 6 mm od glass tubes covered with rubber septa, as in our previous studies.⁷

3. Results and discussion

The different rates of reactions of hexane isomers in the carbocationic isomerization are rationalized by changes in rates of the mechanistic steps of the reaction (eqns. (5)–(7)) and changes in the rate-determining step.^{1a,4b,12}



For the TFMSA-catalyzed reaction, the relative reactivity of 3MP and hexane in the isomerization mode was about the same (almost 1000) as for the reaction catalyzed by HF-based superacids.⁴ At longer reaction times, the consecutive isomerization steps connecting all the hexane isomers^{4b} were observed. In the cracking mode, however, the reactivity ratio shrank to about ten, because the reaction of hexane was accelerated much more than the reaction of 3MP.⁷ Hexane isomers were observed as 80% of the products from 3MP and 20% from hexane in the cracking mode. It is not clear, however, how much of these were formed by isomerization and how much by disproportionation, together with the ≤C₅ and ≥C₇ products. Some peculiarities in the product distribution were observed for the reactions of hexane.^{7b} A careful study of the products from 3MP has since revealed similar features, namely: the absence of olefinic products (they are retained as alkenyl cations in the acid layer), formation of 2,2DMB as a primary product, albeit in smaller proportions than from hexane, and an excess of the branched isomers over the equilibrium value for butanes and pentanes (ratios *iso:normal* of 20–40) even more pronounced than from hexane (ratios *iso:normal* of 7–9).

In the heavier fraction, 2,4-dimethylpentane, two methylhexanes, two methylheptanes and some octane and nonane isomers were identified by GC-MS from both hexane and 3MP.

We noted, however, that hexane always contained at least 0.2% of MCP (see Experimental section)^{7b} and that the induction period for the cracking mode was somewhat shorter for the purest reagent than for hexane from other sources, which contained 0.4–0.6% MCP. We found no report of hexane isomerization or cracking using synthetic hexane, which suggests that all the literature studies were conducted with reactant as pure (or impure) as ours, at best. Most disturbing, however, in the work of Brouwer and Oelderik the catalyst was generated by the reaction of the acid (HF–SbF₅) with an excess of MCP, which was cleaved to *tert*-hexyl cations and then converted by hydride transfer to methylcyclopentyl cations. There was no free antimony pentafluoride left.^{4b} Unnoticed before by us and apparently by others was the mention that 1% MCP was added to the feed, “to prevent runaway cracking”.^{4b} It is likely that the methylcyclopentyl cations in the acid layer were not replaced by the less stable¹³ cations of the reactant. It was also reported that the interconversion of methylpentanes (2MP, 3MP) with hexane had the hydride transfer as rate-determining step.^{4b} The two hydride transfer steps could have then involved in one step the pool of methylcyclopentyl cations and reactant molecules and

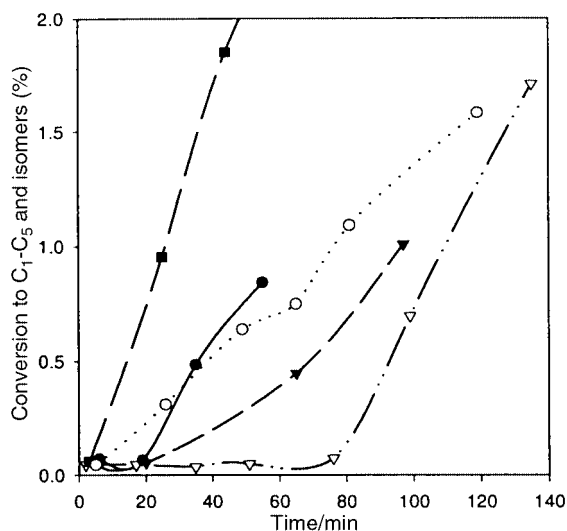
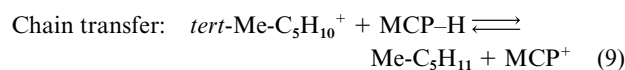
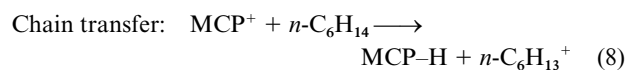


Fig. 1 The effect of MCP content on the isomerization and disproportionation–cracking of hexane with TFMSA. ■, ● 0%; ○ 0.28%; ▼ 0.36%; ▽ 0.47%.

in the other step the product cations and MCP in the feed (eqns. (8) and (9)).



We next conducted a study of the reaction of synthetic hexane, containing no MCP, with TFMSA and then we checked the effect of the addition of controlled quantities of MCP and other cycloalkanes upon the reaction. The role of the hydride transfer step and the possible intervention of olefinic intermediates were examined in reactions in which one component (hexane, MCP, or TFMSA) was labeled with deuterium. The experiments with the deuterated hydrocarbons were run at very low conversions, to evidence the initial isotope distribution, unaltered by secondary and subsequent reactions or by reversibility.

In the reaction of synthetic hexane with TFMSA at 42 °C, which is near the higher end of the temperature range employed for this reactant,⁷ the induction period was reduced essentially to zero. Addition of traces of MCP had no effect, but larger amounts inhibited the chain disproportionation and slowed the development of the yellow color in the acid layer near the interface, signature of the substituted allyl cations connected to the initiation of the cracking mode reaction. The conversion values measured for the reaction of pure hexane exhibited some dispersion, as expected for a chain-type reaction. This feature is illustrated by the comparison of two runs with pure hexane in Fig. 1. It is clear, however, that the chain reaction starts earlier in the absence of MCP than in its presence. A threshold of about 0.3–0.4% MCP may be established for the inhibition of the disproportionation at this temperature (Fig. 1). Some retardation of the allyl cation formation was seen even at slightly lower MCP concentrations (Fig. 2). Mixtures containing more than 1.7% MCP showed very little cracking even after 16 days. Addition of 5% MCP to a reaction mixture already in the cracking mode restored the isomerization mode, as shown in Fig. 3. The change in the growth of isomers (Fig. 3) indicates that in the cracking mode they were formed for the most part by a different mechanism than in the isomerization mode. The product distribution in the two reaction modes has been detailed earlier.^{7b}

A possible rationalization of these results was the intervention of hydride transfer catalysis by MCP,¹⁴ that is, the scheme

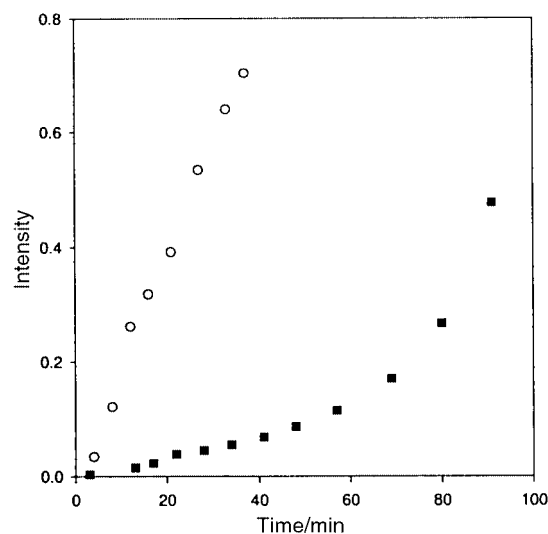


Fig. 2 The effect of the MCP addition on the development of the UV absorption (λ 300–320 nm, shifting in time⁷) in the reaction of hexane with TFMSA. ○ No MCP; ■ 0.25% MCP.

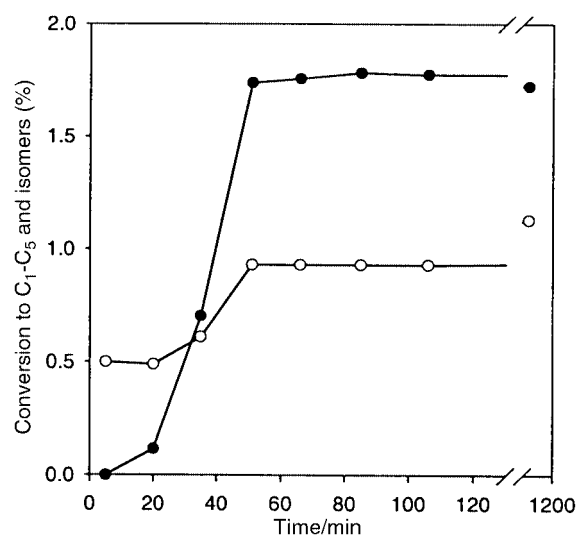


Fig. 3 Suppression of the cracking mode of the reaction of hexane by addition of larger amounts of MCP. The reactant contained 0.05% 2MP and 0.44% 3MP. ● Cracking products; ○ hexane isomers (2MP + 3MP + 2,3DMB).

of cationic isomerization of hexane (eqns. (5)–(7)) is extended to include eqns. (9) and (8). Because of very low conversions, the reaction reversibility should have no observable effects in our experiments and it was neglected in the equations, except for the transfer of a hydride tertiary on both sides of eqn. (9). If hydride transfer catalysis intervened, it would result from the rate of eqn. (8) being higher than that of eqn. 7 (Curtin–Hammett principle).¹⁵

It was found, however, that the inhibition of the chain disproportionation reaction can also be achieved by the addition of cyclohexane (CH, Fig. 4) and cyclopentane (CP, Fig. 5). Both CH and CP contain only secondary C–H bonds and are expected to contribute to the hydride transfer step much less than MCP, if at all. The cycloalkanes have, therefore, an effect in retarding the oxidation that generates allyl cations.^{7b} In fact, the effect of MCP can be counteracted by the addition of ferric ions.

The existence of a minor effect of MCP on the “clean” isomerization rate was established by the addition of MCP to a reaction stabilized against disproportionation by 13% CP, at room temperature. In the absence of MCP, the reaction in the isomerization mode occurring under these conditions also shows an induction period (Fig. 6). Upon addition of 0.3% of

Table 1 Distribution of label in reactants and products of reaction of hexane with MCP-*I-d* (1.8%) and TFMSA (at room temperature, with stirring)

Time/h	Conv. (%)	Hexane ^a	2MP ^a	3MP ^a	MCP ^a	MCP conv. ^b (%)	CH ^a
42	0.20	<0.01	0.86	— ^c	0.93	0.23	0.18
67	0.27	<0.01	0.86	0.86	0.90	0.33	0.18
92.5	0.38	<0.01	0.80	0.76	0.86	0.41	0.18
142	0.61	<0.01	0.70	0.70	0.80	0.68	0.18
186	0.89	<0.01	0.63	0.55	0.76	0.92	0.19

^a Number of deuterium atoms per molecule. ^b CH is the only observed product from MCP and TFMSA. ^c The amount of 3MP was too small to allow accurate measurement.

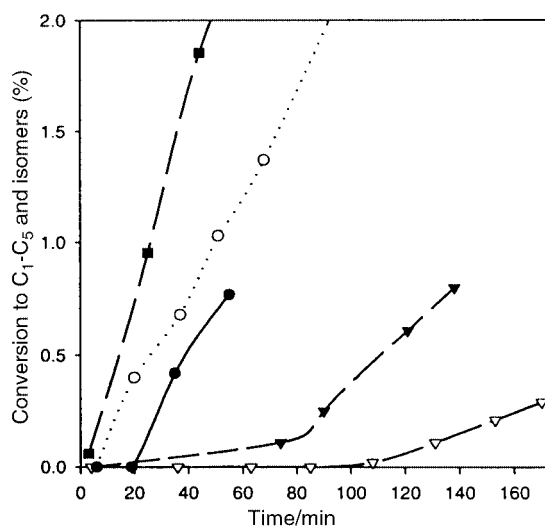


Fig. 4 The effect of CH content on the isomerization and disproportionation–cracking of hexane with TFMSA. ■, ● 0%; ○ 0.66%; ▽ 1.75%; ▽ 2.40%.

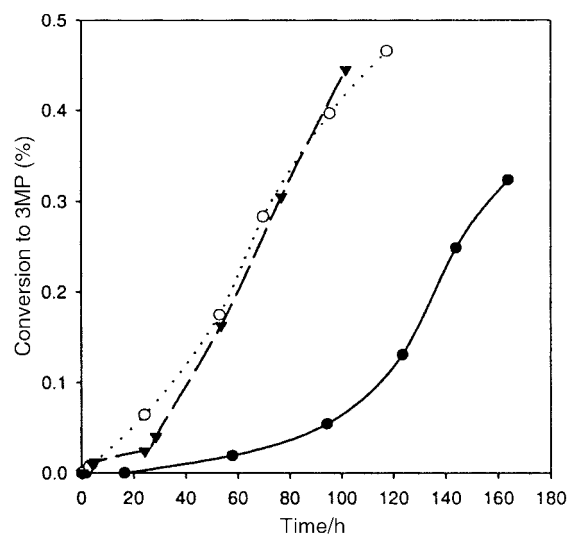


Fig. 6 The effect of MCP and 3-methylhexane (3MH) on the reaction of hexane stabilized by 13% CP with TFMSA. ● Pure hexane; ○ 0.3% MCP; ▽ 0.3% 3MH.

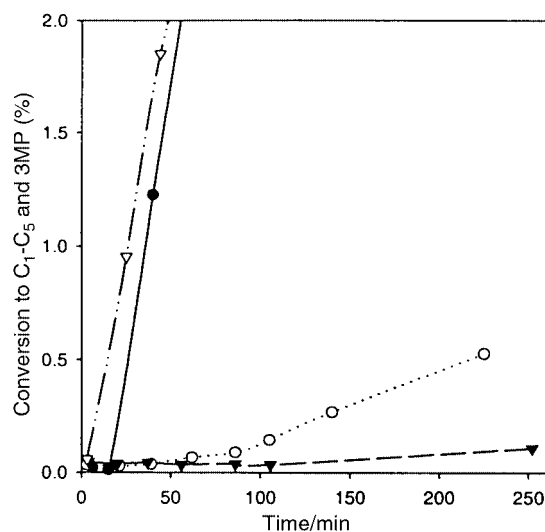


Fig. 5 The effect of CP content on the isomerization and disproportionation–cracking of hexane with TFMSA. ▽, ● 0%; ○ 2.66%; ▽ 3.29%.

MCP, the isomerization begins immediately, but the rate is similar to that observed after the induction period without MCP. It was tempting to assign the rate increase in the absence of MCP to the isohexanes (2MP and 3MP) formed (*ca.* 0.1%) at the end of the induction period. Addition of 0.3% of the branched acyclic homolog 3-methylhexane at the beginning of reaction had an effect indistinguishable from that of MCP (Fig. 6). The explanation of this effect as hydride transfer catalysis is undermined, however, by the observation that increases of MCP concentration above the threshold did not affect the rate and larger amounts (up to 8%) cause a slight decrease in the isomerization

rate. On the other hand, the (branched) reaction product *cannot* act as a hydride transfer catalyst, as proposed,¹⁴ in *any* reaction system. Of the two intervening carbocationic intermediates, the hydride transfer from the product to the reactant cation has a retarding effect (it is the reverse reaction), whereas the hydride transfer to the product cation is an identity reaction and has no effect whatsoever. (Rigorously speaking, the addition of product should reduce the rate, because of reaction reversibility.) Alternative explanations are required for all the cases in which acceleration of acid-catalyzed reactions of *n*-alkanes by the reaction products was observed. Minor effects like an increase in surface tension or an increase in solubility of the reactant in the acid layer because of a slightly higher content of ions¹⁶ would suffice in our case.

The above results do not mean that MCP does not participate in hydride transfer reactions with the cationic or cationoid intermediates of the reaction of hexane. Information about this reaction step was obtained from the study of the reaction in the presence of MCP-*I-d*. Examination of reaction mixtures at very low conversions allows the evaluation of the initial label distribution in the reaction products, when the deuterium source is still in large excess over the (deuterated) product formed. Addition of 1.8% MCP-*I-d* to the reaction of H gave predominantly deuterated 2MP and 3MP (more than 85% MP-*d* at 0.2–0.27% conversion), whereas the CH product was extensively de-deuterated and MCP was de-deuterated to a significantly smaller extent (Table 1). The material balance did not equate exactly, because some deuterium was lost to the acid, as shown below, and the loss was more pronounced from the reaction products than from MCP-*d*.

In a hydride transfer step, MCP-*I-d* competes with hexane as the hydride/deuteride source. For a nonselective reaction, the ratio MP-*d*:MP-*h* should be the same as the ratio MCP-*I-d*:hexane \approx 1:50. Instead, we found MP-*d*:MP-*h* \approx 5.7:1

Table 2 Content (%) and distribution (mole fraction) of label in reactants and products of reaction of hexane-U- $d_{4,3}$ (30.7% deuterium content) with MCP (2.24%) and TFMSA (at room temperature, with stirring)

Time/h	Conv. ^a (%)	Hexane ^b	2MP ^b	MCP ^b	CH ^b					
24	0.39	30.12	5.78	0.51 d_0	3.98	0.65 d_0	4.50	0.60 d_0		
				0.29 d_1					0.26 d_1	0.30 d_1
				0.12 d_2					0.06 d_2	0.08 d_2
				0.04 d_3					0.01 d_3	0.02 d_3
				0.03 d_4						
49	0.63	30.33	6.58	0.43 d_0	6.38	0.49 d_0	5.89	0.51 d_0		
				0.34 d_1					0.34 d_1	0.33 d_1
				0.16 d_2					0.12 d_2	0.12 d_2
				0.05 d_3					0.04 d_3	0.03 d_3
				0.02 d_4					0.01 d_4	0.01 d_4
	0.01 d_5									
74	0.98	30.35	8.27	0.33 d_0	8.58	0.37 d_0	7.30	0.44 d_0		
				0.35 d_1					0.36 d_1	0.35 d_1
				0.20 d_2					0.18 d_2	0.15 d_2
				0.08 d_3					0.06 d_3	0.05 d_3
				0.03 d_4					0.02 d_4	0.01 d_4
	0.01 d_5	0.01 d_5								

^a Some initial cracking occurred and it is included in the conversion figures. ^b The deuterium content is given as a percentage D of total (D + H).

(85:15), a 285-fold reversion. This number has to be corrected for three factors. The first is the primary isotope effect, which multiplies it. As the position of the transition state along the reaction coordinate connecting two similarly stable tertiary cations is likely to be near the midpoint, the isotope effect may be close to the maximum value of 8 at room temperature.¹⁷ Because of the same isotope effect, as soon as nondeuterated MCP appears in the mixture, it participates in hydride transfer preferentially to MCP- d and reduces the amount of deuterium observed in MP-s. The second factor operates if the reaction occurs in the acid layer, rather than at the interface, because of the different solubility of H and MCP in the acid. This factor cannot in any case be larger than two. Finally, the measured value has to be increased to account for the loss of deuterium from the product to the acid. Altogether, the rate constant for hydride transfer to the cations of MP-s should then be at least three orders of magnitude greater for MCP than for hexane as hydride donors. It follows that in the reactions of hexane containing 0.3–8% MCP the hydride transfer step involves the latter predominantly or exclusively, yet the effect on the reaction rate is minor. This breakdown of the rate-product correlation¹⁸ suggests that the hydride transfer is not the rate-determining step in the *n*-hexane isomerization.

The isomerization of MCP occurring concomitantly to the reaction of hexane was peculiar in that it went beyond the equilibrium composition. In the end, CH was the only isomer present in the reaction mixture. We have no explanation for this observation other than that it was theoretically predicted long ago for isomerizations in which isomers undergo side reactions of different kinetic orders.¹⁹

In another series of experiments, the hydrogen transfers during the reaction were examined for deuterated hexane and regular MCP. The partially but uniformly labeled hexane is much cheaper than the fully deuterated material. Moreover, differences in the label content of products from it could give information about the relative importance of the isotope effect-sensitive hydride transfer step in their formation.

The reaction of hexane-U- $d_{4,3}$ was conducted in the presence of 2.24% MCP. The deuterium content and the isotopomer distribution in reactants and products are shown in Table 2. It is seen that 2MP had lost the majority of its deuterium. The same observation was made for 3MP, but that peak was small and the results less accurate, therefore they were not entered in Table 2. The loss cannot be assigned to the addition of one hydrogen per molecule of product coming from MCP in the hydride transfer

step or from any possible isotope fractionation. For a starting material with 5.3% hexane- d_0 and 9.8% hexane- d_1 ($d_1:d_0 = 1.85$) and the label distributed statistically among all the methyl and methylene groups, the ratio 2MP- d_1 :2MP- d_0 could vary from 1.52 to 1.71, for a primary KIE between one and infinity, only slightly reduced by secondary KIE. This is far from the 2MP- d_1 :2MP- $d_0 = 0.6$ measured at 0.39% conversion. At the same time, deuterium was incorporated into CH and even MCP. As shown in Table 2, trideuterated CH and MCP were seen already at 0.39% conversion and the tetradeuterated species at 0.98% conversion. These results show that the carbocations formed at the acid strength of TFMSA, by no matter what process, are converted to the corresponding alkenes, which undergo multiple reprotonations and eliminations. The alkenes may be in equilibrium with the esters. The evolution of deuterium content of 2MP with time, lowest in the earliest sample and increasing with conversion, indicates full randomization of the label with the acid at all times. The deuterium content of the starting hexane did not change, but the conversions examined were very low, anyway.

The isotope equilibration of the C–H bonds with the acid hydrogen was also evidenced by comparison of the intensity ratio of the ²H NMR signals of the fresh acid and spent acid (reacted for four days to 1.3% hexane conversion) to the signal of the natural-concentration deuterium in a chloroform standard. Also, upon shaking the spent acid with toluene for 2 min at room temperature,²⁰ we observed isotope exchange, leading to the formation of mono- and dideuterated toluene. These tests demonstrated that the acid was significantly deuterated. On the other hand, the reaction of synthetic hexane with TFMSA- d at 0.2% conversion, just before the onset of the cracking mode, gave nearly 76% deuterated 2MP, that is, containing 10.5 D atoms per molecule. The H/D exchange of saturated hydrocarbons with sulfuric acid²¹ and with solid acids²² has been reported.

The cracking products were also polydeuterated (Table 3). At higher conversions, the deuterium content of all products decreases, as calculated for the isotopic dilution of the acid by exchange. Significantly, the starting material, hexane, contains negligible amounts of deuterium (less than 0.1%), up to 9.11% conversion. In fact, the deuterium contents of hexane in Table 3 are below the uncertainty limit of the measurements and were entered in the table for the sake of not withholding any data. If 0.05% D at 0.20% conversion were meaningful, the deuterium content at a conversion 45 times higher (9.1%) should be significant, rather than still below the error limit.

Table 3 Content of deuterium in the reactant and products of reaction of hexane with TFMSA-*d* (at room temperature, with stirring)

Time/h	Conv. ^a (%)	Hexane ^b	Isobutane ^b	Isopentane ^b	2MP ^{b,c}
45	0.20	0.05	—	—	75.5
86	0.75	0.05	44.33	45.2	61.7
89	3.36	0.07	14.2	16.5	27.4
92	9.11	0.07	6.25	7.75	9.72

^a The first entry represents “clean” isomerization, the other entries cracking–disproportionation. ^b Percentage D of total (D + H). ^c The smaller peak for 3MP had similar D content with 2MP in each case.

Table 4 Content of deuterium in the products of reaction of hexane-U-*d*_{4,3} (30.7% deuterium content) with CP (14%) and TFMSA (at room temperature, with stirring)^a

Time/h	Conv. ^b (%)	Isopentane ^b	2MP ^b	3MP ^b	CP ^b
6	0.45	3.00	6.65	8.43	0.35
19	1.00	4.29	9.92	10.88	1.50
24.5	1.14	8.02	10.22	11.15	1.60

^a Hexane showed no loss of D. ^b Percentage D of total (D + H).

To study the reaction of hexane with MCP-*d* in the cracking mode, ferric ions were added to the mixture.^{7b} The transfer of deuterium from MCP-*d* to all the reaction products and to the acid was at least as important as for the reaction in the isomerization mode, but the unreacted hexane showed again no deuteration above the limit of our analysis.

Extensive deuterium exchange was also seen in the reaction of labeled hexane containing 14% CP, but no MCP, as shown in Table 4. The GLC peak of CP covered that of the 2MP product, but the deuterium content of the latter was accurately measured from the intensities of the peaks of the molecular ion of the *d*₀ (*m/z* 86) and the corresponding deuterated species, even though the content of 2MP in the mixture could not be determined. Of the cracking products, the deuterium content of isopentane formed is also shown. It exhibits a large deuterium loss. In this, as in the experiments described in the previous paragraphs, the measured deuterium content of the hydrocarbon products roughly matches the distribution calculated for full exchange with the acid (statistical distribution).

The lack of return to the reactant was not manifested in the corresponding reaction of 3MP with TFMSA-*d*, conducted in the isomerization mode, presented in Table 5. Slow, but steady, deuterium incorporation in 3MP was observed. On the other hand, the deuteration of the product did not show a maximum at the earliest time, but increased up to a conversion of 3.37% and then decreased because of the isotopic dilution of the acid. The differences in behavior of 3MP and hexane could be most simply rationalized by the control of the reaction of the latter by the hydride transfer step. The observation of higher conversions for the reaction of hexane-U-*d*_{4,3} with MCP (Table 2) than for the reaction of hexane with MCP-*d* (Table 1) points in the same direction. The lack of appreciable acceleration by the added MCP shown in Fig. 6 contradicts this hypothesis, however, and remains puzzling. There is, of course, the possibility that the “classical” isomerization mechanism comprising only initiation (mainly by protonation), 1,2-shifts (over protonated cyclopropanes) and hydride transfers (eqns. (5)–(7) or (5)–(9)) needs amending. At least some of the results can be rationalized if the initial activation of the alkane is oxidative, which is consonant with the existence of an induction period, rather than by acidolysis. Each molecule that reacts goes through the olefinic state several times before forming the product, even though no alkene is seen in the products. The alkenes or esters (mechanistically equivalent to the alkyl cations) are in part oxidised to alkenyl cations, the complexity and stability of which increase in time. A tertiary hydrogen from a branched alkane or, even better, from MCP, can be transferred to the initial, secondary alkenyl cations, thus reverting them to reactive

Table 5 Content (%) and distribution (mole fraction) of deuterium in the reactant and product of the reaction of 3MP with TFMSA-*d* (at room temperature, with stirring)

Time/min	Conv. ^a (%)	2MP ^b	3MP ^{b,c}		
10	1.23	11.63	0.58 <i>d</i> ₀	0.31	0.98 <i>d</i> ₀
			0.16 <i>d</i> ₁		0.01 <i>d</i> ₁
			0.11 <i>d</i> ₂		0.01 <i>d</i> ₂
			0.08 <i>d</i> ₃		
			0.03 <i>d</i> ₄		
25	3.37	20.47	0.35 <i>d</i> ₀	1.53	0.93 <i>d</i> ₀
			0.11 <i>d</i> ₁		0.02 <i>d</i> ₁
			0.09 <i>d</i> ₂		0.01 <i>d</i> ₂
			0.08 <i>d</i> ₃		0.01 <i>d</i> ₃
			0.08 <i>d</i> ₄		0.01 <i>d</i> ₄
			0.07 <i>d</i> ₅		
			0.07 <i>d</i> ₆		
			0.05 <i>d</i> ₇		
			0.03 <i>d</i> ₈		
			0.02 <i>d</i> ₉		
42	5.33	19.13	0.29 <i>d</i> ₀	1.72	0.92 <i>d</i> ₀
			0.15 <i>d</i> ₁		0.03 <i>d</i> ₁
			0.13 <i>d</i> ₂		0.02 <i>d</i> ₂
			0.11 <i>d</i> ₃		0.01 <i>d</i> ₃
			0.10 <i>d</i> ₄		0.01 <i>d</i> ₄
			0.07 <i>d</i> ₅		
			0.05 <i>d</i> ₆		
			0.04 <i>d</i> ₇		
			0.02 <i>d</i> ₈		
			0.01 <i>d</i> ₉		
70	7.15	15.06	0.33 <i>d</i> ₀	1.90	0.90 <i>d</i> ₀
			0.21 <i>d</i> ₁		0.04 <i>d</i> ₁
			0.15 <i>d</i> ₂		0.02 <i>d</i> ₂
			0.10 <i>d</i> ₃		0.01 <i>d</i> ₃
			0.07 <i>d</i> ₄		0.01 <i>d</i> ₄
			0.05 <i>d</i> ₅		
			0.04 <i>d</i> ₆		
			0.03 <i>d</i> ₇		
			0.01 <i>d</i> ₈		
			0.01 <i>d</i> ₉		

^a Only 2-MP is formed. ^b The deuterium content is given as a percentage D of total (D + H). ^c Starting material.

alkenes. This process explains both the data of Fig. 6 and the reduction in rate observed when MCP is replaced by MCP-*I-d*.

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