

The Mechanism of Isobutane Cracking over Amorphous and Crystalline Aluminosilicates

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The acid catalyzed cracking of isobutane over a silica-alumina catalyst and several zeolites was studied. The activity of these catalysts, for whatever reason, increased in the order silica-alumina < H-ZSM-5 < H-Y < H-M, i.e., the same order found in a closely related study of neopentane. The higher the activity the lower was the temperature required to achieve a given conversion, the higher was the paraffin-to-olefin ratios, and the greater was the isomerization of iso- to normal hydrocarbons. It was demonstrated that with all these catalysts two primary reactions occurred resulting in the formation of CH₄ and H₂ and concomitantly the t-butyl and isopropyl cations. The latter either desorbed as the corresponding olefins or underwent secondary reactions. So long as the latter were relatively unimportant the C₃ + C₄ hydrocarbons formed nearly equaled the isobutane reacted. However, the sum of the CH₄ and H₂ produced was generally less than this value. Evidently hydrogen transfer is more important in the conversion of isobutane than of neopentane. This chemistry is discussed. © 1988 Academic Press, Inc.

INTRODUCTION

The mechanism of paraffin cracking remains, even after many years of industrial application, a controversial subject (1-17). The most argued matters include the nature of the initiation step and whether or not the protolysis of a C-C or C-H bond may play a role in the initiation of the reaction or as an alternative pathway of cracking (11-19) as it does in superacid systems (20).

In a recent study (21) we have demonstrated that the protonation of a C-C bond of neopentane is the preferred pathway to crack this paraffin, producing CH₄ and t-C₄H₉⁺ in the *primary* reaction step. This carbenium ion either decomposed to form isobutene or reacted further (by *secondary* processes) to yield expected products. Its stability varied with the acidity of the catalyst. This reaction was studied on a variety of solid acids ranging from silica-alumina

to a very active, slightly dealuminated, mordenite.

Isobutane cracking has been advocated as a useful probe for the characterization of solid acids (11). This small paraffin contains one tertiary C-H bond which is more labile than the primary C-H bonds of neopentane and therefore offers an alternate point for proton attack and subsequent propagation steps. Other authors have explored the reactions of larger paraffins containing tertiary hydrogens with similar objectives (13, 14).

McVicker *et al.* (11) noted that the products formed in the primary step of the cracking of isobutane were identical with those formed in the homogeneous gas-phase free radical reactions. On this basis, they suggested that the reaction was initiated by an electron transfer from isobutane to an electron acceptor site which was said to be present on the surface of solid acids. The radical ion formed was then supposed to decompose into CH₄, H₂, and the corresponding carbenium ions, the remaining chemistry following from this. This idea is, therefore, an alternative to the concept of a

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primary protolysis forming H_2 and the *t*-butyl cation or CH_4 and the isopropyl ion as described by Haag and Dessau (14) and by ourselves (21). Isobutane, however, was not the reactant in either of these works. One of the present objectives was to discriminate between these possibilities.

Grady and Gorte (22) concluded that stable carbenium ions were formed on adsorption of *t*-butanol and other aliphatic alcohols at room temperature on H-ZSM-5 and most recently Zardkoochi *et al.* (23) have presented a ^{13}C MASNMR spectrum showing a peak at 250 ppm downfield from TMS attributed to the partially shielded isopropyl ion. The corresponding ions are stable in "magic acid" (20) and this is in accord with the observations of McVicker *et al.* (11) that ultrastable Y-zeolite acts as a superacid in the reactions of the 2-methylpen-tenes. In their work a flow reactor was used; complete mass balances could not be obtained; e.g., H_2 could not be determined quantitatively during the cracking of isobutane. In the present work this difficulty was circumvented by using pulse or static experiments. Thus, we have extended our previous work (21) so that the decomposition of isobutane can be compared with that of neopentane over the same set of catalysts and some additional perspective shed on the work of McVicker *et al.*

EXPERIMENTAL

Catalyst preparation and pretreatment. The commercial silica-alumina catalyst (Houdry M-46) was from the same batch used in many of our earlier studies. Two samples of H-ZSM-5 were used. One was obtained from the Pittsburgh Energy Technology Center and had a Si/Al ratio of 74. The other was a gift from Mobil Oil Corp. with a Si/Al ratio of 34.7. The Linde Y-zeolite was dealuminated to match its Si/Al ratio with that of a very active slightly dealuminated mordenite. Thus, the extensive factors of the acidity of these two materials should be similar although the intensive factors may be very different. The

starting materials for the preparation of these catalysts were the Linde LZ Y62 and the Norton Z900H. The former (NH_4NaY) was first calcined in a static muffle furnace for 2 h at 540°C and then twice exchanged by refluxing in 0.9 M NH_4NO_3 (200 g zeolite/liter solution) for 1 h; this process was repeated. The resulting material was then heated to 815°C for 2 h in a static muffle furnace; its Si/Al was 2.65. This material was then further treated with 1.0 M HCl for 2 h, resulting in Si/Al = 8.1. The mordenite as received had Si/Al = 5.9. It was refluxed for 2 h with 4 M HNO_3 and then thoroughly washed with deionized water to increase its Si/Al ratio to near that of the H-Y. The physicochemical data of the catalysts are given in Table 1. In neither case was the extralattice alumina completely removed.

Preliminary tests revealed that the results were insensitive to treatment temperatures between 400 and 500°C; i.e., the reaction product distributions were not significantly different. Therefore, following the conditions most often reported in the literature, all the catalysts were calcined in flowing dried O_2 for 1 h at 500°C (70 ml/min) followed by evacuation to less than 10^{-5} Torr during another hour.

Reactants. Research-grade isobutane, neopentane, and *n*-butane were employed. The He carrier gas was passed through a Matheson Purifier; its maximum impurity level was determined to be <1 ppm. The hydrogen was diffused through a palladium-silver alloy thimble.

Reaction procedures. The catalytic experiments were performed in either the pulse or the batch mode using the same glass system as that described previously (21). Provision was also made for the *in situ* treatment of the catalyst in flowing gas.

Hydrogen measurements. H_2 was removed from mixtures of hydrocarbon gases as follows. In a typical experiment the gas to be analyzed was first passed through an empty glass bead trap at -195°C which removed all the products but CH_4 and H_2 . The latter were quantitatively adsorbed

TABLE 1
 Physicochemical Properties of the Catalysts

	SiO ₂ -Al ₂ O ₃	H-ZSM-5(74)	H-ZSM-5(35)	H-Y(8.1)	H-M(7.3)
Chemical analysis					
SiO ₂ (%)	87.5	98.9	97.6	90.2	88.7
Al ₂ O ₃ (%)	12.5	1.1	2.4	9.3	10.1
(Al atoms/g) × 10 ⁻²⁰	14.8	1.3	2.8	11.0	11.9
Si/Al (chemical)	5.9	74	34.7	8.1	7.3
Si/Al (framework)	—	74	35	13	11
Pore volume (cm ³ /g)	0.6	0.10 ^a (0.2)	0.18 ^a (0.2)	0.28 ^a (0.3)	0.21 (0.2)
Source of the starting material	Houdry (M-46)	PETC	Mobil	Linde LZY62	Norton Z-900H

^a Calculated from oxygen saturation adsorption values; expected values from crystal structure are indicated between parentheses.

from the effluent He stream onto a 5A molecular sieve trap at the same temperature. The second trap was then transferred to another glass system in which CH₄ and H₂ were separated chromatographically and the latter was converted to water before passing through a TCD detector. The accuracy of these determinations was estimated to be ~5%.

Residue (coke) measurements. These were made in an attached glass circulation system using 200 Torr O₂ at 500°C. The CO₂ and H₂O were removed from the circulating gas in a U-loop trap cooled to -195°C. The CO₂ could be released at -78°C and the H₂O retained. Thus, these gases could be separated and each of them transferred and measured in a gas burette. After a given kinetic experiment the reactor was evacuated to ~5 × 10⁻⁵ Torr at the reaction temperature before admitting the oxygen.

RESULTS

Pulse experiments. Tables 2 and 3 show the product distributions obtained when 1.54 × 10¹⁹ molecules of isobutane were passed over 400 mg of catalyst in a purified He carrier gas stream (90 cm³/min) at low or higher conversion, respectively. Note the much lower temperature, 200 vs 400°C, required to limit the conversion on the very active H-mordenite (Table 2). The product

distributions obtained at higher conversions and temperatures are shown in Table 3. Another catalyst has been included here, viz., H-ZSM-5(74), whose behavior fits in between those of silica-alumina and H-ZSM-5(35) as expected. Both silica-alumina and H-ZSM-5 yielded C₃ and C₄ olefins as primary products.

If the *primary* reactions are protonation of a carbon-carbon single bond yielding CH₄ and the isopropyl cation or a carbon-hydrogen bond forming H₂ and either a *t*-butyl or a *sec*-butyl ion, the mass balances work out remarkably well in most cases; i.e., the sums of the C₃ + C₄ products are in fair agreement with the amounts of isobutane converted, and the CH₄ formed in most cases bears a reasonable resemblance to the total C₃ fraction. The results are of course disguised by products formed in *secondary* reactions. That oligomerization occurs is indexed by the appearance of pentanes in the products and by paraffin-to-olefin ratios greater than zero. The data suggest that the extent of these reactions was small with silica-alumina and H-ZSM-5, but became important with H-Y and especially with H-M. Of course, some of these products are the result of secondary cracking of oligomers.

It was not possible to determine the amount of H₂ formed in the pulse experiments with satisfactory accuracy because

TABLE 2
Isobutane Cracking over Solid Acids (Conversion <5%)^a

	SiO ₂ -Al ₂ O ₃	H-ZSM-5(35)	H-Y(8.1)	H-M(7.3) ^b
Reaction temperature (°C)	400	400	400	200
Conversion (%)	0.8	1.0	2.3	3.1
Molecules × 10 ⁻¹⁷ or (molecules formed/100 molecules reacted) ^c				
Isobutane converted	1.2 —	1.5 —	3.6 —	4.8 —
Methane	0.0 (0)	0.4 (27)	0.6 (17)	6.4 (133)
Ethane + ethene	0.1 (8)	1.2 (80)	0.2 (6)	0.2 (4)
Propane	0.1 (8)	0.0 (0)	0.5 (14)	2.2 (46)
Propene	0.2 (17)	0.5 (33)	0.7 (19)	0.0 (0)
<i>n</i> -Butane	0.0 (0)	0.0 (0)	0.4 (15)	1.2 (25)
Isobutene	0.8 (70)	0.3 (20)	0.9 (25)	0.0 (0)
<i>n</i> -Butenes	0.2 (17)	0.1 (7)	0.4 (15)	0.0 (0)
Pentanes	0.0 (0)	0.0 (0)	0.6 (10)	0.2 (4)
C ₃ + C ₄	1.3 (108)	0.9 (45)	2.9 (80)	3.4 (71)
C ₃ /C ₃ ²⁻	0.4 —	0.0 —	0.7 —	∞ —
C ₄ /C ₄ ²⁻	0.0 —	0.0 —	0.4 —	∞ —

^a Pulse reactor, 400 mg of catalyst; pulse size 1.54×10^{19} molecules. He carrier flow rate 90 cm³/min.

^b These are data from the first pulse. This catalyst showed pronounced deactivation with pulse number. The amount of residue formed is not included in the isobutane converted because it was below detection limits.

^c Molecules formed per 100 molecules of isobutane reacted are shown in parentheses.

TABLE 3
Isobutane Cracking over Solid Acids (High Conversion)^a

	SiO ₂ -Al ₂ O ₃	H-ZSM-5(74)	H-ZSM-5(35)	H-Y(8.1)	H-M(7.3) ^b
Reaction temperature (°C)	500	500	500	500	400
Conversion (%)	7.4	10.9	18.0	16.3	86.0
Molecules × 10 ⁻¹⁷ or (molecules formed/100 molecules reacted) ^c					
Isobutane converted	11.4 —	16.7 —	27.8 —	25.2 —	132.3 —
Methane	1.6 (14)	9.5 (57)	14.8 (53)	5.5 (22)	34.5 (26)
Ethane + ethene	0.2 (2)	0.8 (5)	9.9 (36)	3.5 (14)	12.4 (9)
Propane	0.0 (0)	0.9 (5)	2.9 (10)	5.5 (14)	132.1 (100)
Propene	2.1 (18)	8.6 (51)	15.1 (54)	7.6 (30)	0.0 (0)
<i>n</i> -Butane	0.4 (4)	0.5 (3)	0.4 (1)	3.4 (13)	15.5 (12)
Isobutene	5.8 (51)	3.6 (22)	3.0 (11)	3.6 (14)	0.5 (0.4)
<i>n</i> -Butenes	3.0 (26)	2.8 (17)	2.3 (8)	2.3 (9)	0.3 (0.2)
Pentanes	0.0 (0)	0.0 (0)	0.0 (0)	2.4 (10)	1.9 (14)
C ₃ + C ₄	11.3 (99)	16.4 (98)	23.7 (85)	22.4 (89)	148.3 (110)
C ₃ /C ₃ ²⁻	0.0 —	0.1 —	0.2 —	0.7 —	∞ —
C ₄ /C ₄ ²⁻	0.1 —	0.1 —	0.1 —	0.6 —	21 —

^a Reaction conditions, see Table 2.

^b Same as in Table 2.

^c Same as in Table 2.

of the small amounts of isobutane reacted. The methane production in molecules formed per 100 molecules reacted was sufficient to account for 15 to 60% of the primary reaction. In the batch experiments (see below) comparable amounts of H₂ were determined. Hence in the activation of isobutane, hydride transfer to smaller carbenium ions, e.g., the isopropyl cation, is more important than that with neopentane (21). This was not unexpected since the latter contains only primary C-H bonds whereas isobutane has a tertiary one.

The hydrogen transfer activity became important with H-Y (C₃/C₃⁻ and C₄/C₄⁻ approached unity) but over H-M the effect was dramatic. In all cases most of the isobutane converted can be accounted for by the (C₃ + C₄) products. In contrast with our neopentane results (21), however, in all cases except for H-M the amounts of CH₄ produced were much smaller than those of the reactant converted.

To explore further the chemistry of hydride transfer the paraffin/olefin ratios were determined over a wide range of temperatures (200–500°C). The data are shown in Table 4. Interpretation is complicated somewhat by the fact that the isopropyl cation is a primary product whereas the *sec.*-butyl ion is not. A clear trend can be seen only for H-M, and these data are remarkably similar to those reported earlier (21) for neopentane.

In order to check for the possible effect of diffusion limitations in the smallest pore

zeolite, H-ZSM-5, the reactivity order of neopentane, isobutane, and *n*-butane was determined on both this catalyst and H-M(7.3). The reaction conditions were the same for the three reactants. On both catalysts the reactivity order was neopentane > isobutane ≧ *n*-butane, coincident with the electron donor ability of the σ-C-C and σ-C-H bonds of these paraffins. This crude test indicates that the extent of transport limitations in H-ZSM-5 was not large enough to disguise the activity data. However, it may affect the extent of secondary reactions.

Batch experiments. A static system was used to obtain easily measurable amounts of H₂ at the same reaction temperature with all the catalysts. As an extra bonus this provided a means to ascertain the fate of all the reactant molecules through a complete mass balance including the H₂ and the residues formed. The results of these experiments are given in Tables 5 through 8. The 350°C reaction temperature was chosen as a compromise for catalysts of varying activity and because it was low enough to preclude any possible contribution from a homogeneous gas-phase free radical mechanism and yet a useful conversion could be obtained even with the least active catalyst.

In all four cases, good mass balances on both C and H were obtained. In all these experiments, however, the amount of CH₄ + H₂ produced was significantly less than the number of molecules of isobutane converted showing that a portion of the lat-

TABLE 4
Effect of Temperature on the Paraffin/Olefin Ratio^a

Catalyst:	SiO ₂ -Al ₂ O ₃				H-ZSM-5(35)			H-Y(8.1)			H-M(7.3) ^b					
	400	450	500	600	400	450	500	400	450	500	200	250	300	350	400	450
Propane/propene	0.4 ^c	0.4 ^c	0.0	0.0	0.0	0.1	0.2	0.7	0.8	0.7	∞	∞	∞	∞	∞	∞
<i>n</i> -Butane/butenes	0.0	0.0	0.1	0.1	0.0	0.0	0.1	0.4	0.5	0.6	∞	∞	74	39	22	7
											(∞)	(∞)	(65)	(41)	(23)	—

^a Reaction conditions; see Table 2.

^b Figures between parentheses show that data obtained when neopentane was the reactant. The C₃/C₃⁻ was also ∞ for this reactant at all temperatures.

^c Conversion <2%. Due to the presence of C₃H₈ impurity these ratios are uncertain.

TABLE 5
Mass Balance of Isobutane Reacting on Silica-Alumina at 350°C^a

Products	Molecules $\times 10^{-17}$	(Molecules formed per 100 molecules reacted)
i-C ₄ H ₁₀ (converted)	18.4	—
H ₂	5.5	(30)
CH ₄	3.4	(19)
H ₂ + CH ₄	8.9	(49)
C ₂ H ₄ + C ₂ H ₆	1.7	(9)
C ₃ H ₈	2.5	(14)
C ₃ H ₆	3.4	(19)
n-C ₄ H ₁₀	0.0	(0)
i-C ₄ H ₈	2.6	(14)
n-C ₄ H ₈	1.2	(7)
i-C ₅ H ₁₂	3.7	(20)
n-C ₅ H ₁₂	0.0	(0)
C ₃ + C ₄	9.7	(53)
i-C ₄ H ₁₀ (unreacted)	444	
Conversion to gaseous products + residues = 4.0%		
C and H Balance	C atoms $\times 10^{-17}$	H atoms $\times 10^{-17}$
Gaseous products (rec.)	1834	4588
Residues	15.6	15.6 (H/C = 1.0)
Total recovered	1850	4604
Reactant	1924	4810
Loss	74 (3.9%)	206 (4.3%)

^a Fresh catalyst—batch reactor (400 mg of catalyst, 5.9×10^{20} Al), 350°C. Initial amount of reactant was 481×10^{17} molecules of i-C₄H₁₀.

ter formed carbenium ions by conventional hydride transfer to other carbenium ions. Nevertheless, the paraffin/olefin ratios followed the same trend in going from silica-alumina to H-mordenite as was found in the pulse experiments (Tables 2–4) although they were displaced toward higher values reflecting the higher partial pressures of hydrocarbons in contact with the catalyst for longer times.

An interesting feature of these experiments was the differing abilities of these catalysts to isomerize both the C₄ and the C₅ fractions. Note that as one goes from silica-alumina to H-M the isomerization activity increased sharply. Table 5 shows that neither *n*-butane nor *n*-pentane was present in the products obtained over silica-alumina. At the other extreme H-M

produced iso- and *n*-pentanes in almost equilibrium amounts plus a large proportion of *n*-butane. These data support the idea that longer lifetimes of the carbenium ions result from larger intensive factors of the acidity and thus promote an increase in the extent of isomerization.

Effect of pre-reduction of the catalyst.

To test for the possible role of electron acceptor (EA) sites in the initiation step, as suggested by McVicker *et al.* (11), the catalyst [H-ZSM-5(35)] was pre-reduced in H₂ at 500°C before injecting a pulse of reactant. This should eliminate most of the postulated EA sites (24, 25) and greatly reduce the reaction rate. H-ZSM-5 was chosen because of published evidence (26) of its ability to form cation radicals from C₆ olefins. Table 9 shows that neither the hydrogen re-

duction nor its use as carrier gas modified the activity or product distribution significantly. Similar results were obtained for neopentane cracking (21).

DISCUSSION

As was the case with neopentane (21) the present data demonstrate that the protonation of a C–C bond of isobutane provides a route to crack this paraffin. With the latter, significant amounts of H₂ were also produced suggesting that C–H bonds are also attacked.

In the acid-catalyzed cracking of long-chain paraffin molecules, olefin formation is mainly the result of β -scission of the initially formed carbenium ions; dehydrogenation is not significant. Garten (27) recognized as early as 1967 that smaller paraffins such as isopentane must involve a dehydro-

genation step and attributed this to impurity centers (perhaps Fe) in the silica–alumina catalyst; he reported that at 0.6% conversion, 80 moles of pentene was produced per 100 moles of isopentane reacted. This work was followed up by Brenner and Emmett (13), who confirmed these results and established that the dehydrogenation activity of the catalyst was *intrinsic* and not the result of trace impurities. The dehydrogenation activity was not related to the ability of the catalyst to hydrogenate ethylene. The latter reaction could be effectively poisoned by H₂S without much effect on the isopentane reaction. Although H₂ was not reported, CH₄ was and it is clear that these results are consistent with those reported herein for isobutane and hence with those (Table 10) of McVicker *et al.* (11). Moreover regardless of mechanism, the primary

TABLE 6
Mass Balance of Isobutane Reacting on H-ZSM-5(35) at 350°C^a

Products	Molecules $\times 10^{-17}$	(Molecules formed per 100 molecules reacted)
i-C ₄ H ₁₀ (converted)	85.2	—
H ₂	8.3	(10)
CH ₄	31.5	(37)
H ₂ + CH ₄	39.8	(47)
C ₂ H ₄ + C ₂ H ₆	7.0	(8)
C ₃ H ₈	48.7	(57)
C ₃ H ₆	5.5	(6)
n-C ₄ H ₁₀	8.8	(10)
i-C ₄ H ₈	2.6	(3)
n-C ₄ H ₈	1.5	(2)
i-C ₅ H ₁₂	4.1	(5)
n-C ₅ H ₁₂	0.5	(0.6)
C ₃ + C ₄	67.1	(79)
i-C ₄ H ₁₀ (unreacted)	403	
Conversion to gaseous products + residues = 17.5%		
C and H Balance	C atoms $\times 10^{-17}$	H atoms $\times 10^{-17}$
Gaseous products (rec.)	1894	4804
Residues	58.3	54.4 (H/C = 0.9)
Total recovered	1952	4859
Reactant	1956	4890
Loss	4 (0.2%)	31 (0.6%)

^a Fresh catalyst—batch reactor (400 mg of catalyst, 1.1×10^{20} Al). Initial amount of reactant was 489×10^{17} molecules of i-C₄H₁₀.

TABLE 7
Mass Balance of Isobutane Reacting on H-Y(8.1) at 350°C^a

Products	Molecules × 10 ⁻¹⁷	(Molecules formed per 100 molecules reacted)
i-C ₄ H ₁₀ (converted)	76	—
H ₂	30.8	(41)
CH ₄	22.2	(29)
H ₂ + CH ₄	53.0	(70)
C ₂ H ₄ + C ₂ H ₆	4.1	(5)
C ₃ H ₈	38.4	(50)
C ₃ H ₆	0.5	(0.7)
n-C ₄ H ₁₀	17.4	(23)
i-C ₄ H ₈	0.9	(1)
n-C ₄ H ₈	0.5	(1)
i-C ₅ H ₁₂	2.5	(33)
n-C ₅ H ₁₂	0.6	(1)
C ₃ + C ₄	57.7	(76)
i-C ₄ H ₁₀ (unreacted)	416	—
Conversion to gaseous products + residues = 15.5%		
C and H Balance	C atoms × 10 ⁻¹⁷	H atoms × 10 ⁻¹⁷
Gaseous products (rec.)	1902	4853
Residues	66.4	79.7 (H/C = 1.2)
Total recovered	1968	4932
Reactant	2032	5080
Loss	64 (3.2%)	148 (2.9%)

^a Fresh catalyst—batch reactor (400 mg of catalyst, 4.4 × 10²⁰ Al). Initial amount of reactant was 508 × 10¹⁷ molecules of i-C₄H₁₀.

products formed in all cases are CH₄ or H₂ and the corresponding carbenium ions. Given the latter more carbenium ions can be produced from the reactant by hydride transfer. These results can be explained

most simply (for isobutane) by the generalized reaction pathway written below, which has precedent in the work of Olah *et al.* (20) where the carbenium ions formed are stabilized in magic acid,

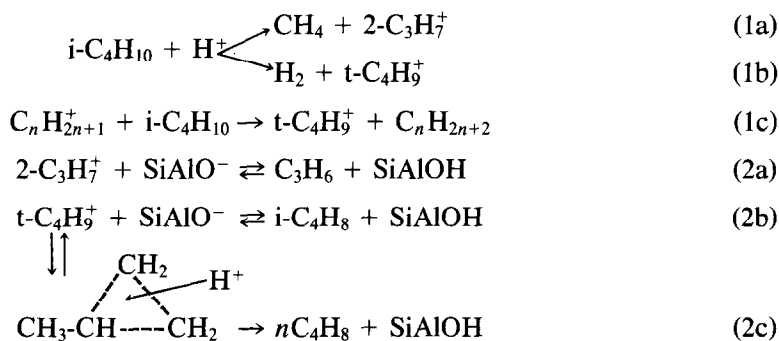


TABLE 8
Mass Balance of Isobutane Reacting on H-M(7.3) at 350°C^a

Products	Molecules × 10 ⁻¹⁷	(Molecules formed per 100 molecules reacted)
i-C ₄ H ₁₀ (converted)	220	—
H ₂	17.0	(8)
CH ₄	44.8	(20)
H ₂ + CH ₄	61.8	(28)
C ₂ H ₄ + C ₂ H ₆	6.6	(3)
C ₃ H ₈	159	(86)
C ₃ H ₆	0.0	(0)
<i>n</i> -C ₄ H ₁₀	29.6	(13)
i-C ₄ H ₈	0.1	(~0)
<i>n</i> -C ₄ H ₈	0.0	(~0)
i-C ₅ H ₁₂	3.5	(2)
<i>n</i> -C ₅ H ₁₂	1.0	(~0)
C ₃ + C ₄	188.5	(99)
i-C ₄ H ₁₀ (unreacted)	286	
Conversion to gaseous products + residues = 43.4%		
C and H Balance	C atoms × 10 ⁻¹⁷	H atoms × 10 ⁻¹⁷
Gaseous products (rec.)	1820	4760
Residues	202	286 (H/C = 1.4)
Total recovered	2022	5046
Reactant	2108	5270
Loss	86 (3.2%)	224 (4.3%)

^a Fresh catalyst—batch reactor (400 mg of catalyst, 4.8 × 10²⁰ Al) 350°C. Initial amount of reactant was 527 × 10¹⁷ molecules of i-C₄H₁₀.

TABLE 9
Effect of Hydrogen on Isobutane Conversion over H-ZSM-5(35)^a

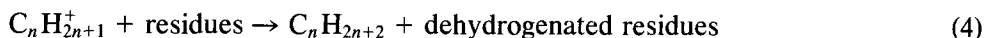
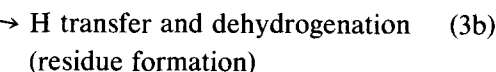
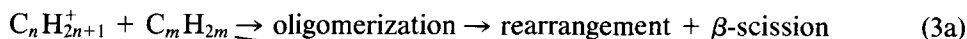
Carrier conversion (%):	Oxidized catalyst		Reduced catalyst			
	Pulse 1 ^b	Pulse 8	Pulse 9 ^c	Pulse 15	Pulse 16 ^d	Pulse 17
	He	He	H ₂	H ₂	He	He
	2.6	3.6	2.8	3.6	4.0	4.1
	Molecules × 10 ⁻¹⁷					
i-C ₄ H ₁₀ converted	4.0	5.5	4.2	5.5	6.2	6.2
Methane	3.0	3.8	3.1	3.6	3.8	3.5
Ethane + ethene	0.6	0.7	0.7	0.8	0.8	0.8
Propane	0.7	0.8	0.8	0.9	1.0	1.0
Propene	2.2	2.5	2.1	2.4	2.7	2.8
<i>n</i> -Butane	0.0	0.3	0.0	0.7	0.6	0.6
Butenes	0.8	1.4	0.9	1.1	1.4	1.5

^a Pulse reactor, 400 mg of catalyst, pulse size = 1.54 × 10¹⁹ molecules. The flow rate of He or H₂ was 90 cm³/min. The reaction temperature was 450°C.

^b The catalyst received the standard oxygen pretreatment before this pulse; the next seven pulses followed on this preparation.

^c Before pulse 9 the catalyst was reoxidized and then reduced in H₂ at 500°C. The following six pulses were in H₂ carrying gas.

^d After pulse 15 the system was switched to He carrying gas and left overnight at 450°C. Pulses 16 and 17 were passed the following morning.



Reactions (2) describe the role played by the intensive factor of the acidity (the strength of the acid–base interaction). The energetics of these equilibria govern the stationary concentrations or lifetimes of the carbenium ions and, hence, the propensity for secondary reactions ((3) and (4)), but most specifically hydride transfer. Therefore, the product distribution will be affected by the interplay between the basicity of the intervening olefins and the strength of the solid acid. The lifetimes of the carbenium ions reflect the acid strength of the solid. Reactions between the olefins released and these carbenium ions become more probable with increasing lifetime. These produce C_6^+ , C_7^+ , and C_8^+ species which can rearrange by simply hydride and methyl shifts into isomeric ions which can then be cleaved by β -scission forming C_3 – C_5 olefins and for example the 2-propyl ion

which, being less stable, desorbs as propene or reacts with either the reactant isobutane or residues and desorbs as propane. Evidently this hydrogen (hydride) transfer reaction increases in going from silica–alumina to H–mordenite and is also strongly affected by the residence time and the partial pressure of hydrocarbons.

Table 4 provides some indirect information on the variation of the lifetime of carbenium ions on the catalyst studied. As expected the most active catalyst, H–M, which has been suggested to show superacidity (28), yields paraffin/olefin ratios at least two orders of magnitude higher than H–Y. Furthermore, this catalyst effects reaction at temperatures as low as 250°C. Interestingly Hattori and co-workers (29) have reported the isomerization of *n*-pentane to isopentane and the cracking of the latter to isobutane at 0°C over a silica–alu-

TABLE 10

Comparison of the Results of McVicker *et al.* (11) with Those from this Work^a

Catalyst:	SiO ₂ –Al ₂ O ₃		H–Y Zeolite				
	McV	Ours	McV	McV	Ours	McV	Ours
Reaction temp (°C):	500	500	500	500	500	450	450
Conversion (%):	6.9	23.2	7.2	25.4	16.3	9.4	5.1
Moles/100 moles product							
Methane	17.5	18.3	11.4	8.2	16.4	3.9	8.8
C ₂ H ₄ + C ₂ H ₆ ^b	2.3	4.2	6.8	7.2	10.4	4.9	4.7
C ₃	21.0	22.1	36.4	41.0	38.7	28.5	31.3
C ₃ /C ₃ ⁺	(0.06)	(0.11)	(3.55)	(12.9)	(0.7)	(13.25)	(1.65)
C ₄	59.2	55.4	34.0	30.8	27.5	46.1	47.8
C ₄ /C ₄ ⁺	(0.04)	(0.29)	(2.75)	(5.27)	(0.6)	(5.68)	(1.13)
Pentanes	0.0	0.0	11.4	12.8	7.0	16.6	7.3

^a McVicker *et al.* (11) conditions: Flow reactor, $P_T = 1$ atm, $\bar{P}_{i-C_4H_{10}} = 190$ Torr, 1 g catalyst. Ours: Pulse reactor, pulse size: 0.57 cm³ STP, 400 mg of catalyst.

^b McVicker *et al.* gives C₂ and other compounds as “minor products.” They state that C₂ is its main component.

mina catalyst onto which SbF_5 had been sublimed. This is certainly superacid behavior and part of the common chemistry described herein.

Additional indirect evidence of the longer lifetime of the C_4 and C_5 carbenium ions is included in the data shown in Tables 5 through 8. The isomerization of isobutane was nonexistent on silica-alumina and increased in the order $\text{H-ZSM-5} < \text{H-Y} < \text{H-M}$. The same trend was observed in the isomerization of the pentanes where the iso-/normal ratio goes from ∞ on silica-alumina to 3.5, a value close to equilibrium, on H-M.

Indeed, if a way could be found to determine the equilibrium constants $K_{2a} = (2\text{-C}_3\text{H}_7^+)/(\text{C}_3\text{H}_6)$ and $K_{2b} = (\text{t-C}_4\text{H}_9^+)/(\text{C}_4\text{H}_8)$, a true measure of the catalyst acidity would be achieved and could be quantified by application of the van't Hoff relation.

In our previous study of the decomposition of neopentane, reactions corresponding to (1b) and (2c) were not observed and (1c) was much less important. The more labile tertiary C-H bond of isobutane evidently can be attacked by catalyst protons and carbenium ions much more readily than the primary C-H of neopentane and this complicates the product distribution. The data show that significantly more isobutane was reacted than $\text{CH}_4 + \text{H}_2$ produced. Hence, half or more of the reaction may proceed via t-butyl ions formed by hydride transfer to less stable ions on the surface. In the case of neopentane, at least at low conversions, the amount of neopentane reacted was very close to that of the methane produced.

It is interesting to compare our data with those obtained by McVicker *et al.* (11) on silica-alumina and H-Y using a flow reactor (Table 10). Given the difference in the reactors used, and to a certain extent in the catalysts studied, the agreement is excellent. The higher paraffin/olefin ratios reported by McVicker *et al.* on H-Y may be a consequence of the higher partial pressure of reactant and longer contact times in their

experiments. A similar effect is evident in our data when the product distributions from static (batch) experiments (Tables 5-8) are compared with those shown in Table 3 (pulse experiments) for the same catalysts. Thus McVicker *et al.* (11) had essentially the same data to interpret as we had. Indeed we agree that H_2 , CH_4 , and the corresponding olefins are produced in a primary step and this is followed by secondary acid-catalyzed reactions. The difference arises in that they attribute these primary products to a radical reaction which we feel is unnecessary and unwarranted by the data. The initiation step in their proposed mechanism was the transfer of an electron from i- C_4H_{10} to EA sites on the solid forming radical cations which were then assumed to react following the decomposition pathways of their gas-phase counterparts, yielding i- $\text{C}_4\text{H}_8 + \text{H}_2$ and $\text{C}_3\text{H}_6 + \text{CH}_4$. The olefins so formed may then be protonated and further react following classical carbenium ion chemistry. They studied the cracking of isobutane on $\gamma\text{-Al}_2\text{O}_3$, Cl- and F-aluminas, silica-alumina, and Y-zeolite. To estimate the radical-like cracking contribution they used the molar product ratio (methane + ethene + propene + butenes)/total conversion products. Using this parameter they concluded that on all the above catalysts, except H-Y, the radical contribution was $>90\%$. They attributed the different behavior of the weaker acid catalysts from that of H-Y by assuming that true carbenium ion intermediates form only on the latter; alkoxide species were suggested to function in a related way on the former. We explain these same data with the reasonable assumption that short lifetimes diminish the extent of secondary reactions. The lifetime is presumed to reflect the intensive factor of the acidity and thus H-Y is intermediate in its action between H-M and H-ZSM-5 or silica-alumina.

Radical reactions, once initiated, are not confined to a surface. The gas-phase reactions have high activation energies and usu-

ally become unimportant below 450°C. However, McVicker *et al.* (11) did not assume thermal initiation; they assumed that isobutane is oxidized to the cation radical. This kind of reaction has been observed (24) on aluminum silicates with polynuclear aromatic compounds (low ionization potential molecules) and the oxidizing agent has been traced to reducible oxygen (25). These studies revealed that the EA sites could be mainly eliminated by reduction with H₂ at 500°C. The lack of an effect of pre-reduction and of the use of H₂ as a carrier gas on the activity and product distribution obtained on H-ZSM-5 (Table 9) strongly suggest that radical cations do not play a significant role in the catalytic decomposition of isobutane. Furthermore, nobody has demonstrated that simple paraffins, such as isobutane, may be converted into cation radicals by any solid acid of the kind used in this or their work. An authoritative discussion of this subject is given by Bard *et al.* (30).

The product distributions obtained by either McVicker *et al.* or by us can be rationalized in terms of Reactions (1)–(4). The less active catalysts, silica–alumina and H-ZSM-5, produce very low paraffin/olefin ratios and either no or very little isomerized C₄ and C₅ products. This is consistent with Reactions (2) being displaced toward the right making Reactions (3) and (4) reactant starved. H-M is located at the other extreme. This partially dealuminated mordenite is extremely active; the carbenium ions are stabilized on the solid and therefore have ample opportunity to react with product olefins or isomerize, leading to low olefin production and high proportions of *n*-butane and *n*-pentane in the products. H-Y shows an intermediate behavior. Interestingly, the rating of these solids using neopentane as a reactant was exactly the same (21).

The trends established in the present work illustrate the increasing complexity anticipated when using longer unbranched hydrocarbons, e.g., *n*-hexane. The data of

Haag and Dessau (14) suggest a less important yet significant role for direct protonation vis-a-vis hydride transfer with this feedstock. Taken together with the present data, it can be seen that the α -test measures the ability of a catalyst to generate carbenium ions both by direct protonation and by stabilizing such ions to enhance hydride transfer.

As discussed previously (21), the notion of Marczewski (12) that Lewis acid sites are directly involved in the reaction mechanism can be dismissed for lack of evidence. If hydride ions could be removed by Lewis sites, certainly this would be observed with triphenylmethane which forms a stable (C₆H₅)₃C⁺ ion on H⁻ removal. Wu and Hall (31) showed that whereas this ion indeed forms on acid catalysts, the reaction is proton catalyzed, not direct H⁻ removal by Lewis sites. Marczewski's catalyst yielded results essentially identical to those reported for silica–alumina and the zeolites (21).

In summary, these studies of the cracking of isobutane, together with the related ones using neopentane (21) and other small paraffins (13–15, 27, 29), have produced new insight into the functions of solid acid catalysts. Evidence for the involvement of pentacoordinated carbonium ions in the reactions of paraffins has been obtained. This has been a much debated issue in recent years. The isobutane data show additionally the participation of the protonation of the tertiary C–H bonds in the cracking mechanism, a pathway energetically unfavored in the case of neopentane, where no H₂ production was detected (21). These studies have clarified considerably the chemistry which is occurring in these systems. It is now possible to envisage a generalized mechanism for the cracking of paraffins in which the relative rates of the several reactions are affected by the nature of the reactant, the acidity of the catalyst and the process variables.

In closing, a word of caution should be added. Zeolite crystals are never perfect.

Although a constant activity per site has been demonstrated for high-silica H-ZSM-5 and H-Y catalysts (32–34), it has been recognized for many years that in certain cases very substantial enhancement of the site activity may be brought about by dehydroxylation or dealumination (35) or by promotion with divalent or polyvalent cations (36). Most recently Lago *et al.* (37) have demonstrated a site activity enhancement by a factor of about 50 on mild steaming of H-ZSM-5. This they attributed to a Lewis acid enhancement of the remaining Brønsted sites by a pairing interaction. In particular, our mordenite samples exhibited a nonlinear increase with Al/g of analogous character (38). Therefore care must be taken in attributing differences in catalytic behavior to changes in zeolite structure, particularly since it has been pointed out by Haag and Chen (39) that in carefully controlled circumstances the intrinsic site activities of H-Y and H-ZSM-5 are identical.

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