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Peculiarities Observed in H–D Exchange between Perdeuterioisobutane and H-Zeolites

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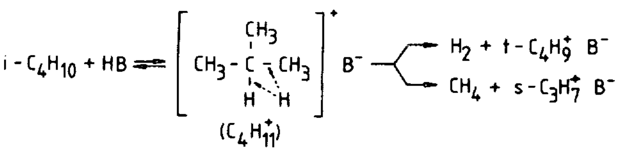
H–D exchange between perdeuterioisobutane and NaH–Y-zeolites and H-mordenite (H-M) was studied using the pulse technique. Nine of the ten D atoms in the isobutane molecule were exchanged for H on the most acidic Y-zeolites at the lowest temperature (200°C) where H–D exchange was observed, while other transformations of isobutane were not. The reaction is thought to be initiated by protonation of the tertiary C–D bond on the Brønsted acid sites of the catalyst and the exchange to proceed via the *t*-butyl carbenium ion intermediate. Release of the ion from the surface occurs via hydride transfer conserving the identity of the tertiary position. At higher temperatures and over the more acidic H-mordenite at even lower temperature (125°C) an extensive intermolecular H–D exchange occurs between perdeuterioisobutane and its exchanged products. A more detailed understanding of this reaction chemistry is developed herein. © 1995 Academic Press, Inc.

INTRODUCTION

Nowadays it is generally accepted that cracking of alkanes on solid acids proceeds via carbenium chain mechanisms (1–7). There are, however, various ideas concerning the initial formation of the carbenium ion intermediates. For reasons described in detail elsewhere (8), we think that the chains for isobutane decomposition are initiated by proton attack on C–H or C–C bonds, i.e., where HB is the Brønsted acid site of the catalyst and $C_4H_{11}^+$ is a pentacoordinated carbonium ion suggested to form in superacids by Olah *et al.* (9) (Scheme 1).



SCHEME 1

Once carbenium ions are formed, the subsequent chemistry proceeds by rearrangement:

$$t\text{-}C_4H_9^+B^- \rightleftarrows s\text{-}C_4H_9^+B^-, \qquad [1]$$

followed by hydride transfer

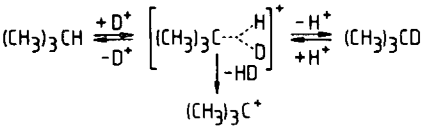
$$\left\{\begin{matrix} s\text{-}C_3H_7^+B^- \\ s\text{-}C_4H_9^+B^- \\ t\text{-}C_4H_9^+B^- \end{matrix}\right\} + i\text{-}C_4H_{10} \rightarrow \left\{\begin{matrix} C_3H_8 \\ n\text{-}C_4H_{10} \\ i\text{-}C_4H_{10} \end{matrix}\right\} + t\text{-}C_4H_9^+B^{-1}, \qquad [2]$$

where the last reaction is degenerate.

Chain termination occurs by deprotonation of carbenium ions resulting in formation of olefins and restoration of Brønsted acid sites:

$$\left\{\begin{matrix} s\text{-}C_3H_7^+B^- \\ s\text{-}C_4H_9^+B^- \\ t\text{-}C_4H_9^+B^- \end{matrix}\right\} \rightarrow HB + \left\{\begin{matrix} C_3H_6 \\ n\text{-}C_4H_8 \\ i\text{-}C_4H_8 \end{matrix}\right\}. \qquad [3]$$

In previous studies (9) H–D exchange provided strong evidence for the mode of protolytic attack on isobutane molecules. When isobutane was treated with deuterated superacids ($DSO_3F:SbF_5$ or $DF:SbF_6$) *at low temperature* (−78°C), the *initial* H–D exchange was observed exclusively at the tertiary carbon (Scheme 2). The formation of HD and isobutane with methine H–D exchange could be best explained as proceeding through a two-electron, three-center-bond pentacoordinated carbonium ion.



SCHEME 2

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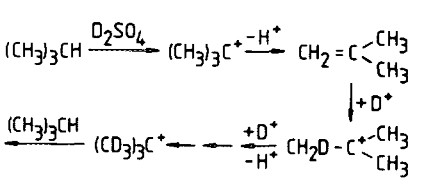
Under superacidic conditions the carbenium ions are stable at low temperature, thus no olefin formation from carbenium ions occurs; consequently reversible isobutylene protonation cannot be involved in the exchange reaction. Actually H–D exchange on the methine group may take place via the carbonium ion in parallel with carbenium ion formation.

Another type of H–D exchange has been observed when the reaction proceeds via carbenium ions. In concentrated D_2SO_4, Otvos *et al.* (10) found at room temperature the eventual exchange of all nine methyl hydrogens but not the methine hydrogen in isobutane. They supposed that a small amount of metastable *t*-butyl cation was formed in an oxidative step which deprotonated to isobutylene that rarely escaped the solution phase. The reversible protonation (deuteration) of isobutylene was responsible for the H–D exchange on methyl groups (Scheme 3).



SCHEME 3

The reason that only 9 of the 10 H in isobutane could be exchanged to D according to Otvos *et al.* is that the carbenium ion must be released as isobutane by the transfer of the tertiary hydride ion from reactant isobutane to carbenium ions at the gas/solution interface. In effect, a carbenium ion (or its corresponding olefin) can rarely escape the solution phase except by H^- transfer from another paraffin. At the gas/solid interface escape should in principle be much easier. This is apparently true with weak solid acids, but not with stronger ones, e.g., H–M and some H–Y-zeolites. Here we think the adsorbed complex is stabilized by forming an alkoxide in equilibrium with the carbenium ion (*vide infra*).

Results similar to those of Otvos *et al.* (10) were obtained by Larson and Hall (11) in H–D exchange between isobutane and deuterated amorphous silica–alumina. Nine of the ten H atoms in isobutane could be exchanged. The 10th, and the one that could not be, was the tertiary hydrogen. It was clear from their results that a given isobutane molecule, once chemisorbed, remained on the surface for a time long relative to the transport of H (or D) by diffusion across the surface. The 9 hydrogens remaining on the *t*-butyl carbenium ion apparently exchanged freely with available catalyst –OD groups, perhaps by the mechanism of Scheme 3. The identity of the tertiary ion was conserved by hydride transfer from reactant molecules.

Recently Mota *et al.* (12, 13) published the results of H–D exchange at 100°C between 3-methylpentane and perdeuterated zeolites under conditions where neither olefin nor other cracking products were found. Deuterium was incorporated in primary, secondary, and tertiary positions, but in more constrained zeolites preferentially in primary positions. They regarded this result as evidence for the formation and rearrangement of pentaccordinated carbonium ions. Although the initial attack is on the tertiary C–H bond, exchange may not occur for steric reasons. Therefore a rearrangement was suggested to result in the migration of deuterium within the carbonium ion to more accessible primary and secondary positions.

A quite different and rather peculiar exchange pattern was observed by us for exchange between perdeuterioisobutane and H–Y-zeolite. At the lowest temperature (200°C) where the first exchanged product appeared, already 9 of the 10 D in the isobutane were exchanged. We shall show that this peculiarity provides indirect evidence for the carbenium chain initiation by protonation on Brønsted acid sites. In this paper our attention is focused on processes taking place between isobutane and H-zeolites at temperatures sufficiently low that conversion of isobutane by decomposition was negligible.

EXPERIMENTAL

Catalysts. The catalysts used and their properties are listed in Table 1. Their acidities, expressed as percent H_2SO_4, were determined by the method of Umansky *et al.* (14). Pellets of M–46, a non-zeolitic amorphous silica–alumina obtained from Houdry over 40 years ago, were crushed and sieved. Powder of LZ–210(6) and LZ–210(12) silicon-enriched Y-zeolites, LZ–Y82 ultrastable Y-zeolite, and LZ–M8-mordenite supplied by UOP were pressed into pellets without binder, crushed, and sieved. An aliquot of the 20–40 mesh fraction (0.425–0.85 mm) of each catalyst was heated to and held at 500°C for 5 h in an open quartz crucible. After being covered with a lid, the catalyst was cooled and 400 mg was weighed on a Mettler balance.

Catalytic tests. Catalytic tests were carried out at atmospheric pressure in a continuous-flow quartz U-tube (8 mm i.d.) reactor. The downflow side served as preheater; the catalyst was packed into an approximately 2-cm-long bed held between plugs of quartz wool in the upflow side. In the reactor, the catalyst was treated in flowing dry O_2 at 500°C overnight before being flushed and cooled to the desired reaction temperature in a flow of dried high-purity N_2. The reaction was initiated by switching the reactor from nitrogen to the reactant mixture stream. This mixture was 10% isobutane in N_2 (Matheson, instrument grade), and it was fed at a fixed space velocity ($F/W = 1.1 \times 10^{-5}$ mole isobutane g^{-1} s^{-1}). The effluent gas was sampled and analyzed by online GC for H_2 and C_1 to C_8 hydrocarbons. The data ob-

TABLE 1

Physiochemical Properties of Catalysts

Catalyst	Chemical Analysis (wt%)			[Si/Al][a] atom ratio	[$Al_{F/g}$ × 10^{-20}][a]	Pore vol.[b] (surface area)	[H_2SO_4/H_2O][c] (%)	Source
	SiO_2	Al_2O_3	Na_2O					
M-46	87.5	12.5	n.d.[d]	—	—	(270)	68	Houdry
LZ-210(6)	77.2	20.8	2.0	3.4	22.8	0.33	89	UOP
LZ-210(12)	86.9	12.7	0.46	6.0	14.6	0.33	96	UOP
LZ-Y82	75.7	24.1	0.46	5.2	15.8	0.32	98	UOP
LZ-M8	90.9	9.1	<0.1	8.9	10.6	0.18	>100[e]	UOP

[a] $Al_{F/g}$ is the framework Al/g of catalyst from ^{29}Si MAS NMR; the Si/Al atom ratios are from the same data.

[b] Pore volume (surface area) is given in cm^3/g or (m^2/g) and was calculated from BET measurements.

[c] Concentration of sulfuric acid with acid strength equivalent to the acid sites of the catalysts deduced from the spectral shift of adsorbed 4-nitrotoluene (See Ref. (14)).

[d] Not determined.

[e] $H_2SO_4 \cdot SO_3$ having $H_0 = -13$.

tained at the lowest temperature at which the reaction could be observed were recorded to obtain initial rates. The composition of the effluent was calculated as the mole fractions (X_i) of the total product (including isobutane). As the conversions presented here are below 1%, the differential reaction rates for formation of individual products were calculated as $r_i = X_i\,(F/W)$ mole g^{-1} s^{-1}.

H–D exchange. Exchange reactions were carried out at atmospheric pressure in a pulse reactor system. The same reactor was used as in the flow system. Helium was used as carrier gas (30 cm^3/min). *Only one pulse* was sent through each catalyst except where mentioned otherwise. After being attached to the system, the catalyst was heated to and held overnight at 500°C in flowing dry O_2. Finally, the reactor was flushed with dried He and cooled to the preselected temperature.

The amount of isobutane in a pulse was adjusted by changing the pressure in a calibrated doser (volume = 1.8 cm^3). Products were trapped for 30 min at −195°C after passing the catalyst. Separation, after warming the trap, was carried out on a GC column containing dibenzylamine on Chromosorb P, and TCD was used for detection. The isobutane exiting the TCD was collected in a trap cooled with liquid nitrogen and then was attached to a mass spectrometer. The mass spectra were recorded at the lowest ionization potential (18 eV) applicable in order to minimize fragmentation.

Correction was made for the isotopic distribution obtained for the reactant perdeuterioisobutane processed in a similar way as the exchanged samples except bypassing the reactor. This perdeuterioisobutane (Merck) contained 15.3% i-C_4HD_9 and 6.2% i-$C_4H_2D_8$ as impurities. Before being used the reactant was degassed by repeated cycles of freezing, pumping, and thawing.

RESULTS

Catalytic test. The Brønsted acidities of catalysts, expressed as the equivalent concentration of sulfuric acid, are listed in Table 1. The acidity increased in the sequence M-46 < LZ-210(6) < LZ-210(12) < LZ-Y82 < LZ-M8. The rate of product formation from reaction of isobutane over zeolites increased in the same sequence (Table 2). On mordenite at 225°C, 0.6% of the entering i-C_4H_{10} underwent reaction. The product contained, in addition to n-butane, nearly equivalent amounts of propane and i-pentane. Only 0.8% hydrogen and no CH_4 were present, suggesting that initiation was rare, as was termination (no olefins were detected). Thus the chain length was very long. Once a "bank account" of carbenium ions was established, most of the products were formed by isomerization followed by H^- or CH_3^- transfer from the isobutane reactant (2, 6). Thermodynamics becomes limiting below 250°C, where the equilibrium constant for cracking of i-C_4H_{10} into CH_4 + C_3H_6 is about unity (see the last column of Table 2).

Over LZ-210(12) and LZ-Y82, essentially identical product distributions were obtained at 350°C. This temperature was higher by 125°C than that required for mordenite to maintain the conversion of isobutane about the same. Here again, n-butane was the dominant product, but propene and isobutene were also formed (termination) together with hydrogen and methane (initiation) in about equivalent amounts.

The temperature had to be raised to 450°C to obtain a conversion of the same magnitude over LZ-210(6). Under these conditions, the initiation products H_2 and CH_4, and the products formed by hydride transfer from isobutane to carbenium ions, propane and n-butane, were dominant. Thus, hydride transfer played a less significant role in

TABLE 2

Rates of Product Formation from Reaction of i-C_4H_{10} over H–Y- and H–M-Zeolites[a]

	Catalyst			
	LZ–210(6)	LZ–210(12)	LZ–Y82	LZ–M8
Temperature (°C)	450	350	350	225
H_2	8.2	2.8	3.6	0.8
CH_4	12.8	2.8	4.0	0
C_2H_6	0	0	0	0
C_2H_4	0	0	0	0
C_3H_8	7.9	2.9	5.6	12.5
C_3H_6	8.8	0.5	0.7	0
n-C_4H_{10}	10.5	26.1	40.5	45.6
i-C_4H_8	5.1	2.5	3.3	0
n-C_4H_8	0	0	0	0
i-C_5H_{12}	0	0	2.7	14.0
Conversion (%)	0.26	0.27	0.44	0.60
Conversion rate[b]	31.3	31.9	52.9	72.5
Chain length[c]	0.9	5.2	6.4	90

[a] Rates are given as 10^{-9} mole g^{-1} s^{-1}; 400 mg of each catalyst was used; the reactant was 10% isobutane in N_2 and the flow rate, F/W, was 1.1×10^{-5} mole g^{-1} s^{-1} (for isobutane). Turnover frequencies may be calculated from these data after dividing by the appropriate entry in the sixth column of Table 1.

[b] Conversion = $1/4 \sum_1^5 jr_i$, where j is the number of carbon atoms in the ith product.

[c] Molecules reacted by H^- transfer ($\sum_3^5$ paraffins) per molecules reacted in the initiation reactions yielding H_2 and CH_4.

the conversion than with the other three zeolites. This is marked by the much shorter chain length obtained.

The conversion of isobutane was significantly lower at 450°C on M–46 amorphous silica–alumina than on the least active zeolite (Table 3). No carbenium ion chain was established. H_2, isobutene, CH_4, and propene were the only products detected. The conversion decreased further when the catalyst was pretreated at 650°C instead of 500°C.

H–D exchange. With M–46 silica–alumina (pretreated at 500°C) no H–D exchange between catalyst and perdeuterioisobutane was observed below 450°C. At and above this temperature, decomposition of isobutane was already taking place, but no H-containing species were found in the unreacted i-C_4D_{10}. Of course, exchange does occur with samples pretreated at lower temperatures or when H_2O is added back (11).

With Y-zeolites at the lowest temperature (200°C) where H–D exchange was observed, already isobutane-H_9D_1 appeared in the unreacted i-C_4D_{10} from exchange with the Brønsted hydrogens (Figs. 1 and 2). On more acidic Y-zeolites (Figs. 2A and 2B) i-C_4H_9D was a major reaction product, but a distribution of h_1–h_9 species was obtained as the temperature was increased. This behavior is characteristic of a two-phase system [gas, where exchange does not take place and an adsorbed (or solution) phase where the molecule resides for a relatively long time while it equilibrates with its environment] as for example in the work of Otvos *et al.* (10) using concentrated D_2SO_4 in which the solvated ion is soluble, but the hydrocarbon is not.

LZ–210(12) (Fig. 1) shows the most characteristic changes in the isotopic distribution due to raising the reaction temperature. The concentration of h_9, the most highly exchanged species, first increased with increasing temperature, then passed through a maximum at 300°C. At higher temperature more and more isotopic species appeared, forming an inverted U-shaped distribution as the system moved toward equilibrium. The local maximum moved from h_9 to h_8 at 400°C. At this temperature formation of 3% n-butane formed by isomerization was already observed, presumably via the t-butyl carbenium ion.

On the other two Y-zeolites, similar changes in the isotopic distributions with increasing temperature were observed (Fig. 2). At 300°C the local maximum was at h_9 on LZ–210(12), at h_8 on LZ–210(6), and at h_7 on LZ–Y82.

TABLE 3

Rates of Product Formation from Reaction of i-C_4H_{10} at 450°C over Silica–Alumina Catalyst M–46 Pretreated at Different Temperatures

Product[a]	r_i^b	r_i^c
H_2	3.7	2.0
CH_4	0.8	0.4
C_2H_6	0	0
C_2H_4	0	0
C_3H_8	0	0
C_3H_6	0.7	0
n-C_4H_{10}	0	0
i-C_4H_8	3.5	1.9
n-C_4H_8	0	0
i-C_5H_{12}	0	0
Conversion (%)	0.04	0.02
Conversion rate[a]	4.2	2.0

[a] Rates, r_i, are given as 10^{-9} mole g^{-1} s^{-1}; 400 mg of catalyst was used; the reactant was 10% isobutane in N_2; the flow rate, F/W, was 1.1×10^{-5} mole g^{-1} s^{-1} (for isobutane). The surface area of the catalyst was 270 m^2/g. Rates per unit area may be calculated if desired.

[b] Catalyst was pretreated at 500°C.

[c] Catalyst was pretreated at 650°C.

[d] Rate of conversion = $1/4 \sum_1^4 jr_i$, where j is the number of carbon atoms in the ith product.

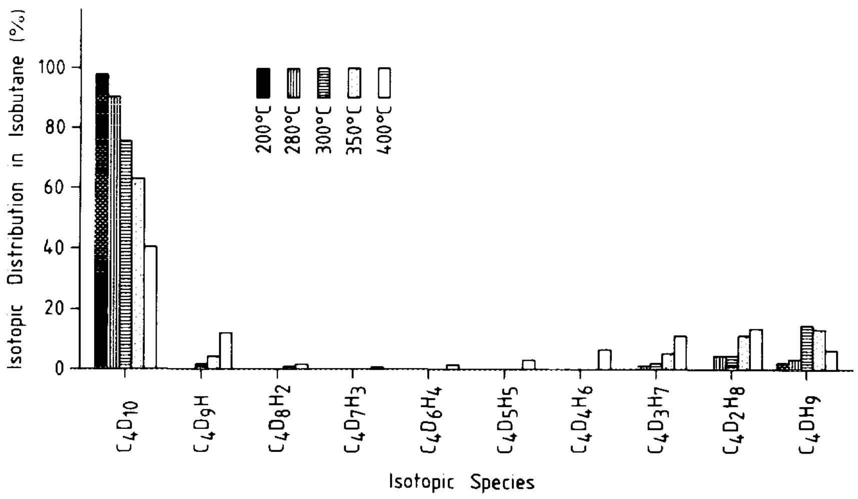


FIG. 1. Isotopic composition of isobutane formed by contacting LZ-210(12) with perdeuterioisobutane at various temperatures; 400 mg catalyst (5.8×10^{20} Al_F). 1.83×10^{19} molec. perdeuterioisobutane and He carrier gas 30 cm^3 min^{-1} were used in pulse experiments. A fresh sample of catalyst was used for each pulse.

On LZ-210(6), lower exchanged species appeared at 200°C. This was observed only at and above 300°C on LZ-210(12). Note that with the most acidic Y-zeolite (LZ-Y82) no d_7–d_9 species were detected at this temperature.

A characteristic isotopic distribution was obtained on LZ-210(6) at 350°C (Fig. 3). A first pulse of i-C_4D_{10} yielded a minimum at h_2 and a local maximum at h_7. As in the case of LZ-210(12), the local maximum moved toward

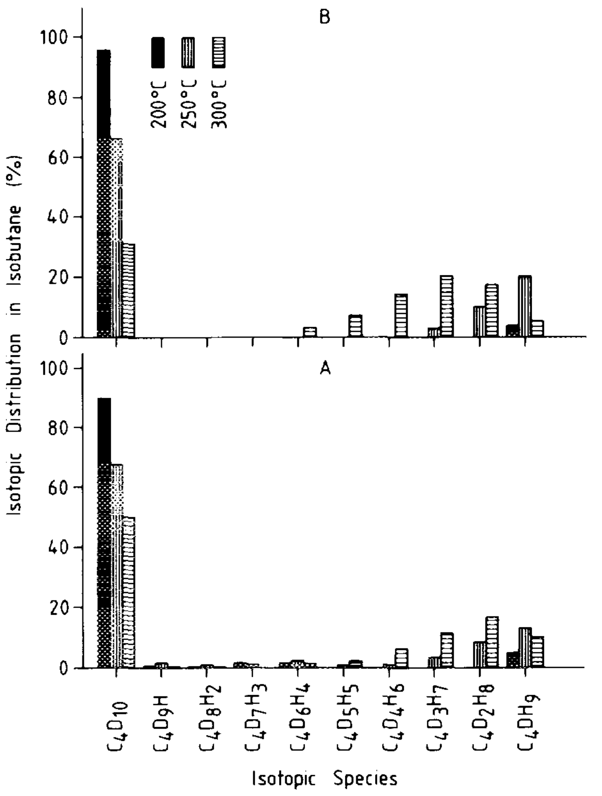


FIG. 2. Isotopic composition of isobutane formed by contacting pulses of perdeuterioisobutane at various temperatures with (A) LZ-210(6)- and (B) LZ-Y82-zeolites; 400 mg catalyst (9.1×10^{20} Al_F and 6.3×10^{20} Al_F, respectively); pulse size was 1.83×10^{19} molec. perdeuterioisobutane and the He carrier gas flow rate was 30 cm^3 min^{-1}.

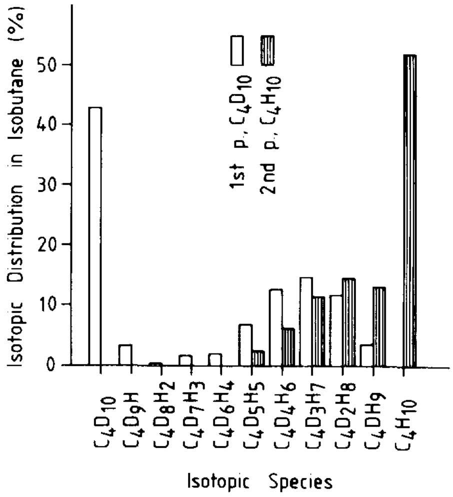


FIG. 3. Isotopic composition of isobutane formed by passing a first pulse of perdeuterioisobutane, then a second pulse of undeuterated isobutane over LZ-210(6)-zeolite at 350°C; 400 mg catalyst (9.1×10^{20} Al_F) and 1.83×10^{19} molec isobutane in He carrier gas (30 cm^3 min^{-1}) were employed.

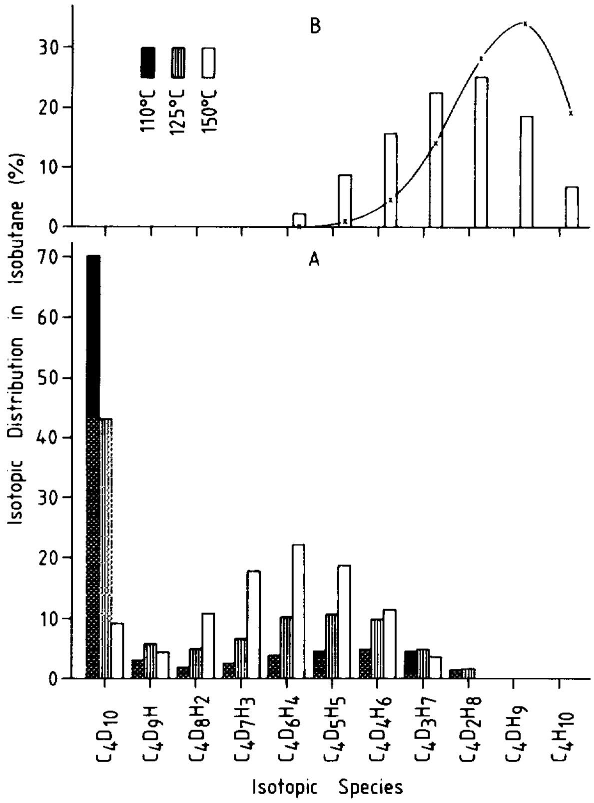


FIG. 4. Isotopic composition of isobutane formed by contacting LZ–M8 at 350°C with (A) perdeuterioisobutane and (B) a second fresh sample with a 50/50 mixture of perdeuterioisobutane and undeuterated isobutane; 400 mg catalyst (4.2×10^{20} Al_F) and 1.83×10^{19} molec. isobutane were used and He carrier gas was flowed at 30 cm^3 min^{-1}. The solid line shows the equilibrium curve expected for random mixing of all the H and D atoms held by the zeolite and in the i-C_4H_{10} + i-C_4D_{10} mixture.

less exchanged species with increasing temperature: from h_9 at 250°C to h_8 at 300°C and h_7 at 350°C.

After the perdeuterioisobutane pulse was passed, a second pulse containing i-C_4H_{10} was sent over the catalyst at the same temperature and the resulting isotope distribution in the product is also shown. This product contained h_5 to h_9 species with a local maximum at h_8.

No hydrocarbon was released from LZ-M8 below 110°C but about 80% of the pulse was recovered at this temperature as "unreacted" isobutane; the remainder could be recovered at 125°C. The character of the isotopic distribution was typical of a system in which a portion of the pulse was adsorbed and a portion not (remaining d_{10}); the first portion appeared as a nearly equilibrated system (Fig. 4A). As the temperature was increased, the first portion of the pulse increased at the expense of the latter portion. The Y-zeolites at much higher temperature (Figs. 1–3) can be seen approaching this kind of distribution. On these zeolites, the concentration of the highly exchanged h_9 species decreased with increasing temperature (see Fig. 1). On mordenite, h_9 was completely missing at 110°C; a rather flat distribution was obtained with a questionable maximum at h_7. As with the Y-zeolites, this local maximum tended to move to h_5 and h_4 species as 125 and 150°C, respectively, and it became more pronounced. Thus, the system can be seen to move toward equilibrium at these mild temperatures with this superacid catalyst. The less acidic Y-zeolites showed the same tendencies, although the move toward equilibrium was much less pronounced even at the higher temperatures employed.

A similar isotopic distribution was obtained (Fig. 4B) when a pulse of 50/50% perdeuterio- and perhydroisobutane was sent through a fresh sample of H-M (LZ–M8) at 150°C. Note that the catalyst added over 4 times as many H into the pool as the C_4H_{10} molecules in the pulse. This explains why the isotopic distribution had its maximum at h_8 instead of h_4 and there was no evidence of d_1 to d_{10} species. The D atoms from the C_4D_{10} reactant that entered the H/D pool resulted in the near equilibrium distribution shown in Fig. 4B. It may be estimated that this pool initially contained about 0.9×10^{20} D atoms and an equal number of H atoms from isobutane. The catalyst supplied 4×10^{20}H, so that H/D = 5.4.

The extent of H–D exchange in perdueterioisobutane pulses on different catalysts and at different temperatures is listed in Table 4. At the highest temperature used for each catalyst, the percentage of the D atoms of i-C_4D_{10} replaced by H was only about half the equilibrium value (last column). Values in parentheses show the percentage of H initially in the catalysts that were replaced with D by one pulse of perdeuterioisobutane. These values were calculated by considering the number of protons in zeolites equal to the number of framework Al ions not neutralized by Na^+ (6).

DISCUSSION

The salient observations of this work were: (a) 9 of the 10 deuterium atoms of the i-C_4D_{10} were exchangeable with the Brønsted sites of the zeolites whereas the 10th was not, confirming earlier work; (b) the nonexchangeable one was the tertiary D (11), but see later; (c) the exchange process acted as expected for a two-phase system where a gas-phase molecule is removed to a chemisorbed (or solution) state where it remained for a time long compared to that required for a single exchange to occur; thus multiple exchange occurred; (d) the extent of exchange increased with temperature and with catalyst acidity; the multiply exchanged species formed a distribution appearing as a system approaching equilibrium. These facts may be understood in terms of the potential energy diagram shown in Scheme 4. This shows the reaction coordi-

TABLE 4

Percent of D(H) Atoms Exchanged per Pulse of Perdeuterioisobutane at Various Temperatures[a]

Catalyst	Temperature (°C) 125	150	200	300	Equilibrium[b] of H (D)
LZ-210(6)			2.0 (0.4)	18.0 (3.5)	83.7 (16.3)
LZ-210(12)			6.2 (1.9)	37.5 (11.4)	76.6 (23.4)
LZ-Y82			3.7 (1.0)	48.4 (13.6)	78.0 (22.0)
LZ-M8	17.5 (7.3)	37.5 (15.8)			70.4 (29.6)

[a] 400 mg of each catalyst was used (the number of H atoms on the catalysts was taken from Ref. (6); pulse size: 1.83×10^{19} molec. perdeuterioisobutane (1.78×10^{20} atom); numbers without parentheses show the percent of D atoms exchanged in perdeuterioisobutane; numbers in parentheses show the percent of H atoms of the catalyst exchanged.

[b] Calculated assuming complete mixing for comparison with observations = D/(H + D) (total available for exchange). The i-$C_4H_1D_9$ and i-$C_4H_2D_8$ impurities in the i-C_4D_{10} have been included in these calculations.

nate for carbenium ion reactions of olefins and alcohols. On chemisorption of an olefin into a precursor state, II (possibly the H-bonded olefin), the carbenium ion may be formed on activation with proton addition. The metastable ion thus formed, III, will be more stable the deeper the well and may even become a stable state in a superacid. The carbenium ion will establish an equilibrium with the alkoxide IV (from which it cannot escape as product in the absence of H_2O), thus allowing for a long residence time of a particular ion–alkoxide pair on the surface. The carbenium ion may be reformed many times before escaping. Now the same ion is produced from isobutane as described in Scheme 1 and is stabilized in the same way. The ion may be released from the surface by H^- transfer, and this is the source of the heavily exchanged isobutanes studied herein. The adsorbed carbenium ion has both the opportunity and ability to undergo multiple exchange with the zeolite hydrogen. This makes the system behave as if it were a solution phase as studied by Otvos *et al.* (10). Note that the sole route for release of olefins is via return to the precursor state (II). This is the route for chain termination described in Table 2. The equilibrium between II and III is the pathway favored by Otvos *et al.* (10), but in D_2SO_4 the corresponding i-C_4H_9-O-SO_3D may also play a role.

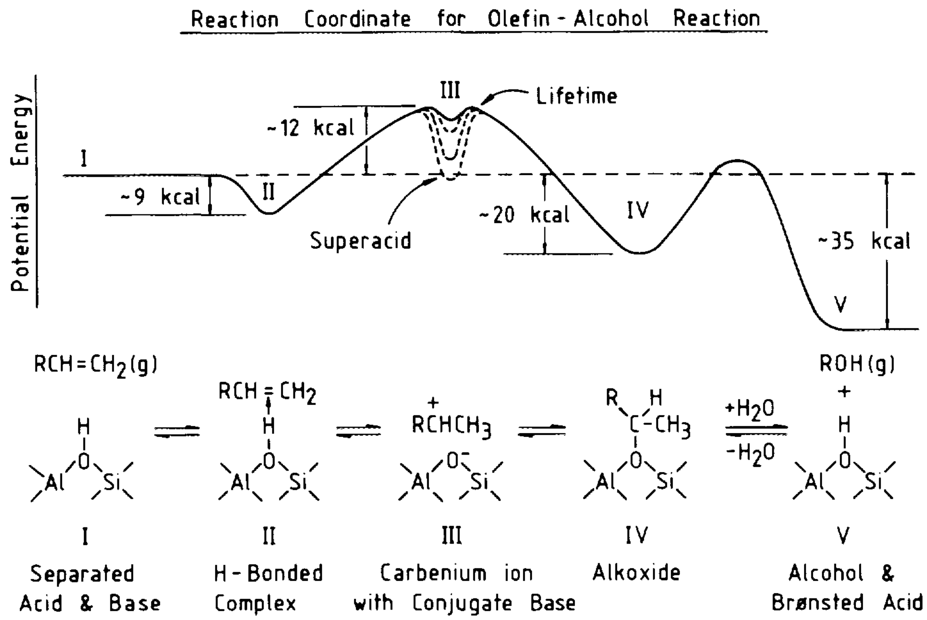
The alumina–silicate catalysts used in this work can be sorted into three categories according to their acidity (14):

(i) Dry amorphous silica–alumina ($-H_0 = 5.8$, equivalent to sulfuric acid of about 70% concentration);

(ii) NaH-Y-zeolites ($-H_0 = 10$ to 12, equivalent to sulfuric acid of 89–100% concentration); and

(iii) H-mordenite ($-H_0 = 13$, stronger than 100% sulfuric acid; equivalent to fumic acid of about 25% SO_3 concentration).

No H–D exchange between dry amorphous silica-alumina and perdueterioisobutane was observed at temperatures below 450°C. This is in contradiction with earlier work (11), where exchange was observed at 150°C, but in a recirculation system where the contact time was infinitely longer. The products formed in isobutane decomposition indicate (Table 3) that no carbenium chain process



SCHEME 4

was occurring, i.e., H^- transfer was unobservable. It should be noted that most of the H held by this catalyst are terminal Si–OH groups, not Brønsted sites.

Both $H_2 + CH_4$ and other paraffins were formed over NaH–Y-zeolites at conversions of isobutane below 0.5% (Table 2). The presence of alkanes in the product indicates that hydride transfer had taken place according to Eq. [2], i.e., a process in which metastable carbenium ion intermediates must be involved. Carbenium ion formation can be best explained by protonation of isobutane on Brønsted acid sites according to Scheme 1. Once formed the reaction pathways shown in Scheme 4 become available. The chain length (expressed as the rate of product formation in hydride transfer steps ratioed to the rate of product formation in the initiation reaction) increased with increasing acidity (Table 2). The chain lengths on LZ–210(12) and LZ–Y82 are comparable; recall that the lifetime (steady-state surface concentration) of carbenium ions depends among other factors on the temperature. The much longer chain length of LZ–M8 results from its much higher acidity. The chain can be terminated only by olefin desorption.

Because as many as 9 of the 10 D in the perdeuterioisobutane molecule were exchanged for H on NaH–Y-zeolites at 200°C (Figs. 1, 2), it is reasonable to expect that this reaction also proceeded through carbenium ion intermediates as it does in concentrated sulfuric acid (Scheme 3). Indeed, the strength of the Brønsted acid sites in LZ–210(12)- and LZ–Y82-zeolites is close to the acidity of concentrated sulfuric acid (Table 1). Thus according to Scheme 3, H–D exchange in deuterated sulfuric acid proceeds through *t*-butyl carbenium ion and isobutylene intermediates by successive deprotonation–deuteration steps.

At low temperature on strong acid sites, the equilibrium between surface-bound carbenium ions and gas-phase isobutylene must be far to the left; i.e.,

$$(CD_3)_3C^+B^- \rightleftarrows DB + CD_2{=}C(CD_3)_2. \qquad [4]$$

With the strongest acid employed, LZ–M8, no olefin could be detected in the reaction products. If isobutylene was released, it was immediately protonated again to reform *t*-butyl carbenium ions. NMR results (16) have shown that the surface protons/deuterons undergo rapid mixing at reaction temperature. Thus, as many as nine D of an adsorbed i-C_4D_{10} can be exchanged during one residence on the catalyst.

H-transfer from reactant molecules to carbenium ions and isobutylene formation according to Eq. [4] are parallel processes. When the intermolecular hydride (deuteride) transfer is much faster than the release of isobutylene, the concentration of the latter in the product may be below the observation limit.

At 350 to 400°C amounts of $h_1 > h_2$ appeared in the exchanged products from LZ–210(12)- and LZ–210(6)-zeolites (Figs. 1 and 3, respectively). This may have resulted from the mechanism of Scheme 2, i.e., via the pentacoordinated carbonium ion. Had the isotopic distribution been governed exclusively by the mechanisms described in the paragraphs above, the concentration of h_1 should be the lowest. It thus seems probable that at least a fraction of h_1 species was formed by methine H–D exchange according to Scheme 2. If pentacoordinated carbonium ions are formed on Brønsted acid sites, methine H–D exchange (restoration of Brønsted acid sites) may take place competitively with formation of the corresponding carbenium ion. The remaining unexchanged Brønsted acid sites are sufficiently abundant to provide for exchange of up to nine hydrogens per carbenium ion. The extent of H–D exchange between perdeuterioisobutane and catalysts increased as the reaction temperature was increased (Table 4), and increasing amounts of h_3 to h_8 species appeared in the products (Figs. 1–3), indicating onset of intermolecular exchange.

The isotopic composition of the products found with Y-zeolites and the H-mordenite, and the way these change with temperature, deserves comment. With the former, only the h_9 product was observed at 200°C, but as the temperature was raised this fraction first increased and then decreased again as important amounts of h_7 and h_8 appeared (Fig. 1). At 400°C small amounts of h_1 to h_8 appeared. This behavior can best be explained by assuming that at 200°C the residence time on a given site is sufficiently long to allow all of its methyl deuterium atoms to exchange with catalyst hydrogen and that intermolecular exchange is a much slower process. The latter is required to move the system to equilibrium.

The distributions shown for equimolar i-C_4D_{10} and i-C_4H_{10} over LZ–HM8 (Fig. 4B) are typical equilibrium curves for exchange of the i-C_4D_{10} with the amount of hydrogen available for exchange; they are concave to the abscissa. The data for the Y-zeolites shown in Figs. 1–3 are initially convex to the abscissa, suggesting a stepwise exchange process. As the temperature is raised, however, these distributions develop a hump at the heavily exchanged end (h_5 to h_9), indicating movement toward the equilibrium distribution and confirming that intermolecular exchange among the adsorbed species is occurring, although much more slowly than the local exchange required to form the h_9 species. The data for LZ–M8 are reminiscent of a similar process in a two-phase system such as isobutene-d_8 in benzene in contact with aqueous H_2SO_4. The result was a nearly completely exchanged paraffin reentering the gas phase.

When a first (perdeuterio) isobutane pulse was passed over LZ–210(6) at 350°C (Fig. 3), the majority of the exchanged species was h_5 to h_9; when a *second* pulse

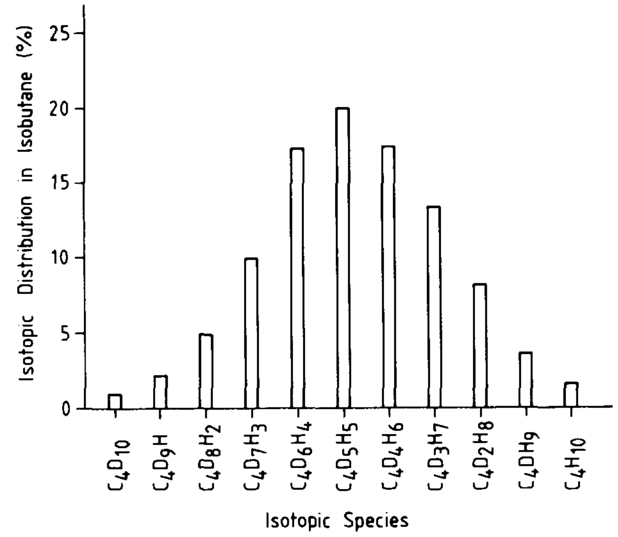


FIG. 5. Isotopic composition of isobutane formed by contacting a 50–50 mixture of perdeuterio- and perhydroisobutane (52% C_4H_{10}, 2% $C_4H_4D_8$, 15% C_4HD_9, 31% C_4D_{10}) with SbF_5–SiO_2–Al_2O_3 at 0°C for 150 min. The distribution was calculated from the data in Ref. (16).

containing i-C_4H_{10} was passed, highly exchanged (d_6–d_9) species were not formed, because of the relatively small population of D atoms put onto the surface by the first pulse (see Table 4). The distributions obtained from both pulses are compared in Fig. 3.

More extensive H–D exchange between perdeuterio-isobutane and H-mordenite was found at 125°C than with H–Y-zeolites at 200°C (Table 4). This suggests that on the more acidic mordenite a greater fraction of Brønsted sites remained populated for much longer times than on the Y-zeolites. The distribution of isotopic species approaching equilibrium (Fig. 4B) shows that the carbenium ions underwent multiple and intermolecular exchange steps before escape from the surface. (The solid line superimposed on the block diagram (Fig. 4B) shows the equilibrium distribution expected from random mixing of all the H and D present in the system). As the temperature was increased, the fraction of the molecules which became protonated at all (Fig. 4A) increased; the maximum in isotopic distribution increased in height and, as expected, shifted noticeably toward less exchanged species as intermolecular mixing became involved.

Results obtained in H–D exchange between 50–50 perdeuterio- and perhydro-isobutane over SbF_5–SiO_2–Al_2O_3 solid superacid at 0°C was reported by Takahashi and Hattori (16). After recirculation in a closed reactor system for 150 min at 0°C, 99.4% of the isobutane remained "unreacted," but extensive intermolecular H–D scrambling resulted in the volcano-shaped isotopic distribution shown in Fig. 5. Although the authors attributed their results to a carbenium ion reaction initiated by H^- abstraction, the commonality of their results with those for LZ-HM-8 shown in Fig. 4 makes this assignment questionable.

The results obtained in H–D exchange between isobutane and H-zeolites by pulse reactor techniques has provided valuable insight into the possible Brønsted acid catalyzed mechanisms operating at low isobutane conversion. At higher temperatures the results obtained became obscured by secondary processes. Nevertheless, the data confirm and support the reaction schemes presented for the acid catalysis and the introduction of the alkoxide species provides a way to explain the storage capacity of the catalyst.

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