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Active Sites and Intermediates for Isomerization and Cracking of Cyclohexane on HY

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Initiation of both isomerization and cracking reactions of cyclohexane on HY at 400°C occurs at Brønsted sites. The absence of molecular hydrogen as a product indicates that protonation of the feed molecule occurs, and the resulting carbonium ion can rearrange through a cracking–realkylation process, or undergo ring cleavage leading to acyclic products. No direct evidence was obtained which would indicate the existence of a chain mechanism proceeding through cyclic carbenium ion intermediates. These observations support a previously proposed mechanism for initiation of cracking of linear paraffins at Brønsted sites. © 1990 Academic Press, Inc.

INTRODUCTION

Although reactions of hydrocarbons on solid acid catalysts have been studied for many years, the detailed mechanisms of these processes are still under debate. Many of the recent reports have focused on the behaviour of acyclic paraffins under cracking conditions (*1–6*), with rather less attention being given to the cycloparaffins (*7–9*). Both classes of hydrocarbons are important components in gas oil feedstocks (*10*), and their respective reactions would be expected to demonstrate many common features.

An overall understanding of a particular cracking mechanism requires both identification of the active catalytic sites on the solid and characterization of the hydrocarbon intermediates involved in passing from reactant to products. These two facets are intimately related, as the types of possible intermediates will be determined by the nature of catalytic sites present, as well as reaction conditions such as temperature. Superimposed upon this will be constraints such as pore dimensions of the catalyst itself (*11, 12*) which can limit formation of certain intermediates, and also influences due to the presence of other hydrocarbon components in the reaction mixture (*13*).

Most of the phenomena associated with reactions of hydrocarbons on zeolites have been interpreted in terms of ionic mechanisms. The intermediates in these processes would be carbonium ions or carbenium ions (*4, 10*) and their formation is generally attributed to interactions with Brønsted or Lewis acid sites on the zeolite surface (*14, 15*). There has also been some recent discussion concerning the role of radical intermediates in these processes (*16–18*). A review of the pertinent literature from the past few years leaves the impression that a coherent and consistent mechanistic picture has not yet emerged, possibly in part because of adherence to different experimental techniques and methods of interpretation.

A continuing series of investigations on catalytic reactions of paraffins and cycloparaffins on aluminosilicates has examined both selectivity and kinetic phenomena in conjunction (*1–3, 19–21*). A plausible mechanistic model has emerged in which reaction is generally initiated at Brønsted sites through protonation to give carbonium ion intermediates. One of the consequences of this simple model is the requirement for rearrangement of protonated species prior to cracking (*1, 20*). Although the rearrangement of carbenium ions is well known, there is much less evidence for isomerization

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through protonated intermediates (without loss of molecular hydrogen). As isomerization is the dominant process observed for reaction of cyclohexane on HY, a detailed investigation of this process has been undertaken.

THEORY

Selectivity

For each reaction product, the time averaged yield from $t = 0$ to t_f can be plotted against $\bar{X}_R$, the integral conversion of feed. This allows the selectivity of products to be described by characteristic curves (*22*). The initial selectivity of a product, given by the slope at zero conversion, is nonzero for a primary product and zero for secondary or subsequent products.

Kinetics

It has been shown (*19, 21*) that reactions of *n*-paraffins on HY can be described by Eq. 1,

$$\frac{dX}{d\tau} = \frac{A(1 - X)/(1 + \varepsilon X)(1 + Gt)^{-N}}{1 + B(1 - X)/(1 + \varepsilon X)}, \quad (1)$$

where X is the instantaneous fractional conversion of the paraffin, τ is the feed contact time, t is the catalyst time on stream, ε is the volume expansion coefficient, G and N are aging parameters, and A and B are constants related respectively to the rate constants for reaction and the Langmuir adsorption constants for the reactant and products. The constants A and B are defined by the expressions

$$A = \frac{\sum_i k_i K[C]_0}{1 + \sum_j K_j n_j [C]_0} \quad (2)$$

and

$$B = [C]_0 \frac{K - \sum_j K_j n_j}{1 + \sum_j K_j n_j [C]_0}, \quad (3)$$

where k_i are the individual rate constants for the i parallel modes of conversion of the feed; K and K_j are Langmuir adsorption constants for the feed C and each product P_j, respectively; n_j are stoichiometric factors accounting for the number of product molecules of type j formed from the feed molecule; and $[C]_0$ is the initial concentration of reactant.

EXPERIMENTAL

Cyclohexane (99.85%) was obtained from Aldrich and used without further purification. Impurities present were 2,3-dimethylbutane, 0.062%; 2-methylpentane 0.012%, 3-methylpentane 0.013%, methylcyclopentane 0.023%; methylcyclohexane, 0.037%. The presence of these impurities was taken into account in calculation of initial selectivities.

HY zeolite (97.3% exchanged) was prepared from NaY (Linde Co., Lot No. 45912, SK40; Si/Al = 2.4) by repeated exchange with 0.5 *N* ammonium nitrate solution. HZSM-5 was provided by SNAM Progetti S.p.A., Milan, Italy. It was prepared according to methods in the patent literature. The sample (Si/Al = 105) was exchanged with aqueous ammonium nitrate.

Catalysts were calcined at 500°C before use. All experiments were carried out using catalysts with mesh size 80/100. Reduction of the catalyst particle size had no influence on the cracking reaction, showing that the reaction was not diffusion controlled.

All experiments were performed by using an integral, fixed-bed gas-phase plug flow reactor with an independently controlled three-zone heater. The experimental apparatus and procedures used were similar to those described in previous studies (*23*). All reactions were carried out at 400°C and 1 atm pressure. Liquid and gas products were analysed by gas chromatography (*23*).

For heat pretreatment experiments at temperatures above 500°C, the reactor temperature was increased to either 600 or 700°C and maintained at the elevated temperature for a period of 4 h. The catalyst was then cooled to reaction temperature in a stream of dry nitrogen.

For rehydration experiments, the reactor

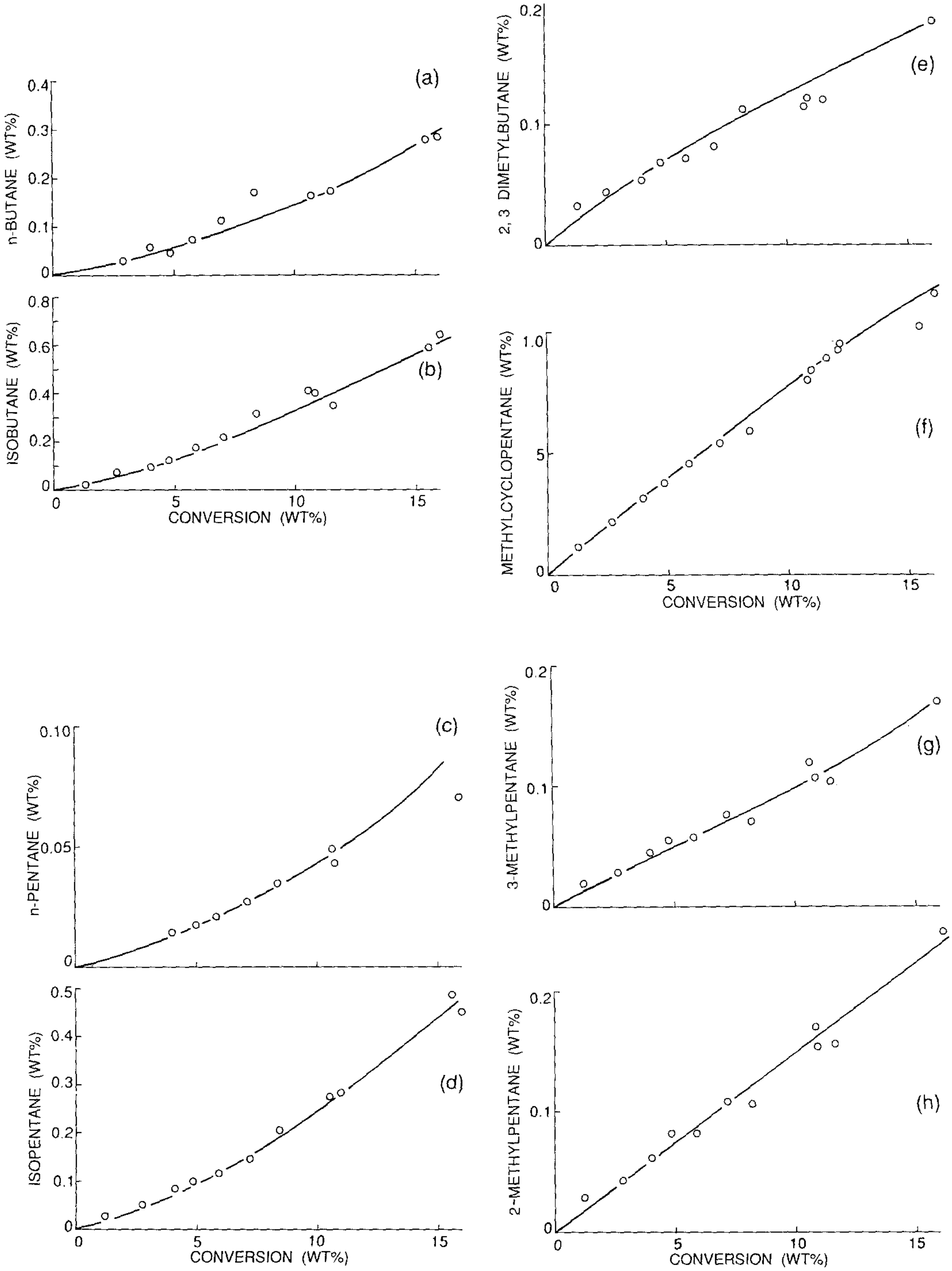

FIG. 1. Plots of yield against conversion for products from reaction of cyclohexane on HY at 400°C (maximum pretreatment temperature 500°C). (a) *n*-Butane, (b) isobutane, (c) *n*-pentane, (d) isopentane (e) 2,3-dimethylbutane, (f) methylcyclopentane (g) 3-methylpentane, (h) 2-methylpentane.

TABLE 1

Initial Weight Selectivities for Reaction of Cyclohexane on HY at 400°C

Product	Type[a]	Initial selectivity
Methane	2s	0
Ethane	2s	0
Propane	(1 + 2)s	0.0200
Propylene	2s	0
Isobutane	(1 + 2)s	0.0137
n-Butane	2s	0
Isopentane	(1 + 2)s	0.0145
n-Pentane	2s	0
2,3-Dimethylbutane	2s	0
2-Methylpentane	(1 + 2)s	0.010
3-Methylpentane	2s	0
n-Hexane	(1 + 2)s	0.017
Methylcyclopentane	1u	0.860
Benzene	(1 + 2)s	0.0200
Dimethylcyclopentanes	(1 + 2)s	0.0143
Methylcyclohexane	(1 + 2)s	0.00846
Trimethylcyclopentanes	2s	0
Toluene	2s	0
Dimethylcyclohexanes	2s	0
C_8 aromatics	(1 + 2)s	0.0033
C_9 aromatics	2s	0
Coke	(1 + 2)s	0.015
		Total 0.996

[a] 1, primary; 2, secondary; s, stable; u, unstable.

was cooled to 100°C, and distilled water injected. The reactor temperature was then raised to 500°C in a stream of dry nitrogen, before cooling to the reaction temperature of 400°C. Catalyst regeneration was carried out at 500°C in a stream of dry air for 24 h (*23*).

RESULTS AND DISCUSSION

Catalytic conversion of cyclohexane on HY at 400°C was studied by variation of the catalyst/reactant ratio and run duration. For each product, yields were plotted against total conversion of feed, as illustrated in Fig. 1. Initial selectivities and product types were obtained from these plots and are given in Table 1. It is clear that the dominant reaction is isomerization under these conditions, to produce methylcyclopentane, which accounts for ~86% of the total initial selectivity. Cracking, hydrogen transfer, and coke formation account for the remainder. As previously reported for reaction of cyclooctane and ethylcyclohexane (*7*), paraffins were the major acyclic products, with little evidence of olefin formation.

Active Sites

Many of the early studies (*24–27*) on catalytic properties of zeolites gave a clear indication that Brønsted sites were active in various types of hydrocarbon reaction. A number of investigations showed correlations between catalytic activity of Y zeolites and the presence of Brønsted centres, identified with the framework hydroxyl groups (*26, 27*). Evidence was provided by examination of effects due to heat pretreatments and water addition to the zeolites, coupled with measurements of catalytic conversions and spectroscopic properties of the solids (*28, 29*).

The Y zeolite used in the present study was subjected to a maximum calcination temperature of 500°C after each exchange process. Selectivity results in Table 1 were obtained for a number of catalyst/reactant ratios, varying the run duration and plotting results as illustrated in Fig. 1. Between each run the catalyst was regenerated in air at 500°C. The HY zeolite was found to fully regain its activity through the regeneration procedure, as reported previously for studies on cracking of other hydrocarbons (*23*).

Figure 2 shows the effects of increasing the catalyst pretreatment temperature above 500°C, for conversion of cyclohexane on HY at 400°C. It is apparant that the conversion of cyclohexane was reduced with a pretreatment temperature of 600°C and declined further when the pretreatment temperature was increased to 700°C. These results are in good agreement with studies of the effects of catalyst pretreatment temperature for cracking of linear paraffins on HY (*28*). Investigations have shown that a maximum in cracking activity is usually observed for pretreatment temperatures ~500–550°C,

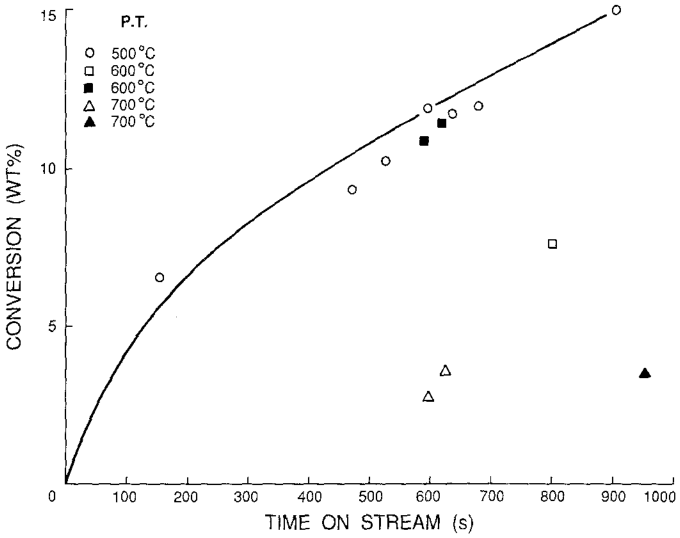

FIG. 2. The effect of catalyst pretreatment temperature and rehydration on total conversion for reaction of cyclohexane on HY at 400°C. Pretreatment temperatures: (○) 500°C; (□) 600°C; (△) 700°C. Solid symbols indicate rehydration. Catalyst-to-reactant ratio is 0.0317.

with activity declining sharply as the temperature is further increased (*28*). This effect has been explained in terms of the dehydration of the zeolite, corresponding to conversion of pairs of Brønsted sites into a Lewis site, with concurrent loss of a water molecule (*29*).

Under some conditions this effect has been found to be reversible. Dehydrated zeolites have been shown to regain catalytic activity on rehydration, attributed to conversion of Lewis sites into Brønsted sites (*26, 27*). This effect of catalyst rehydration is also observed for reaction of cyclohexane on HY. Figure 2 shows the influence of adding water to the catalyst which had undergone pretreatment at 600 and at 700°C. Figure 2 shows that for HY heated to 600°C, the activity is fully restored by water addition, while the process is not reversible when the pretreatment temperature is increased to 700°C. This observation is in agreement with the investigations by Hughes and White (*30*), who found that dehydration of HY occurred without appreciable structural disruption at temperatures up to 600°C, but significant disruption of the zeolite framework took place at 700°C. For other zeolites, such as mordenite, the temperature at which structural degradation occurs may be higher, so that the effects of reversible water addition can be seen even up to 800°C (*27*).

The influence of catalyst pretreatment temperature on product selectivity can also be examined. Figure 3 shows that the selectivity for isomerization of cyclohexane to methylcyclopentane remains unchanged by increasing catalyst pretreatment temperature above 500°C. Therefore, although the total conversion decreases as Brønsted sites are removed, the ratio of isomerized to cracked products remains constant. This suggests that both types of process occur on Brønsted sites on HY zeolite during reaction of cyclohexane. If these reactions occurred on different sites (i.e., Brønsted and Lewis), this ratio should be affected by pretreatment temperature. Figure 4 shows a selectivity plot for total C_6 paraffins produced from reaction of cyclohexane. Again the selectivity is not influenced by pretreatment temperature, indicating that the individual cracking processes again occur on similar sites. It is also interesting to note that selectivity does

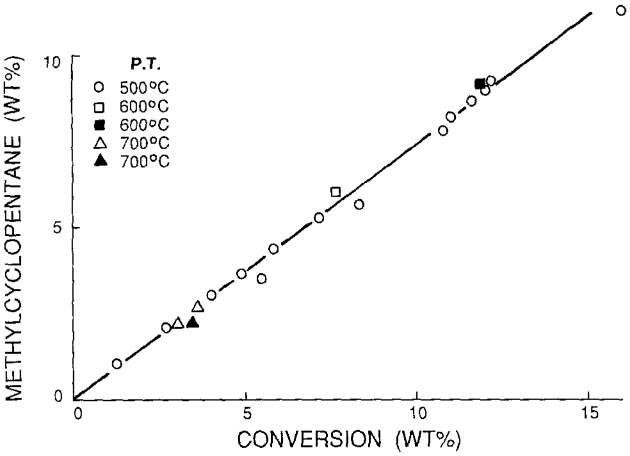

FIG. 3. The effect of catalyst pretreatment temperature and rehydration on methylcyclopentane selectivity for reaction of cyclohexane on HY at 400°C. Symbols as in Fig. 2.

not appear to be influenced for reactions on the rehydrated samples, despite reports that the hydroxyl groups produced during rehydration are not equivalent to those originally present (*26, 30*).

From these results it seems probable that both isomerization and cracking occur on Brønsted sites. The "one site" kinetic model previously applied to reaction of linear paraffins on HY (*19, 21*) was applied to reaction of cyclohexane on HY at 400°C. Cumulative conversions of cyclohexane at various times on stream and catalyst/reactant ratios were fitted by Eq. (1). Experimental points and theoretical lines are shown in Fig. 5. Optimum values of the kinetic parameter *B* are given in Table 2, which also gives values previously obtained for reaction of linear paraffins on HY (*19*).

From Table 2, it is clear that parameter *B* has a positive value for reaction of cyclohexane, while this parameter is close to -1 for reaction of linear paraffins under the same conditions. The significance of $B = -1$ has been discussed previously (*21*), where it was shown that this could be related to strong

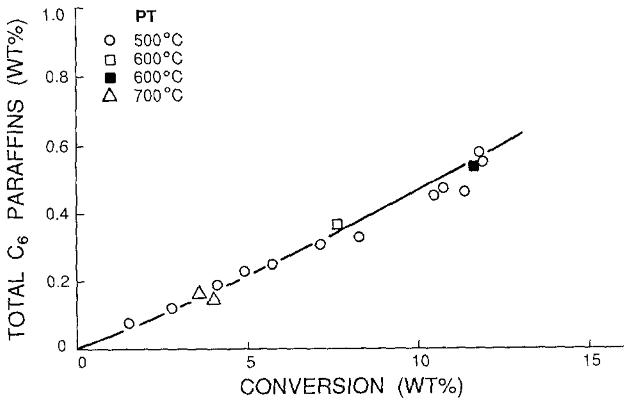

FIG. 4. The effect of catalyst pretreatment temperature and rehydration on C_6 paraffin formation for reaction of cyclohexane on HY at 400°C. Symbols as in Fig. 2.

TABLE 2

Optimum Values of Parameter B for Reaction at 400°C

Reactant	Catalyst	B
Cyclohexane	HY	211
Cyclooctane	HY	65
n-Octane	HY	−0.994 (*21*)
n-Dodecane	HY	−0.996 (*21*)
n-Hexadecane	HY	−0.998 (*21*)
n-Octane	HZSM-5	−0.18

inhibition of the cracking reaction by formation and subsequent adsorption of olefins at the active sites. During cracking of linear paraffins on HY, olefins are a major product at all levels of conversion (Table 3). These unsaturated species are more strongly adsorbed at Brønsted sites than the paraffin feed, producing carbenium ions which are much less effective in causing cracking of the feed than the original sites (*1, 19*).

The absence of strong inhibition during reaction of cyclohexane ($B = 211$) is reasonable here in view of the lack of olefinic products in this case (Table 1). A similar magnitude for parameter B was also obtained by kinetic analysis of results for isomerization of cyclooctane on HY at 400°C (*7*) as shown in Table 2. Introduction of a small quantity of an olefin (1.6% 1-hexene) to the cyclohexane feed produced a significant reduction in measured conversion (Fig. 6), which can be attributed to inhibition by preferential adsorption of the olefin at Brønsted sites.

There is conflicting evidence in the literature on the influence of olefin addition during reaction of linear paraffins on solid acid catalysts. Some authors report an accelerating effect on the cracking process when small amounts of olefin are added to the feed paraffin (*31–34*), and this has been attributed to an autocatalytic process (*31*). Other studies have shown that there is little or no influence on reaction due to trace amounts of olefin (*35–37*). For reaction on the HY zeolite used in the present study, no accelerating influence due to olefin addition has been found during cracking reactions of *n*-hexane at 500°C (*35*). In further studies, addition of 1-hexane to *n*-octane in amounts ≤10% (by weight) produced a reduction in conversion of the linear paraffin. For example, at 400°C, conversion of *n*-octane on HY was found to decrease from 5% to less than 1% after adding 10% olefin to the feed. For reaction of linear paraffins, the reasons for these differences in reported behaviour due to olefin addition are not clear. However, it is interesting to note that at very low levels of olefin addition during *n*-octane cracking

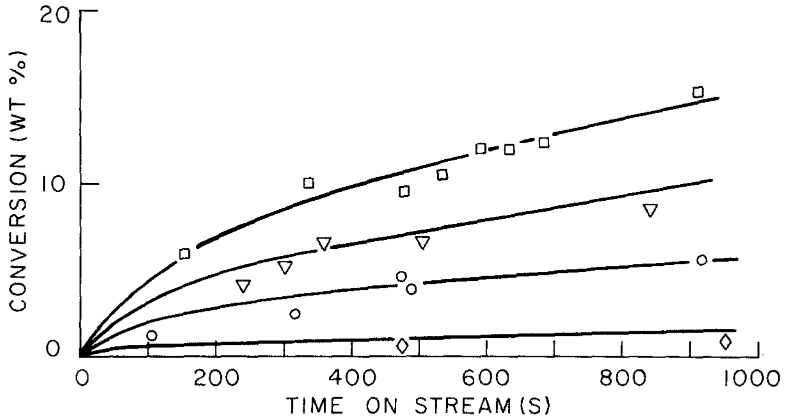

FIG. 5. Experimental points and theoretical lines for conversion of cyclohexane on HY at 400°C fitted by Eq. (1). Catalyst-to-reactant ratios: 0.0032, 0.0127, 0.0128, 0.0317.

TABLE 3

Product Types and Initial Weight Selectivities for Reaction of *n*-Octane on HY and HZSM-5 at 400°C

Product	Type[a]		Initial weight selectivity	
	HY	HZSM-5	HY	HZSM-5
Hydrogen	—	2s	0	
Methane	—	1s	0	0.0050
Ethane	2s	(1 + 2)s	0	0.0285
Ethylene	2s	1s	0	0.025
Propane	(1 + 2)s	1s	0.0500	0.162
Propylene	1u	1u	0.1045	0.156
n-Butane	(1 + 2)s	(1 + 2)s	0.1125	0.123
Isobutane	(1 + 2)s	(1 + 2)s	0.1952	0.0360
trans-2-Butene	1u	1u	0.0593	0.0526
cis-2-Butene	1u	1u	0.0409	0.0376
Isobutene	1u	1u	0.1178	0.125
n-Pentane	1s	1s	0.0281	0.0677
2-Methylbutane	(1 + 2)s	(1 + 2)s	0.1431	0.0125
trans-2-Pentane	1u	1u	0.0124	0.0191
cis-2-Pentene	1u	1u	0.0063	0.00953
3-Methyl-1-butene	1u	1u	0.0022	0.0039
2-Methyl-1-butene	1u	1u	0.0210	0.0269
2-Methyl-2-butene	1u	1u	0.0482	0.0679
1-Pentene	1u	1u	0.0032	0.00529
n-Hexane	2s	(1 + 2)s	0	0.01168
2-Methylpentane	2s	(1 + 2)s	0	0.0018
3-Methylpentane	2s	(1 + 2)s	0	0.0018
2,3-Dimethylbutane	2s	—	0	0
C_7	2s	2s	0	0
C_8 paraffins	(1 + 2)s	2s	0.036	0
C_6 olefins	(1 + 2)s	2s	0	0.0164
C_8 aromatics	(1 + 2)s	2s	0.0125	0.010
C_9 aromatics	(1 + 2)s		0.0038	0
Coke	(1 + 2)s		0.0180	0
			1.014	1.005

[a] 1, primary; 2, secondary; s, stable; u, unstable.

(*31*), no accelerating effect was observed, while effects of any autocatalytic process should be most noticeable under these conditions.

For reaction of branched paraffins on HY zeolite and amorphous silica–alumina, there is clear evidence of an autocatalytic process (*1*, *19*). Addition of small amounts of olefin produce a very significant increase in reaction rate of the feed hydrocarbon. In these cases, the tertiary hydrogen atom is susceptible to abstraction by the adsorbed carbenium ions (i.e., Lewis sites) and cracking via this route occurs more easily than through protonation of the branched molecules.

The evidence here shows that Brønsted sites are active during both cracking and isomerization of cyclohexane on HY zeolite. Isomerization of linear paraffins has been attributed to catalytic reaction at Brønsted sites for *n*-pentane on H-mordenite (*38*) and for reaction of *n*-butane on the solid superacid $AlCl_3$–sulfonic acid resin complex (*39*). Other studies have concluded that Lewis sites are active during isomerization of cyclohexane to methylcyclopentane on metal oxides of the type TiO_2–ZrO_2–V_2O_5 (*40*) and on the solid superacid SbF_5–SiO_2–Al_2O_3 (*41*, *42*). For catalysts which do not have Brønsted sites of suitable acid strength present in sufficient concentration, it is indeed possible that isomerization does occur via hydride ion abstraction at Lewis sites. However, as pointed out recently (*5*), one cannot be entirely sure that all traces of water have been completely eliminated from these catalysts, so that Brønsted sites may still be present and contribute to the observed activity.

Nature of the Hydrocarbon Intermediates

Identification of the active catalytic sites for reaction of hydrocarbons on solid acids is generally much easier than a description of the hydrocarbon species as it is transformed from reactant through to final products. Isomerization and cracking processes have been described in terms of ionic intermediates (*1–10*). These are either carbenium ions produced by hydride abstraction or carbonium ions formed via proton addition. The validity of discussing these carbocations in isolation from the site (i.e., bearing a discrete positive charge) is a matter of conjecture. However, it is worthwhile to examine the reaction of cyclohexane on HY in this context as it gives support to previous discussions on the mechanism for cracking of linear paraffins on this catalyst (*19*).

Isomerization of cyclohexane to methylcyclopentane on a solid super acid catalyst occurs through hydride abstraction at Lewis sites (*41*, *42*). The resultant secondary carbenium ion then undergoes rearrangement to the tertiary methylcyclopentyl carbenium ion, which can desorb as the product methylcyclopentane. This type of mechanism is

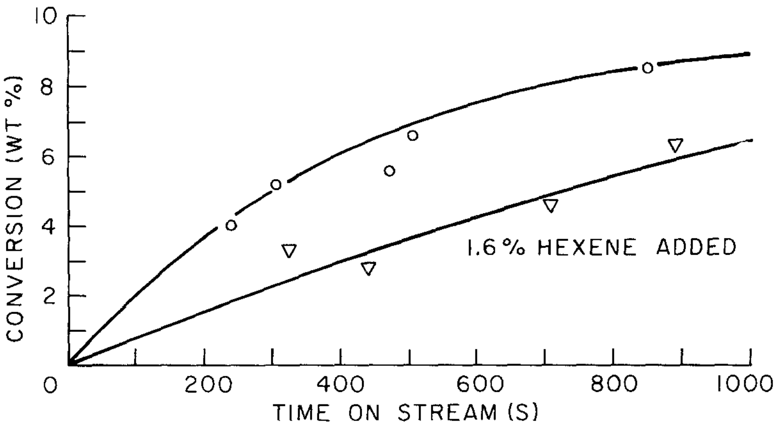

FIG. 6. The effect of olefin addition (1.6% 1-hexene by weight) to cyclohexane feed for reaction on HY at 400°C. Catalyst-to-reactant ratio 0.0317.

illustrated in Fig. 7A. However, as it has been established that Brønsted sites are active during isomerization on HY zeolite, this mechanism cannot apply. Recent studies (*43*) on reactions of 3-methylpentane on the same HY zeolite at 500°C have also failed to detect participation of Lewis acid sites during isomerization processes. No increase in selectivity for these processes relative to cracking reactions could be detected after reversible heat pretreatment experiments. It would appear even more unlikely that initiation via hydride ion abstraction would occur in the absence of tertiary C–H bonds, as in the case of the cyclohexane feed.

Isomerization of cycloparaffins has been studied in liquid superacid media (*44*). Protonation of cyclohexane is thought to occur under these conditions (*44*), and theoretical calculations (*45*) have shown that various protonated structures are stable. Loss of molecular hydrogen from the carbonium ion can lead to the secondary cyclohexyl carbenium ion, which can then undergo rearrangement to yield the tertiary carbenium ion (Fig. 7B). Alternatively the protonated ring can undergo C–C bond cleavage, rather than C–H cleavage to produce an acyclic carbenium ion. Both types of process have been reported by Olah, and reaction temperature determines which process is most favourable (*44*).

The present evidence suggests that on HY zeolite at 400°C reaction of cyclohexane occurs at Brønsted sites. Ring cleavage of a protonated intermediate would lead to an acyclic carbenium ion which can undergo cracking and hydrogen transfer reactions ultimately leading to the observed paraffins and unsaturated species such as aromatics and coke (Table 1). Isomerization to methylcyclopentane, the dominant initial process, cannot occur through loss of hydrogen and subsequent rearrangement of a carbenium ion (Fig. 7B), as molecular hydrogen was not detected. This is not surprising, as molecular hydrogen has not been detected for reaction of linear paraffins such as *n*-octane on HY at 400°C (Table 3). In both cases, the propensity toward formation of molecular hydrogen will be limited by the ease of hydride abstraction at a secondary carbon atom. These structures do not contain "tertiary" hydrogen atoms which are much more easily abstracted to yield molecular hydrogen (*20*). This appears to leave two alternatives as shown in Fig. 7C. First, it is possible that the protonated cyclohexane evolves to yield a species in which hydrogen is loosely bound to a carbenium ion and does not leave during skeletal rearrangement (*41*,

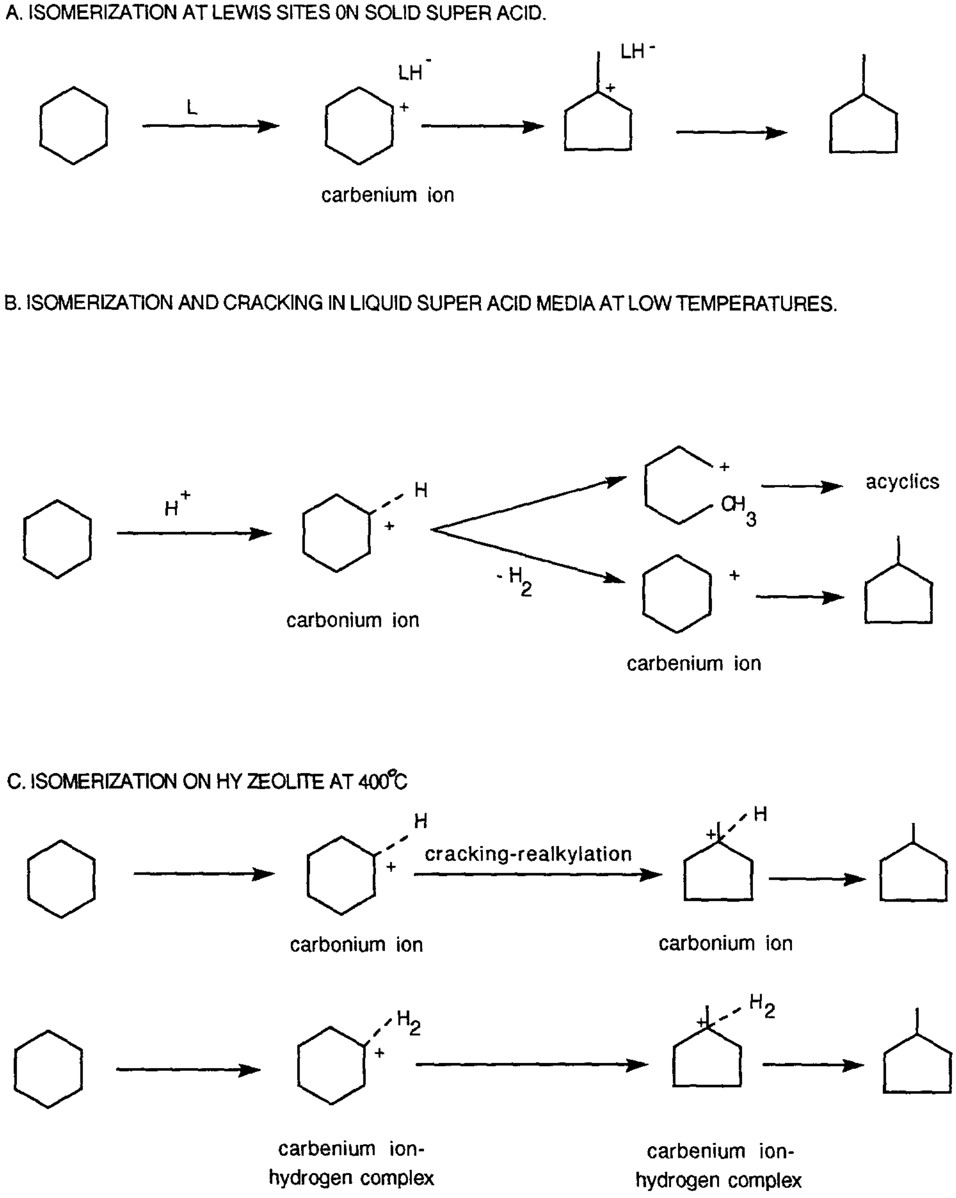

FIG. 7. Reaction mechanisms for isomerization and cracking of cyclohexane through carbonium ion and carbenium ion intermediates.

42). Alternatively, we can envisage rearrangement of the carbonium ion taking place through a cracking–realkylation sequence (*19*).

A cracking–realkylation mechanism has been suggested (*19*) to explain the appearance of branched paraffins as initial products during cracking of linear paraffins on zeolite catalysts, as shown in Table 3, which gives initial selectivity values for reaction of *n*-octane on HY (*23*) and HZSM-5 at 400°C. These values were also calculated from yield-conversion plots as illustrated for reaction of *n*-octane on HZSM-5 in Fig. 8.

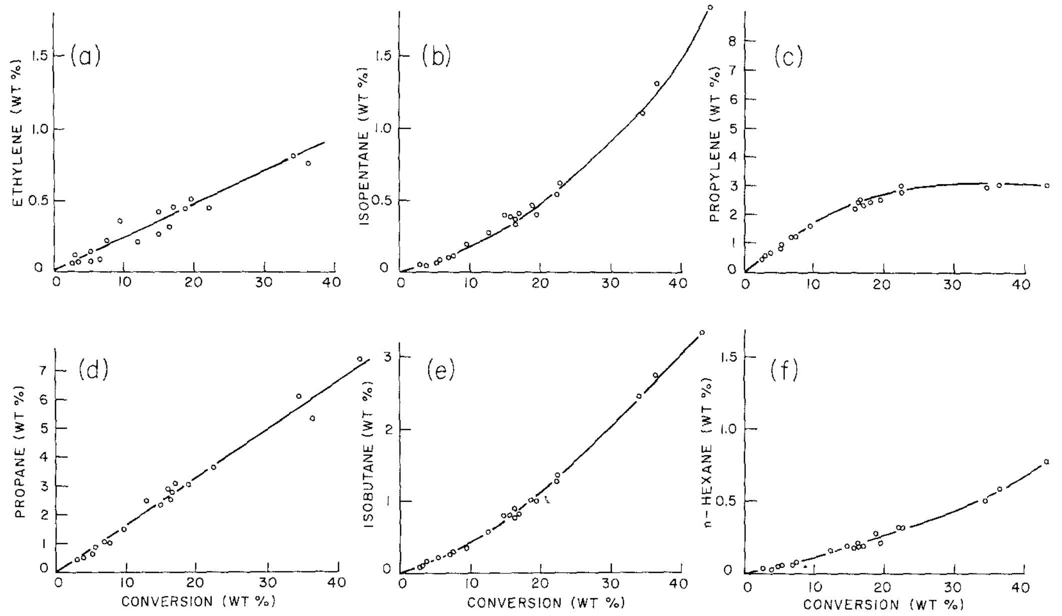

FIG. 8. Plots of yield against conversion for products from reaction of *n*-octane on HZSM-5 at 400°C. (a) Ethylene, (b) isopentane, (c) propylene, (d) propane (e) isobutane, (f) *n*-hexane.

Table 4 shows that branched paraffins are in fact dominant in the range C_4–C_6 for reaction on HY, while the preference for linear paraffins on HZSM-5 can be explained by pore size constraints. In the absence of molecular hydrogen as an observable product, this mechanism removes the requirement of two distinct types of site (Brønsted and Lewis) as proposed by Corma *et al.* (*14, 15*). It is interesting to note that a cracking–realkylation type of mechanism does not appear to have been considered for skeletal rearrangements of paraffins or cycloparaffins in liquid superacids, where isomerization seems to be represented generally by rearrangement of a carbenium ion. However, it should also be noted that the two components of such a mechanism (i.e., C–C bond cleavage of a carbonium ion to produce a carbenium ion and a neutral paraffin, followed by alkylation of a paraffin by a carbenium ion) have both been discussed in detail (*46–48*).

TABLE 4

Ratios of Branched to Linear Paraffins Initially Formed from Reaction of *n*-Octane at 400°C

Catalyst	Branched/linear ratio		
	C_4	C_5	C_6
HY	1.74	5.1	—
HZSM-5	0.29	0.18	0.31

Once the reaction has been initiated, the catalytic process can continue after desorption of products and reconstitution of the original Brønsted site. Alternatively it is possible for the reaction to continue via a chain mechanism in which hydride ion abstraction from feed molecules by adsorbed methylcyclopentyl ions would lead to a new carbenium ion. There is clear evidence for this type of mechanism for reactions of branched paraffins on HY (*19*) where hydride ion abstraction is facile. The effect can be demonstrated by the acceleration caused by olefin addition due to increased surface carbenium ion concentration (*1*). The existence of the chain process can also be demonstrated by changes in selectivity with conversion, as product distributions from initiation (via protonation) can be significantly different from those produced via a chain mechanism (via hydride abstraction). This has been demonstrated for reaction of 3-methylpentane on HY at 500°C (*43*).

For reaction of various feedstocks on a zeolite catalyst under given conditions, there appears to be a relationship between the ease of formation of molecular hydrogen from the feed molecule and the tendency for propagation of the reaction via a chain mechanism (*49*). This is reasonable as both processes involve hydride ion abstraction, the former at a Brønsted site and the latter by a carbenium ion adsorbed at a Brønsted site. As mentioned earlier, molecular hydrogen was not detected as a product for reaction of cyclohexane on HY. The inhibiting influence of an olefin added to the feed also casts doubt that a chain reaction via carbenium ion intermediates (*50*) is the dominant mode of propagation for reaction of cyclohexane on HY.

CONCLUSION

This study shows that both isomerization and cracking of cyclohexane on HY zeolite occur at Brønsted sites. Isomerization of cyclohexane proceeds without loss of molecular hydrogen, and this observation supports the proposal that linear paraffins undergo reaction via rearrangement of a protonated intermediate species prior to cracking (*19*). This would account for the initial formation of branched paraffins, without the requirement for Lewis sites as the dominant active centres on the zeolite framework (*14, 15*). For other types of catalyst, Lewis sites may indeed play a role in isomerization of hydrocarbons (*51*). However, the mechanism presented here, utilizing only Brønsted sites, may also be worth considering in other systems where insufficient molecular hydrogen has been observed to account for stoichiometry (*52, 53*).

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