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The Influence of Reaction Temperature on the Cracking Mechanism of 2-Methylhexane

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The cracking of 2-methylhexane on USHY has been studied in the temperature range 400–500°C. It was found that this reaction leads to the formation of hydrogen, paraffins, olefins, and aromatics ranging from C_1 to C_{10}. Of these only hydrogen, C_1–C_7 compounds, and coke were found to be primary products. Mechanistic considerations indicate that two main processes take place during 2-methylhexane conversion on USHY: (1) initiation by protolysis on pristine Brønsted sites; (2) chain processes involving isomerization, hydrogen transfer, and disproportion. At low temperatures, conversion of 2-methylhexane proceeds to a significant extent via both mechanisms, while at higher temperatures protolytic cracking is the dominant process by far. We find that protolysis accounts for 67, 83, and 94% of total conversion of 2-methylhexane at 400, 450, and 500°C, respectively. The average activation energy for protolytic cracking of 2-methylhexane on USHY was found to be 159 kJ/mol. The unexpectedly low activation energy for protolysis vis-à-vis the comparable value in 2-methylpentane cracking (246 kJ/mol) is discussed in terms of temperature effects on active site densities and in terms of the compensation effect in protolysis. Hydride abstraction from gas phase 2-methylhexane by $C_6H_{13}^+$ and $C_7H_{15}^+$ ions leads to the formation of the paraffinic C_6 and C_7 skeletal isomers found in the primary products. In addition to hydride transfer, the set of active bimolecular chain reactions involves some but not all possible disproportionations between feed molecules and carbenium ions in the range $C_2H_5^+$ and $C_5H_{11}^+$. The reasons for this specificity in disproportionation are discussed. The probability of initial coke formation was found to decrease with increasing temperature, suggesting a diminished rate of bimolecular reaction between adjacent carbenium ions at higher temperatures. We explain this as being the result of lower surface coverage by carbenium ions at elevated temperatures.

INTRODUCTION

Recent kinetic and mechanistic studies of the reactions of C_6 paraffins, carried out on ultrastable HY and other large pore zeolites, have indicated that the cracking of these molecules follows both protolytic and chain reaction modes (1–4). Selectivity data and optimum values of the kinetic parameters obtained from fitting experimental conversion data as a function of time on stream showed that the relative importance of these reaction modes depends on the properties of the catalyst and on reaction temperature. Our recent 2-methylpentane studies on USHY (4) have shown how monomolecular protolysis processes can act as initiation steps for the carbenium-ion-based chain reactions and how their contribution to overall conversion increases with increasing reaction temperature. Bimolecular chain-propagating reactions involving hydride transfer, disproportionation, and isomerization play a dominant role only at low reaction temperatures in that molecule.

Here we broaden the scope of our investigation of the mechanisms of branched paraffin cracking by reporting on a branched C_7 paraffin molecule. The effect of reaction temperature on product distribution and kinetics in the cracking of 2-methylhexane is described below.

EXPERIMENTAL

The feedstock, 2-methylhexane (99.90% pure), was obtained from Aldrich and used without further purification. The only impurity we detected was *n*-heptane (0.03%). HY zeolite was prepared from NaY obtained from BDH Chemicals by exchange with 0.5 *M* NH_4NO_3 solution at ~20°C for 24 h. Between exchanges, the catalyst was dried at 110°C for 24 h, then calcined in air at 500°C for 2 h. This exchange, drying, and calcining cycle was repeated ten times, resulting in a ~99.8% Na-exchanged HY catalyst. The catalyst powder was pelletized, then steamed for 24 h at 300°C to form ultrastable HY (USHY) which had a bulk Si/Al ratio of 2.31, determined by neutron activation energy, and a framework Si/Al ratio of 6.14, determined by X-ray diffraction.

All experiments were performed in a plug-flow glass reactor (60 × 1.6 cm I.D.) with an independently controlled three-zone heater. The experimental method, as well as a typical run, has been described in previous work (4, 18). Gaseous products in the range C_1–C_4 were analyzed by a Carle SX 1156 gas chromatograph which also

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allowed for direct hydrogen determination. Liquid products were analyzed by a Varian 6000 gas chromatograph with a 60-m SE54 capillary column and a flame ionization detector. The identification of the components of our liquid products was performed using a Hewlett–Packard 5890-A GC/MS.

RESULTS

Thermal Cracking

Preliminary thermal cracking experiments were carried out by pumping 2-methylhexane through a reactor packed with inert silica which had been thoroughly cleaned with 36% HCl solution and rinsed with distilled water. These experiments were performed in order to determine the extent of the contribution of noncatalytic cracking to the total conversion of 2-methylhexane. All reaction conditions and the amounts of feed used were the same as those used in the presence of the catalyst. The conversions due to thermal cracking at the longest time on stream (i.e., at the lowest space velocity) were 0.48, 0.73, and 1.51% at 400, 450, and 500°C, respectively.

The product distribution from thermal processes was noticeably different from that due to catalytic cracking. Nonetheless, thermal products consisted mainly of hydrogen, paraffins, and olefins in the range C_1–C_7. The presence of such thermal cracking products show that thermal reaction products can influence the interpretation of initial catalytic selectivity data. For this reason, initial selectivities of catalytic products were determined by subtracting thermal product yields from the total yields observed in cracking experiments with catalyst present.

Catalytic Cracking

Product distributions obtained during the catalytic cracking of 2-methylhexane over our ultrastable zeolite are presented in Tables 1–3 at three temperatures. The products include hydrogen, paraffins, olefins, and aromatics in the range C_1–C_{10}. Of these, only hydrogen, C_1–C_7 compounds, and coke were found to be primary products. Initial selectivities and product types were obtained by interpolating optimum performance envelopes for the products and determining selectivity behaviour at zero conversion (5). Figures 1–4 show some examples of OPE plots in 2-methylhexane cracking at 400, 450, and 500°C. Product types and initial weight and molar selectivities for primary products at 400, 450, and 500°C are listed in Tables 1, 2, and 3, respectively.

TABLE 1

Types of Products from the Cracking of 2-Methylhexane over USHY in the Temperature Range 400–500°C

Product	Type[a] 400°C	450°C	500°C
H_2	1S	1S	1S
Methane	(1 + 2)S	1S	1S
Ethane	1S	1S	1S
Ethylene	1S	1S	1S
Propane	(1 + 2)S	(1 + 2)S	(1 + 2)S
Propylene	(1 + 2)S	1U	1U
C_4-Paraffins	(1 + 2)S	1S	1S
C_4-Olefins	(1 + 2)S	1S	1S
C_5-Paraffins	(1 + 2)S	(1 + 2)S	(1 + 2)S
C_5-Olefins	(1 + 2)S	(1 + 2)S	(1 + 2)S
C_6-Paraffins	1U	(1 + 2)S	(1 + 2)S
C_6-Olefins	(1 + 2)S	(1 + 2)S	(1 + 2)S
C_7-Paraffins	1U	1S	1S
C_7-Olefins	1U	1U	1U
Coke	(1 + 2)S	(1 + 2)S	(1 + 2)S

[a] 1, primary; 2, secondary; S, stable; U, unstable.

The product distribution from 2-methylhexane cracking is similar at all three temperatures. The major initial products were C_3, C_4, and C_7 olefins and paraffins, including various skeletal isomers of the feed: mostly 3-methylhexane and *n*-heptane. These made up about 90% of all initial products at all three temperatures. Other important initial products include hydrogen, methane, ethylene, and C_5-paraffins as well as C_6-paraffins and olefins. Much smaller amounts of ethane, C_5-olefins, and coke were also observed as initial products.

The initial selectivities for the formation of hydrogen and all C_1–C_5 species increased with increasing temperature, while those for all C_6 and C_7 skeletal isomers of the feed and coke decreased. A similar change of initial product selectivities with temperature was observed in the reactions of *n*-heptane over USHY by Corma *et al.* (6). Furthermore, the trend in the changes of the selectivities of isomeric products with temperature agree qualitatively with results from 2-methylpentane cracking on USHY in the temperature range 400–500°C (4). In that case, isomeric products were dominant at temperatures ≤400°C, followed by a sharp decline in isomeric products, accompanied by a pronounced increase in C_1–C_5 species, with increasing temperature. It seems that at low temperatures isomerization reactions are highly favoured in C_6 paraffin molecules, while significant protolytic and β-cracking are already active in C_7 paraffin molecules at 400°C. We see immediately, without any calculation, that there must be an unexpectedly large difference in rate constants for analogous processes in the two molecules.

In addition to primary products, we observed the formation of secondary products. These consisted largely of

TABLE 2

Initial Weight Selectivities for Cracking Products of 2-Methylhexane over USHY in the Temperature Range 400–500°C

Product	Initial weight selectivity[a] 400°C	450°C	500°C
H_2	0.0005	0.0006	0.0008
Methane	0.0032	0.0038	0.0049
Ethane	0.0013	0.0016	0.0022
Ethene	0.0074	0.0096	0.0106
Propane	0.0778	0.0879	0.0985
Propene	0.1766	0.2411	0.2689
C_4-Paraffins	0.2762	0.3345	0.3462
C_4-Olefins	0.0614	0.0923	0.1212
C_5-Paraffins	0.0294	0.0312	0.0331
C_5-Olefins	0.0019	0.0033	0.0093
C_6-Paraffins	0.0357	0.0241	0.0155
C_6-Olefins	0.0334	0.0182	0.0067
C_7-Paraffins	0.2155	0.0971	0.0392
C_7-Olefins	0.0656	0.0416	0.0374
Coke	0.0150	0.0123	0.0053
Total	1.0009	0.9992	0.9998

[a] Initial weight selectivities were determined from initial slope of the yield vs conversion plots.

TABLE 3

Initial Molar Selectivities for Cracking Products from 2-Methylhexane over USHY in the Temperature Range 400–500°C

Product	Initial molar selectivity[a] 400°C	450°C	500°C
H_2	0.0250	0.0273	0.0400
Methane	0.0200	0.0238	0.0306
Ethane	0.0043	0.0053	0.0073
Ethene	0.0264	0.0343	0.0379
Propane	0.1768	0.1998	0.2239
Propene	0.4205	0.5740	0.6402
C_4-Paraffins	0.4762	0.5767	0.5969
C_4-Olefins	0.1096	0.1648	0.2164
C_5-Paraffins	0.0408	0.0433	0.0460
C_5-Olefins	0.0027	0.0047	0.0133
C_6-Paraffins	0.0415	0.0280	0.0180
C_6-Olefins	0.0398	0.0217	0.0080
C_7-Paraffins	0.2155	0.0971	0.0392
C_7-Olefins	0.0669	0.0424	0.0382
Coke	0.0150	0.0123	0.0053
Total	1.6810	1.8555	1.9612

[a] Initial molar selectivities were calculated from initial weight selectivities in Table 1 using the relationship: molar selectivity = weight selectivity * (molecular wt of feed/molecular wt of product).

C_8-olefins and C_7–C_{10} aromatics. Aromatization led mainly to the formation of toluene, dimethylbenzenes, trimethylbenzenes, ethyldimethylbenzenes, and tetramethylbenzenes as shown in Fig. 4. The aromatics were detected only at conversions higher than 5%, and their yield increased sharply with increasing conversion. We take this to indicate that such products arise mainly, or even solely, from the secondary reactions of product olefins with carbenium ions. They are probably also related to the majority of the coke formed at long time on stream and at high conversions.

Reaction Mechanism

The formation of initial hydrogen and both the initial C_1–C_7 paraffins and olefins can be explained as follows: the initiation process involves the protonation of 2-methylhexane on a Brønsted site to form a $C_7H_{17}^+$ carbonium ion (7). This carbonium ion decomposes to form either hydrogen and a 2-methylhexyl carbenium ion ($C_7H_{15}^+$) or a small paraffin ($C_{7-n}H_{2(7-n)+2}$) and a small carbenium ion ($C_nH_{2n+1}^+$) which replaces the proton on the Brønsted base. The above general picture can be made more specific by writing the following initiation processes:

$$C_7H_{16} + H^+B^- \longrightarrow C_7H_{17}^+B^-$$

$$\xrightarrow{X_{00}} H_2 + C_7H_{15}^+B^- \qquad [1]$$

$$\xrightarrow{X_{01}} CH_4 + C_6H_{13}^+B^- \qquad [2]$$

$$\xrightarrow{X_{02}} C_2H_6 + C_5H_{11}^+B^- \qquad [3]$$

$$\xrightarrow{X_{03}} C_3H_8 + C_4H_9^+B^- \qquad [4]$$

$$\xrightarrow{X_{04}} C_4H_{10} + C_3H_7^+B^- \qquad [5]$$

$$\xrightarrow{X_{05}} C_5H_{12} + C_2H_5^+B^-. \qquad [6]$$

Depending on the probabilities of various events, the carbenium ion in Eqs. [1]–[6] can either desorb as an olefin or participate in bimolecular chain reactions. The second option represents the following general bimolecular disproportionation reaction between a carbenium ion and a gas phase 2-methylhexane molecule,

$$C_7H_{16} + C_nH_{2n+1}^+B^- \xrightarrow{X_{nj}} C_mH_{2m+2} + C_kH_{2k+1}^+B^- \quad (n \neq m), \qquad [6a]$$

where $2 \leq n \leq 7$, $2 \leq m \leq 7$, and $2 \leq k \leq 7$. A detailed set of disproportionation reactions possible in this case is presented in Table 4.

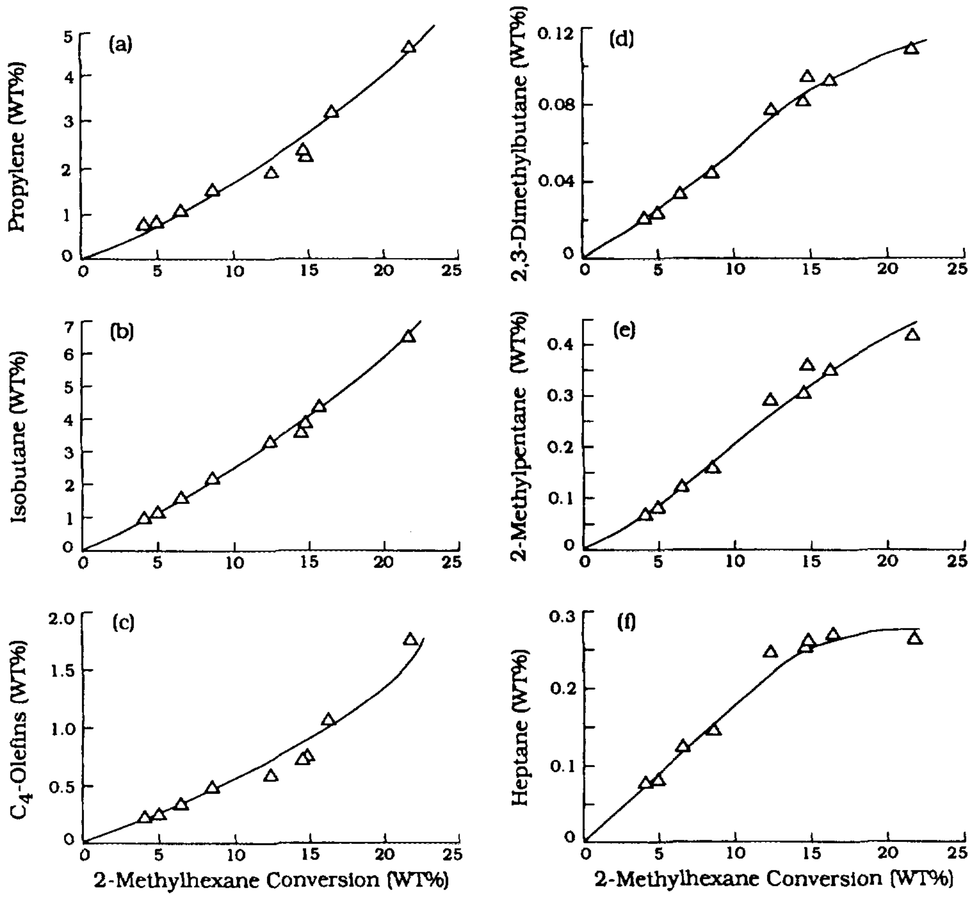

FIG. 1. Optimum performance envelopes for products of reaction of 2-methylhexane on USHY at 400°C. (a) Propylene; (b) isobutane; (c) C_4-olefins; (d) 2,3-dimethylbutane; (e) 2-methylpentane; (f) heptane.

The chain reaction steps may also involve "chain transfer" processes which involve the rearrangement of adsorbed carbenium ions before disproportionation or desorption occurs. When such rearrangement is followed by a hydride transfer from 2-methylhexane to the rearranged carbenium ion, isomeric paraffins are produced according to the general equation:

$$C_7H_{16} + i - C_nH^+_{2n+1}B^- \xrightarrow{X_{nj}} i - C_nH_{2n+2} + C_7H^+_{15}B^-. \quad [6b]$$

Such hydride transfers to 2-methylhexyl ions which have undergone a number of methyl shifts while residing on the surface lead to the formation of a variety of C_7 isomers.

The termination step involves the desorption of a carbenium ion as an olefin, before or after β-scission as shown in Eqs. [24]–[26] in Table 4. One more reaction remains to be taken into account: the formation of coke, which can be written as in Eq. [23] in Table 4.

Determination of the reaction pathway probabilities can now be made using the reactions listed in Table 4 and the molar selectivities of the initial products from Table 3. For each initial product, the total molar selectivity $\mathcal{F}_i$ can be expressed as a linear combination of the appropriate reaction pathway probabilities which lead to its formation. The resulting equations can be written in matrix form as

$$\mathbf{F} = \mathbf{A} \cdot \mathbf{X}, \quad [7]$$

where

$$\mathbf{F} = [\mathcal{F}_{H_2}, \mathcal{F}_{P_1}, \mathcal{F}_{P_2}, \mathcal{F}_{P_3}, \mathcal{F}_{P_4}, \mathcal{F}_{P_5}, \mathcal{F}_{P_6}, \mathcal{F}_{P_{7SI}} \; \mathcal{F}_{O_2}, \mathcal{F}_{O_3}, \mathcal{F}_{O_4}, \mathcal{F}_{O_5}, \mathcal{F}_{O_6}, \mathcal{F}_{O_7}, \mathcal{F}_{\text{coke}}]^T \quad [8]$$

$$\mathbf{X} = [X_{00} \; . \; . \; . \; X_{b74}]^T, \quad [9]$$

$\mathcal{F}_{P_i}$, $\mathcal{F}_{P_{7SI}}$ are the molar selectivities of ith product paraffin and 2-methylhexane isomers, respectively, $\mathcal{F}_{O_i}$, $\mathcal{F}_{H_2}$, $\mathcal{F}_{\text{coke}}$ are the molar selectivities of ith product olefin, hydrogen, and coke, respectively, and **A** is a 15 × 26 matrix of stoichiometric coefficients taken from Eqs. [1]–[26]. In this particular reaction we see that we lack eleven linear equations in order to arrive at a unique solution for the values of the RPPs. To deal with this difficulty and solve for the RPPs we have used the program GAMS (General Algebraic Modelling System). This linear-equation solver allows us to introduce nonlinear equations such as $X_{20}/X_{21} = X_{30}/X_{31} = X_{40}/X_{41}$. Such ratios are used to affirm that analogous reactions will exhibit similar ratios of probabilities when they take place on carbenium ions of

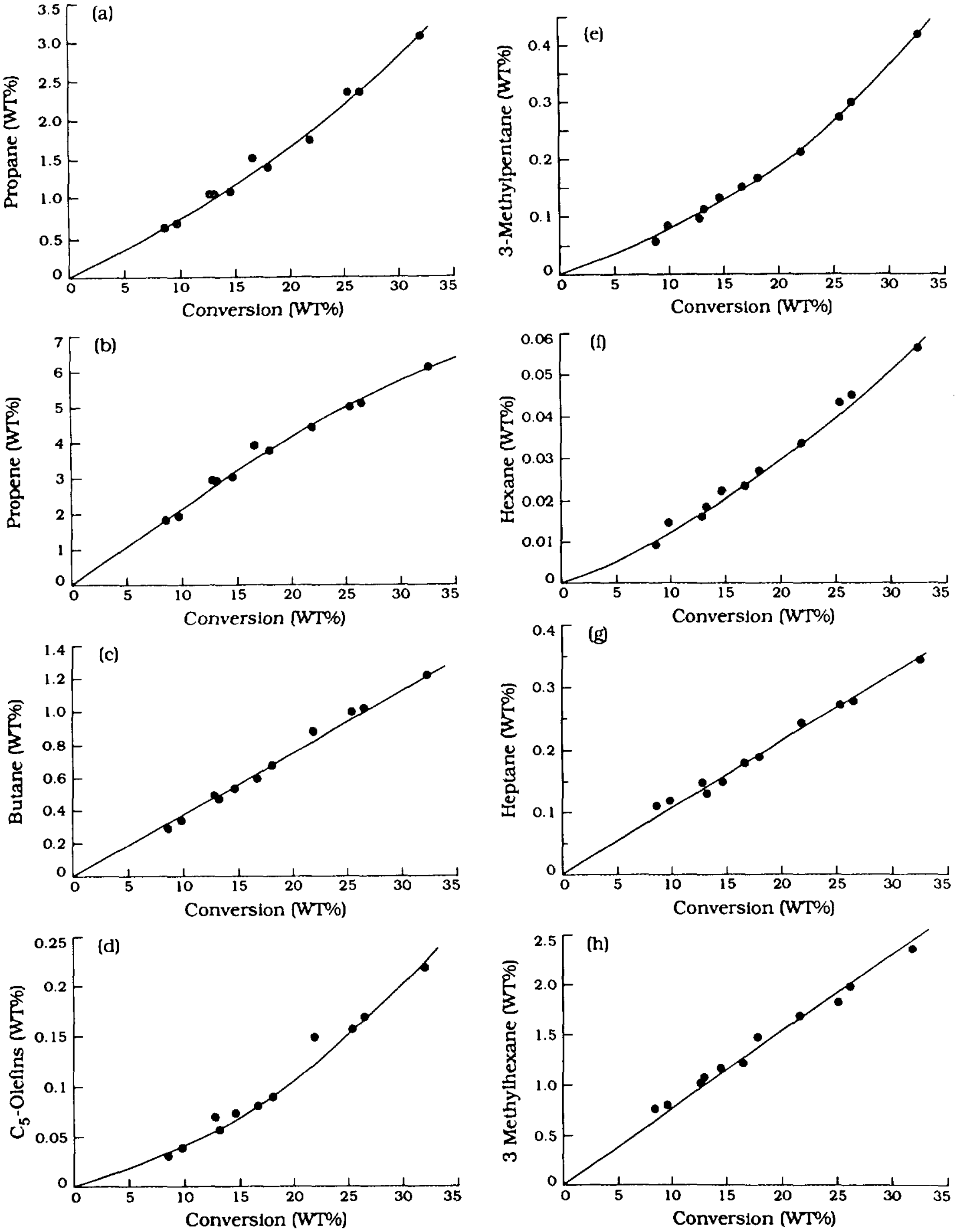

FIG. 2. Optimum performance envelopes for products of reaction of 2-methylhexane on USHY at 450°C. (a) Propane; (b) propene; (c) butane; (d) C_5-olefins; (e) 3-methylpentane; (f) hexane; (g) heptane; (h) 3-methylhexane.

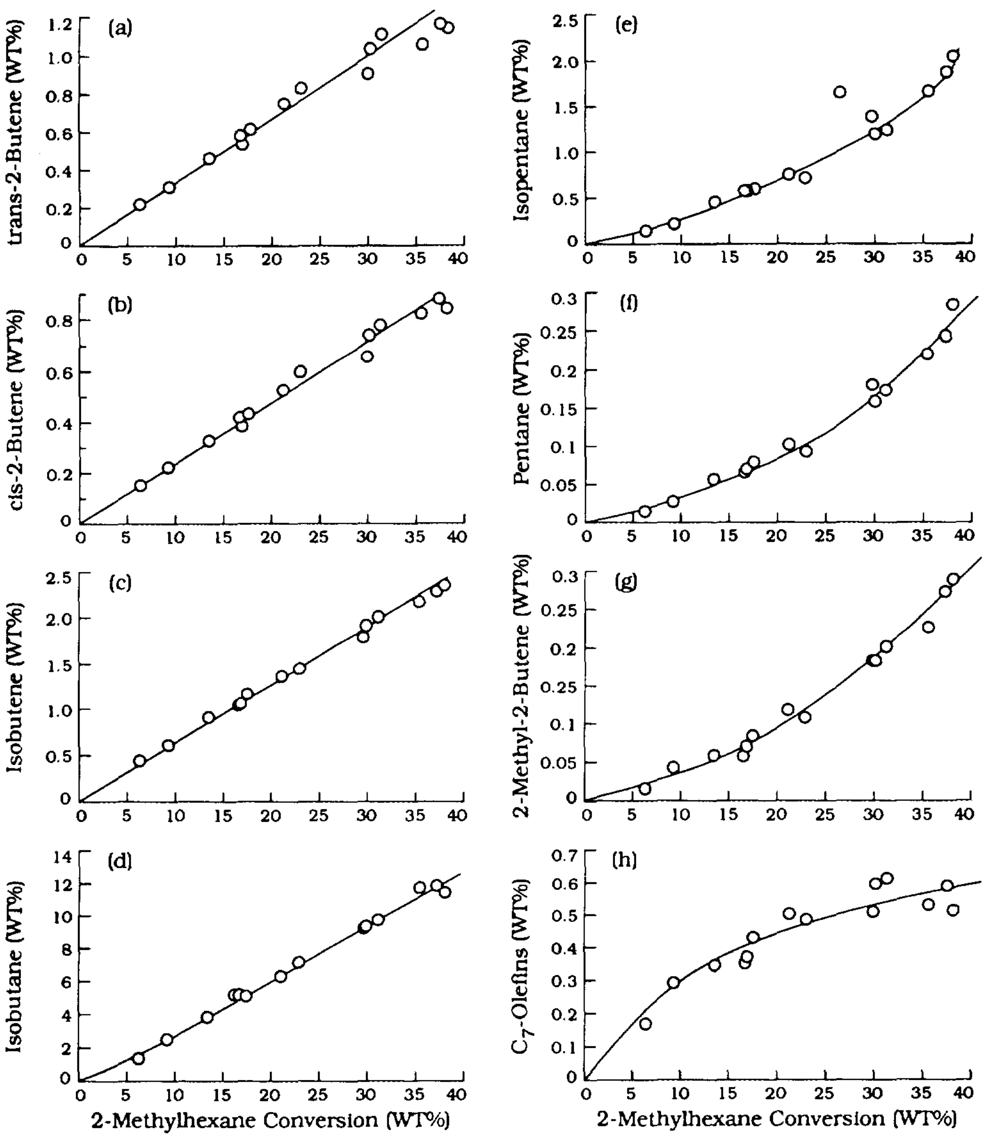

FIG. 3. Optimum performance envelopes for products of reaction of 2-methylhexane on USHY at 500°C. (a) *trans*-2-butene; (b) *cis*-2-butene; (c) isobutene; (d) isobutane; (e) isopentane; (f) pentane; (g) 2-methyl-2-butene; (h) C_7-olefins.

various lengths. Time will tell if this supposition is correct.

Using these additional equations and following the established procedure (4, 11) we have solved for the reaction pathway probabilities (RPPs or X_{nj}) in terms of molar selectivities $\mathcal{F}_i$ of the initial products. The reaction pathway probabilities for cracking reactions of 2-methylhexane calculated in this way are presented in Table 5.

DISCUSSION

Protolytic Cracking

Consideration of the results in Table 5 reveals that cracking of 2-methylhexane proceeds predominantly via monomolecular reactions which grow rapidly in importance with increasing temperature. Protolysis on pristine sites accounts for about 67% of the total 2-methylhexane conversion at 400°C and about 94% at 500°C. The dominant protolytic process is fragmentation of the $C_7H_{17}^+$ carbonium ion to produce C_4-paraffins and propyl ions (process 5); this process accounts for 71% of all protolysis at 400°C. The formation of propane and butyl ions (process 4), which breaks the same bond as process 5, accounts for a further 18% of initiation at the same temperature. Altogether, the protolysis of the γ or δ bond accounts for some 90% of all initiation at 400°C. The protolysis of the β bond, producing pentane and ethyl ions (process 6), follows at 5%, while the complementary reaction produc-

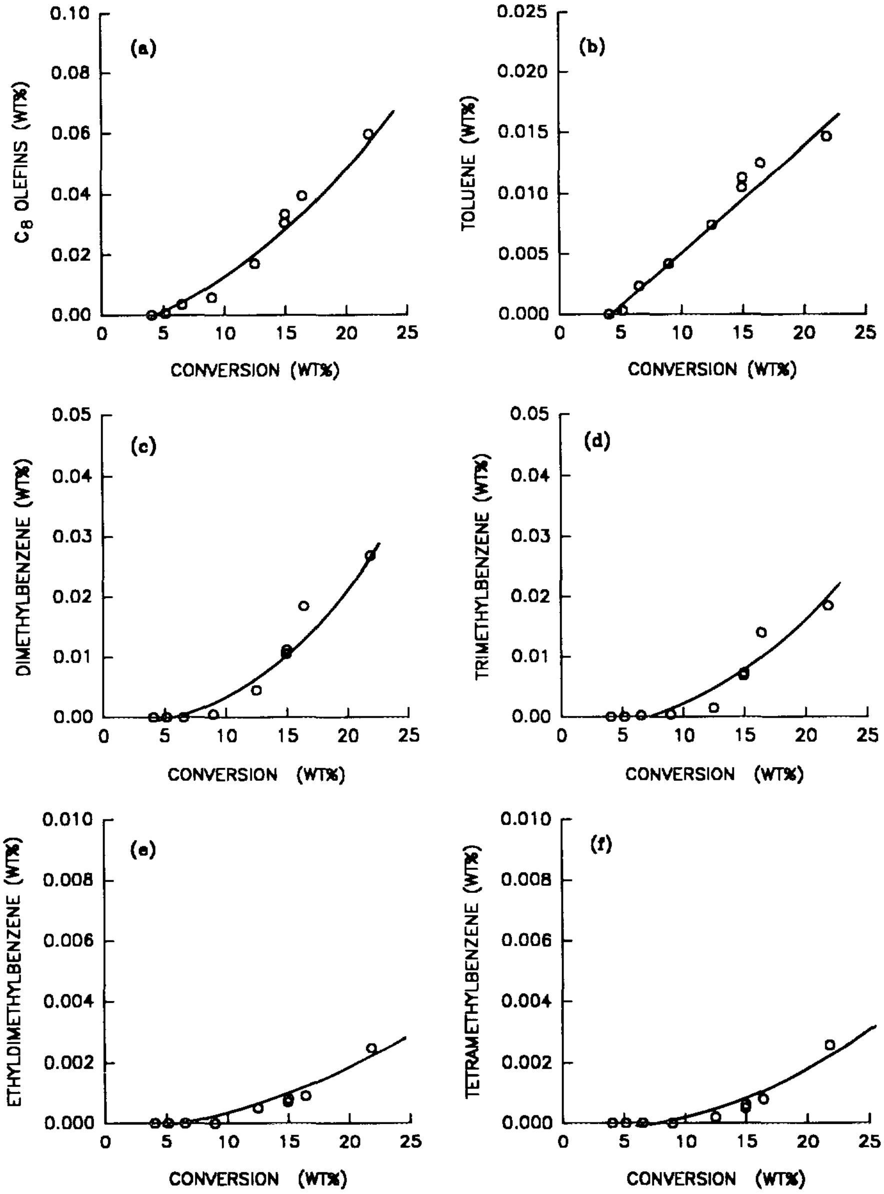

FIG. 4. Optimum performance envelopes for secondary products of reaction of 2-methylhexane on USHY at 400°C. (a) C_8-olefins; (b) toluene; (c) dimethylbenzenes; (d) trimethylbenzenes; (e) ethyldimethylbenzenes; (f) tetramethylbenezenes.

ing ethane contributes less than 1% of the probability of protolysis at 400°C. Other primary protolytic processes involve the formation of methane and $C_6H_{13}^+$ ions (3%) and of H_2 with $C_7H_{15}^+$ ions (1.5%). Note that the probability of protolysis of a $C_7H_{17}^+$ ion to produce a C_5-paraffin and an ethyl ion (process 6) is an order of magnitude higher than that for the production of a C_5 ion and ethane (process 3), at all three temperatures. Similar protolytic cracking behaviour was observed in 2-methylpentane reactions over USHY in the temperature range 400–500°C (4), *n*-heptane cracking over USHY in the 430–470°C range (6) and isobutane reactions on HY at 430°C (12). Why the smaller fragment forms the ion in preference to the larger ion is not clear. The same effect is also seen in the split at the γ or δ bond where the smaller C3 ion is favoured by a factor of 4; this is despite the fact that the C4 fragment could form an iso-C4 ion which should be more stable than the linear C3 ion, which, as we see, is in fact preferred.

This general picture persists all the way up to 500°C, as it does in 2-methylpentane (4). As with that molecule, there is evidence that the X_{03} process and the X_{01} process

TABLE 4

Initial Disproportionation and Hydride Transfer Reactions in the Cracking of 2-Methylhexane at 400–500°C

$C_7H_{16} + C_2H_5^+B^- \xrightarrow{X_{20}} C_2H_6 + C_7H_{15}^+B$ [7]
$\xrightarrow{X_{21}} C_3H_8 + C_6H_{13}^+B$ [8]
$\xrightarrow{X_{22}} C_4H_{10} + C_5H_{11}^+B$ [9]
$\xrightarrow{X_{23}} C_5H_{12} + C_4H_9^+B$ [10]
$\xrightarrow{X_{24}} C_6H_{14} + C_3H_7^+B$ [11]

$C_7H_{16} + C_3H_7^+B \xrightarrow{X_{30}} C_3H_8 + C_7H_{15}^+B$ [12]
$\xrightarrow{X_{31}} C_4H_{10} + C_6H_{13}^+B$ [13]
$\xrightarrow{X_{32}} C_5H_{12} + C_5H_{11}^+B$ [14]
$\xrightarrow{X_{33}} C_6H_{14} + C_4H_9^+B$ [15]

$C_7H_{16} + C_4H_9^+B \xrightarrow{X_{40}} C_4H_{10} + C_7H_{15}^+B$ [16]
$\xrightarrow{X_{41}} C_5H_{12} + C_6H_{13}^+B$ [17]
$\xrightarrow{X_{42}} C_6H_{14} + C_5H_{11}^+B$ [18]

$C_7H_{16} + C_5H_{11}^+B \xrightarrow{X_{50}} C_5H_{12} + C_7H_{15}^+B$ [19]
$\xrightarrow{X_{51}} C_6H_{14} + C_6H_{13}^+B$ [20]

$C_7H_{16} + C_6H_{13}^+B^- \xrightarrow{X_{60}} C_6H_{14} + C_7H_{15}^+B$ [21]
$C_7H_{16} + \text{iso} - C_7H_{15}^+B \xrightarrow{X_{70}} \text{iso} - C_7H_{16} + C_7H_{15}^+B$ [22]

$C_7H_{16} \xrightarrow{X_{Kc}} \text{coke}$ [23]

$C_6H_{13}^+B \xrightarrow{X_{b63}} C_3H_6 + C_3H_7^+B$ [24]

$C_7H_{15}^+B \xrightarrow{X_{b73}} C_3H_6 + C_4H_9^+B^-$ [25]
$\xrightarrow{X_{b74}} C_4H_8 + C_3H_7^+B^-$ [26]

have the highest activation energies. Whether the X_{03} event occurs primarily at the bond next to the tertiary carbon or at the central bond, it seems that the β bond, when it is protolyzed by the X_{05} process, requires less activation energy for protolysis. This may at first be surprising but the two β-cracking processes require the formation of two different carbenium ions. The 02 process leaves behind a C_5^+ ion, while the 05 process leaves behind a C_2^+ ion. It is the process leaving behind the smaller ion that requires the lower activation energy. The values in Table 7 do not therefore represent conventional bond breaking energies but also energies to go from a proton to some other counterion on the surface.

TABLE 5

Reaction Pathway Probabilities for the Reaction of 2-Methylhexane over USHY at Various Temperatures

Process no.	RPP	Reaction pathway probability[a] 400°C	450°C	500°C
1	X_{00}	0.0100 (1.5%)	0.0160 (1.9%)	0.0320 (3.4%)
2	X_{01}	0.0200 (3.0%)	0.0270 (3.2%)	0.0310 (3.3%)
3	X_{02}	0.0040 (0.5%)	0.0050 (0.5%)	0.0070 (0.7%)
4	X_{03}	0.1210 (18%)	0.1590 (19%)	0.2220 (24%)
5	X_{04}	0.4770 (72%)	0.5770 (70%)	0.5970 (64%)
6	X_{05}	0.0340 (5.0%)	0.0430 (5.2%)	0.0460 (5.0%)
Total	Initiation	0.6660	0.8270	0.9350
7	X_{23}	0.0070	—	—
8	X_{24}	—	0.0090	0.0080
9	X_{30}	0.0550	0.0410	0.0020
10	X_{32}	—	—	0.0001
11	X_{33}	0.0003	—	—
12	X_{42}	0.0190	0.0090	0.0060
13	X_{51}	0.0210	0.0090	—
14	X_{60}	0.0010	0.0007	0.0040
15	X_{70}	0.2150	0.0970	0.0390
Total	Propagation	0.3183	0.1654	0.0591
16	X_{Kc}	0.0150	0.0123	0.0053
17	X_{b63}	—	0.0140	0.0180

[a] Reaction pathway probabilities not listed here are equal to zero.

Disproportionation

As reported previously (13), the kinetic treatment of the 2-methylhexane conversion data has shown that cracking of 2-methylhexane takes place not only via monomolecular reactions but also via bimolecular processes. This is confirmed by the data obtained from mechanistic considerations presented in Table 5. Processes 7 to 15 in Table 5 present a set of RPPs representing disproportionation reactions between carbenium ions on the catalyst surface and gas phase 2-methylhexane molecules. This set of probabilities shows that the overall probability of disproportionation between a feed molecule and $C_4H_9^+$ or $C_5H_{11}^+$ ion decreases with temperature. We interpret this as being the result of two factors which reinforce each other. First, there is the tendency of surface populations of carbenium ions to decrease with increased temperature. We have noted this factor before, in discussing 2-methylpentane cracking (4). Second, the transition state between the surface ion and the gas phase molecule is likely to have a shortened lifetime and hence a reduced chance of surviving until a fruitful rearrangement has taken place.

In addition to disproportionation reactions, chain reactions consist of processes involving hydride transfer. Three hydride transfer reactions were found to be active:

(1) significant hydride abstraction by $C_3H_7^+$ ions from the feed molecules to form propane and C_7H_{15} ions;

(2) a very minor contribution by hydride abstraction by the $C_6H_{13}^+$ ions to form C6 isomers and C_7H_{15} ions;

(3) a major contribution from hydride abstraction by $C_7H_{15}^+$ ions to form skeletal isomers of 2-methylhexane and the parent 2-methylhexyl ion.

The C_4 and C_5 ions do not abstract hydride ions to any significant extent, even though they do disproportionate with the feed.

The major contribution to conversion by the hydride abstractions due to parent ions seems to be characteristic of all systems studied to date (4, 19, 24). No doubt it is due to the dominance of parent carbenium ions on the surface. At low temperatures it leads to a significant yield of isomers of the parent molecule. As the temperature rises, and transition state stability and surface populations decline, this reaction diminishes in importance. It is also of lesser importance in molecules which do not show a significant participation of chain processes even at low temperatures (20, 21). Here we see that the reaction pathway probabilities for feed isomerization (process 15) decreased rapidly with increasing temperature. They account for about 22% of conversion at 400°C and only about 4% at 500°C. This fall in probabilities with temperature parallels a substantial increase in the conversion of 2-methylhexane via monomolecular processes, a fact generally observed, for instance in 2-methylpentane (4) and *n*-heptane (6) cracking.

It is not clear why some disproportionation reactions are prominent while other seemingly similar processes are not. It may be due in part to stearic effects involving the "constraint" of the pores, which probably cause a general reduction in bimolecular reactions in HZSM-5 (22, 23). In the case of USHY, however, this is probably not the dominant reason and we must look for other explanations. One that comes to mind is the difference in the configuration of the transition state during the disproportionations; another is the stability of the product molecules. The latter may explain why larger molecules do not disproportionate with their parent ions to form even larger products; the parent carbenium ions will accept a hydride and thus form isomers but do not accept moieties containing carbon atoms. This situation is more likely in reactants of C_5 or less (23).

The other configurational properties of the transition state which may inhibit certain reactions will involve both physical constraints due to accessability and electronic constraints due to the distribution of charge in the various transition states. While it is probably too early to speculate about the details of these matters, we hope these observations may inspire work by researchers interested in theoretical calculations of charge distribution.

β-Cracking

One more process appears in the cracking of 2-methylhexane: *β*-cracking of carbenium ions. Until recently, this classical cracking reaction was used to account for all product distribution phenomena in catalytic cracking. Now we see that it is a minor process in molecules C_6 (4, 19, 24) and here in a C_7 at low temperature. In the cracking of *n*-nonane it becomes noticeable; however, even here it is not the dominant process vis-à-vis protolysis. It seems that this reaction is slow under conditions where chain processes are prominent. We expect that *β*-cracking will be significant only in the cracking of C_7 or larger olefins. This realization represents a major change in our understanding of the processes involved in catalytic cracking.

Coke Formation

Finally, the probability of coke formation was found to decrease with temperature, as has been frequently observed elsewhere (4). Again, the reason is probably connected with the decreased residence times of carbenium ions, which result in a diminished surface coverage. Since we believe that coke formation is due to reactions between adjacent ions, this fits with the previously proposed picture of surface coverage.

Formation of Aromatics

Associated with the process of coke formation is the formation of secondary products, notably the aromatics. These seem to be formed either from adjacent carbenium ions or from the addition of product olefins to carbenium ions. In either case, the process involves cyclization with elimination of small paraffins. The species remaining on the surface is dehydrogenated and thus "sticky," in that the resonances available make it reluctant to desorb. When such ions do desorb, they produce some detectable diolefins and aromatics in great variety (25, 26). Those ions that linger too long on the surface continue to lose hydrogen by a variety of processes and end up as coke, a nondesorbable residue.

Temperature Effects

To extract the apparent activation energies for the individual protolysis reactions, individual reaction rates (IRRs) for 2-methylhexane were calculated by multiply-

TABLE 6

Individual Reaction Rates for 2-Methylhexane Cracking over USHY at Various Temperatures

IRR	Reaction Rate (min^{-1})^{a} 400°C	450°C	500°C
r_{00}	0.056	0.568	4.736
r_{01}	0.111	0.959	4.588
r_{02}	0.022	0.178	1.036
r_{03}	0.668	5.645	32.856
r_{04}	2.662	20.484	88.356
r_{05}	0.189	1.527	6.808
r_{23}	0.039	—	—
r_{24}	—	0.320	1.184
r_{30}	0.312	1.456	0.296
r_{32}	—	—	0.015
r_{33}	0.006	—	—
r_{42}	0.106	0.320	0.888
r_{51}	0.117	0.320	—
r_{60}	0.001	0.004	0.592
r_{70}	1.198	3.444	5.772
r_{kc}	0.084	0.437	0.784
$\Sigma_j r_j^{b}$	5.571	35.662	147.911

[a] Determined by multiplying the RPPs in Table 5 by the total reaction rate, $\Sigma_j r_j$.

[b] Determined from the kinetic parameters for 2-methylhexane conversion (13).

ing the RPPs listed in Table 5 by the total initial rate of reaction calculated using previously described methods (4). These IRRs are listed in Table 6. The activation energies of all protolytic reactions were then calculated from linear regression of the Arrhenius plots and are presented in Table 7. We find that the average value for the activation energy of protolysis in 2-methylhexane is ~160 kJ/mol. Table 7 shows, however, that values for the activation energies of the individual protolytic processes vary around the average, over a range of plus or minus 15% in 2-methylhexane and as much as 25% in 2-methylpentane, whose average activation energy of protolysis is 246 kJ/mol on the same USHY.

TABLE 7

Activation Energies for Protolytic Reactions in the Crackings of 2-Methylpentane (A) and 2-Methylhexane (B) over USHY

Reaction	Activation energy (kJ/mol) (A)	Activation energy (kJ/mol) (B)
r_{00}	330.8	184.7
r_{01}	213.2	154.6
r_{02}	230.2	159.6
r_{03}	240.7	161.9
r_{04}	213.4	145.6
r_{05}	—	148.9
Average	246	159

It seems, therefore, that the length of the carbon chain in a feed paraffin has an unexpectedly large influence on the activation energy of protolysis. This kind of difference applies one-by-one to all the protolysis processes in the two molecules. Since there is no reason to expect the molecular bond strengths to be so different in two such molecules, we are left without an obvious explanation for this phenomenon. We point out, however, that a similar result was observed in an earlier investigation of normal paraffin cracking (14) and is echoed in the frequently reported increase in reaction rate with increasing chain length (20, 27, 28).

We begin the discussion of this matter with a reminder that the rate constants derived by our treatment of the results contain an active-site concentration term, and have the structure

$$k_0 = Ae^{-\Delta E/RT}[S_0], \qquad [10]$$

where A is frequency factor and $[S_0]$ is the initial active site concentration.

The activation energies calculated from the slopes of Arrhenius plots of ln k_0 vs $1/T$ include the effect of temperature on the concentration of the sites active for this reaction (15). It may well be that a molecule which requires a slightly different energy for bond breaking gains significant rate enhancement from a large increase in the number of acid sites capable of providing the necessary protolytic strength. If the site concentration is not influenced by temperature, the site concentration term is incorporated in the frequency factor and has no effect on the activation energy. If, on the other hand, we imagine the number of active sites to be temperature dependent, we will see an overall activation energy which contains a term accounting for the temperature coefficient of the change in active site concentration.

We can assume, with some theoretical justification, that as reaction temperature is increased the number of sites capable of protolysis also increases, in a fashion which mimics the exponential effect of temperature on the rate constant. The sum of the exponential temperature terms belonging to the rate constant and that accounting for the increase in concentration of protolytic sites will then yield an "experimental" activation energy which contains the sum of these two activation energies. We now must consider whether the "activation energy" of the site concentration term is positive and greater for 2-methylpentane or is negative and smaller for 2-methylpentane. A negative "activation-energy-like" exponent (i.e., a positive activation energy) for the site concentration implies that the number of sites capable of protolysis will increase with temperature; this seems intuitively correct. By this reasoning we are brought to the conclusion that the number of sites capable of protolyzing 2-methylpentane increases more rapidly with temperature than those capable of protolyzing 2-methylhexane.

Such an argument means that the ranges of site energies for 2-methylpentane protolysis and for 2-methylhexane protolysis are bounded by upper and lower limits. It is hard to imagine how a range stretching from a molecule-specific lower limit to infinity for each of the molecules would show this kind of behaviour if a single site-energy distribution contains sites appropriate for all protolysis reactions. Such limited ranges of site energy, each appropriate to a specific reaction, have in fact previously been suggested, for similar reasons, in the cracking of cumene (16, 17).

There is also the possibility that a "compensation effect" plays a major role in this series of homologous paraffinic reactants. In this case the argument is as follows. One can write any rate constant in terms of the energy of activation, ΔE, and the entropy of activation, ΔS^*:

$$k_0' = e^{\Delta S^*/R} e^{-\Delta E/RT} [S_0] = e^{\Delta G^*/RT}. \qquad [11]$$

The compensation effect occurs when changes in activation energy are accompanied by parallel changes in the entropy of activation. The increases (or decreases) in both at the same time minimize changes in the Gibbs free energy of activation ΔG^*, so that changes in the observed rate constant are minimized. This phenomenon can be rationalized as being due to the fact that, in a series of similar molecules, a transition state which has more (activation) energy will at the same time be more excited vibrationally and hence have a higher (activation) entropy.

The net effect of this compensation is a tendency for the Arrhenius plots of the rate constants involved to cross at the "isokinetic" temperature (29). Figure 5 shows Arrhenius plots for the protolysis of 2-methylpentane, 2-methylhexane, and *n*-nonane cracking on HY at 400–500°C. The isokinetic temperature seems to lie in the temperature range 415–435°C. It may also be that the site concentration effect and the compensation effect are both present and reinforce each other to produce the observed influence of temperature on protolytic cracking.

A recent paper by Corma *et al.* (30) proposes that a compensation effect may be operating in a given molecule when catalyst formulation is changed. In their considerations these authors invoke linear free energy relationships. We feel that any such linear free energy relationships may be complicated in our work by the effect of temperature on the number of available sites. We are therefore prepared to see the compensation effect as a more diffuse phenomenon, leading not to a unique "isokinetic temperature" but to an "isokinetic region" of temperatures where various molecules show similar rates of reaction.

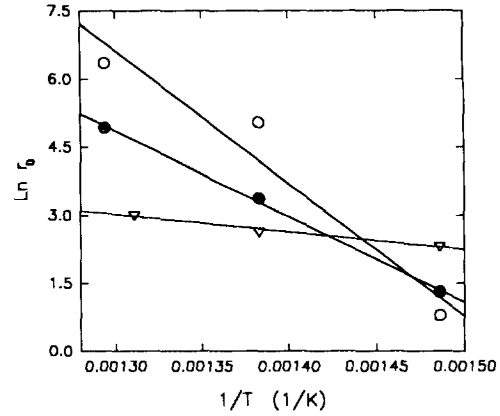

FIG. 5. Arrhenius plots for the protolysis of 2-methylpentane (○), 2-methylhexane (●), and *n*-nonane (▽) cracking on USHY at 400–500°C.

It is interesting to speculate that, if this is so, highly selective cracking of certain components will be possible by making an appropriate choice of reaction temperature.

CONCLUSIONS

Our results show that the conversion of 2-methylhexane proceeds via two main processes:

(1) initiation through protolysis on pristine sites;

(2) chain processes involving isomerization, hydrogen transfer, and disproportionation.

At 400°C, conversion of 2-methylhexane was found to take place via both mechanisms in the ratio of 2 : 1 for protolysis-to-chain conversion, while at higher temperatures conversion proceeds predominantly via protolytic cracking.

We have also explained the production of C_6-paraffins and product skeletal isomers of 2-methylhexane as being the result of hydride-transfer chain reactions between $C_6H_{13}^+$ and $C_7H_{15}^+$ carbenium ions and gas phase feed molecules.

Comparison of the details of the cracking process in 2-methylhexane and 2-methylpentane in Table 7 has revealed large and unexpected differences in the activation energies for the protolysis of the two molecules. We believe that the reason for these differences may be that molecules with relatively minor differences in their requirements for protolytic site strength show unusual activation energies, due to a temperature-induced change in the number of sites available at various acid strengths; or, alternatively, a compensation effect is present in the cracking of paraffins. These two effects may combine to give the observed differences in activation energy reported here. They could also explain the well-documented rapid increase in "crackability" with increasing chain length.

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