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The Reactions of Hexyl Ions on USHY

B. W. Wojciechowski[1] and Y-X. Zhao

Chemical Engineering Department, Queen's University, Kingston, Ontario, Canada

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We have examined the behavior of C_6 carbenium ions in the cracking of 2-methylpentane on USHY. We find that at 400°C, hexyl carbenium ions undergo hydride addition from the feed 10 times faster than proton release to the Brønsted base. This makes the isomerization of the feed a much faster reaction than the production of olefins with the same carbon number. We also find that proton release from a C_6 ion to the Brønsted base requires a higher activation energy than a hydride transfer from the feed to the same ion. At high temperatures isomerization is therefore reduced with respect to olefin production. The presence of steam in the cracking mixture *weakens* the Brønsted bases, and reduces the rates of all reactions but encourages hydride transfer over proton release. This enhances the formation of paraffinic isomers of the feed. At the low steam dilution ratio of 0.07 mol/mol, hydride transfer in 2-methylpentane is as much as 18 times faster than proton release, resulting in a highly isomerized, highly saturated product. The full picture of individual ion fates is presented and gives an important insight into the causes underlying cracking selectivity and the possible methods for its control.

INTRODUCTION

In a series of recent papers we have proposed a quantitative mechanism of paraffin cracking on acid catalysts. The mechanism consists of:

—initiation by protolysis;

—chain propagation by disproportionation of feed molecules with surface-resident carbenium ions; and

—termination by the desorption of olefins (1, 2).

Our approach interprets the measured initial selectivities, obtained from optimum performance envelopes (3, 4), by translating these measurements into reaction path probabilities (RPPs) (2, 5) via a set of equations describing the individual steps in the reaction mechanism being considered (2). The RPP of an elementary reaction path is defined as the fraction of the total rate of conversion of the feed (2) proceeding by this path. For example, for a monomolecular reaction path (0*i*), its RPP is

$$X_{0i} = \frac{r_{0i}}{r_{\text{tot}}} = \frac{r_{0i}}{\sum r_{0i} + \sum r_{jR}},$$

while for a bimolecular reaction path (jR), its RPP is

$$X_{jR} = \frac{r_{jR}}{r_{\text{tot}}} = \frac{r_{jR}}{\sum r_{0i} + \sum r_{jR}},$$

where X is the symbol of the RPP; r is the symbol of the rate; 0*i* represents the mode of protolysis which gives the paraffinic product C_iH_{2i+2} and a carbenium ion; and jR represents the mode of bimolecular reaction involving a carbenium ion $C_jH_{2j+1}{}^+S^-$ and a feed molecule to produce a paraffin $C_{j+R}H_{2(j+R)+2}$ and a new carbenium ion.

Using this approach we have investigated the mechanism of paraffin cracking

—in a variety of molecules (2, 6–8);

—on various catalysts (10, 11); and

—in the presence of various diluents (12, 13).

We have also generalized our observations by unifying the cracking behavior of C_6 paraffin isomers (9) and by explaining how "hydrogen transfer" occurs in catalytic cracking (14).

Here we deepen our examination of the cracking process by concentrating on the formation of the isomers of the feed, and in particular on C_6 olefins and paraffins in 2-methylpentane cracking. In doing this we examine the fate of C_6 carbenium ions which are formed from the feed, isomerize on the surface, and desorb, either by a monomolecular release of a proton to the associated Brønsted base on the lattice, or by abstracting a hydride from the feed.

EXPERIMENTAL

The 2-methylpentane (99+%) was obtained from Aldrich. HY zeolite was prepared from NaY (BDH Chemicals) by exchanging 10 times with 0.5 *M* NH_4NO_3 solution at 20°C for 24 h, drying at 110°C for 24 h; then calcining at 500°C for 2 h after each exchange. The HY zeolite was

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[1] To whom correspondence should be addressed.

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then stabilized by steaming at 400°C for 24 h to produce USHY.

Before we proceeded with the main experimental program, two sets of preliminary runs were carried out: blank runs to determine the extent of thermal cracking and replicate runs to examine the stability of our USHY under our reaction conditions. The thermal reaction was found to be small and the catalyst, stable.

All experiments were performed in a fixed-bed plug-flow glass reactor. Our kinetic runs were done by pumping a set quantity of feed over the catalyst charge. After each run the catalyst was regenerated in air at 500°C. Each catalyst charge was exposed to five or six such runs, each run at a different pumping rate but with the total feed introduced kept constant. This produced runs with constant catalyst/oil ratio and various run durations (or times on stream). The whole procedure was repeated on a series of catalyst charges differing in the amount of catalyst placed in the reactor and then repeated at various temperatures to measure the activation energies.

For the conversion of 2-methylpentane with steam dilution the feed and distilled water, at the designated ratio, are simultaneously pumped into the reactor, fully vaporized, and mixed, before the mixed stream is allowed to contact the catalyst bed.

Products were identified by a Finigan 1020 GC/MS and analyzed by a Carle SX 1156 chromatograph (for gases) or by a Varian 6000 capillary chromatograph (for liquids).

FUNDAMENTALS

The quantitative nature of the chain mechanism of catalytic cracking both requires and explains certain features of the product distribution. The requirements are:

—that the molar selectivity of total paraffins produced in paraffin cracking must be one. *Slightly* higher paraffin selectivities will indicate substantial coke formation involving the elimination of paraffins from "precoke" molecules on the catalyst surface (14). *Substantially* higher initial paraffin selectivities should be viewed with suspicion.

—that in the absence of β-cracking of carbenium ions, the total molar selectivity for olefins is equal to the fraction of total conversion proceeding via the initiation process.

These requirements in turn lead to a more fundamental understanding of the elementary processes which take part in catalytic cracking and provide certain simple measures of some of the properties of the cracking reaction and of the validity of the experimental data.

A total olefin selectivity of one indicates, therefore, that every molecule cracked was converted by an initiation event. No chain propagating setps were present. It also indicates that the kinetic chain length, which is given by

$$CL = \frac{\text{total paraffin selectivity } (=1)}{\text{total olefin selectivity}}$$

will be one in such a case. As propagating reactions become more important, *CL* increases and total olefin selectivity decreases below one.

The "volume expansion" (15, 16) in cracking is then the sum of all paraffin plus all olefin selectivities minus one; it is one when *only* initiation is present; and it is less than one if chain processes are important and β-cracking is negligible. In cases where β-cracking fragments the feed molecule more than once, the volume expansion coefficient can be greater than one, as it is in gas oil cracking.

If β-cracking is important, the situation becomes more complicated. Some of the quick measures described above, such as *CL* and total olefin selectivity, do not reveal the true picture directly. Instead, reaction path probabilities (2) must be extracted from the set of equations describing the chain mechanism (2, 6) and then used to elucidate the details of the reaction. However, certain features of the reaction can still be described on the basis of molar selectivities alone: one such feature is the detailed description of the set of reactions which yield the paraffinic and olefinic isomers of the feed.

There is good reason to believe that most of the paraffinic isomers of the feed are formed by hydride transfer to "parent" carbenium ions; i.e., carbenium ions of the same carbon number as the feed. We will assume that this is so for most of the C_6 paraffins formed. In that case the formation of the C_6 olefin isomers represents alternative fates of the same parent carbenium ions if they shed a proton rather than abstract a hydride ion. The full set of possible interconversions of C_6 carbenium ions which lead to both olefinic and paraffinic C_6 products in C_6 cracking is shown in Fig. 1.

Figure 1 shows all 1–2 methyl and hydride shift processes involving C_6 isomers of carbenium ions. We will ignore the possibility of cyclopropyl ion intermediates forming on the linear portions of the chain since such a postulate is not necessary. If such intermediates are shown to occur on the surface of USHY, appropriate changes in the following interpretation will have to be made.

In Fig. 1 the "originating" hexyl ions (i.e., the "parent" carbenium ions formed from the feed *in the first instance*) are taken to be those formed by the loss of the most readily abstracted hydride and are shown in italics. These ions are formed either by the protolysis of the tertiary hydride in an initiating reaction or by the donation of this hydride to a carbenium ion in a propagating process (1, 2). Various feeds, such as *n*-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane will therefore form different "originating" hexyl ions, listed in Fig. 1 as 4 or 5, 2, 8, 11, and 14, respectively,

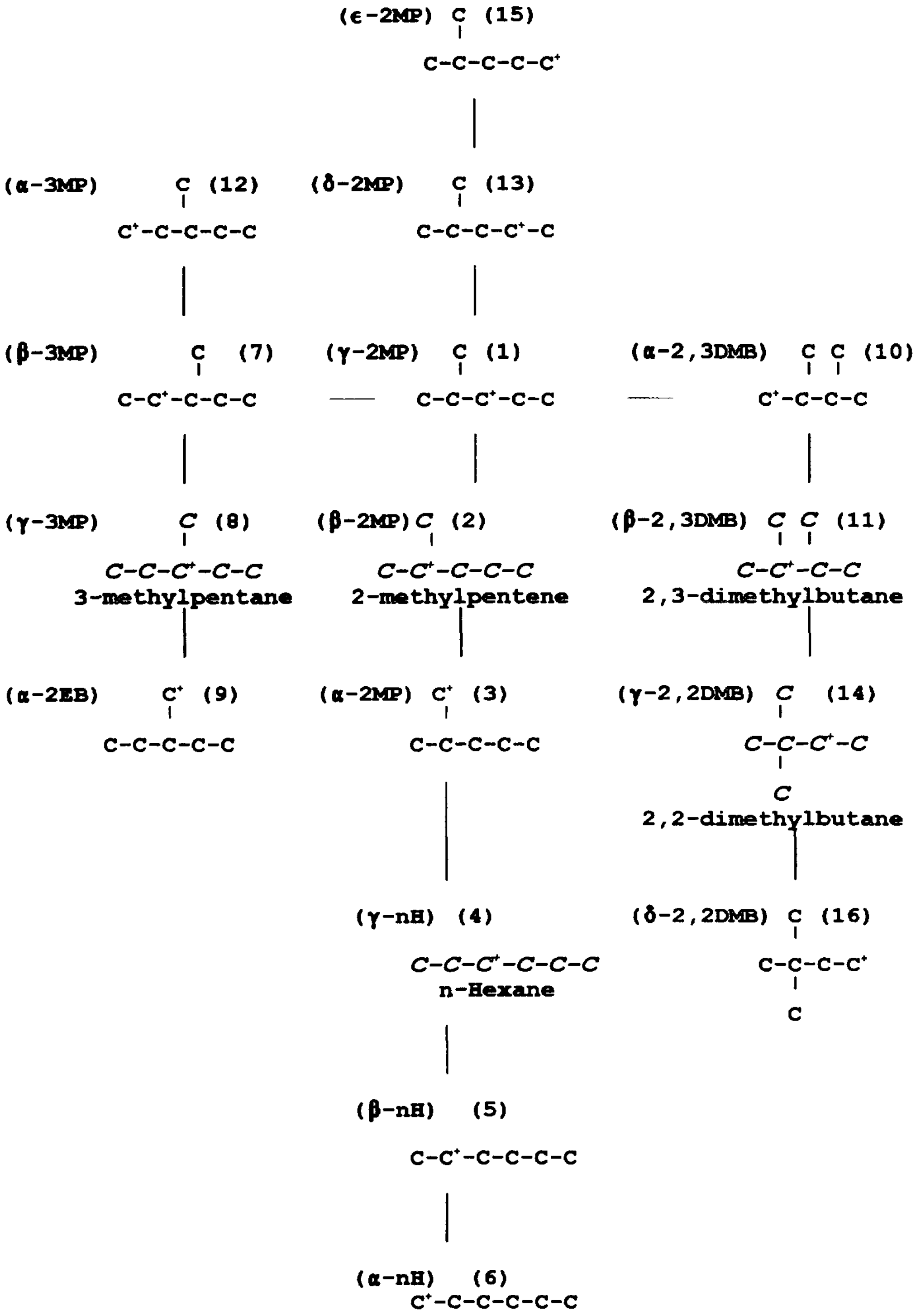


FIG. 1. Scheme of the intraionic rearrangements of hexyl ions on USHY.

TABLE 1

Initial Molar Selectivity of C_6 Olefin and Paraffin Isomers Produced in 2-Methylpentane, 3-Methylpentane, and 2,3-Dimethylbutane Cracking on USHY at 400°C

	Reactants		
	2MP	3MP	2,3DMB
1-Hexene	0.0000	0.0002	0.0000
t-2-Hexene	0.0042	0.0006	0.0015
c-2-Hexene	0.0016	0.0003	0.0007
t-3-Hexene	0.0015	0.0002	0.0004
c-3-Hexene	0.0023	0.0004	0.0012
2-Methyl-1-pentene	0.0056	0.0012	0.0023
2-Methyl-2-pentene	0.0127	0.0017	0.0060
t-4-Methyl-2-pentene	0.0000	0.0000	0.0000
c-4-Methyl-2-pentene	0.0000	0.0000	0.0000
4-Methyl-1-pentene	0.0000	0.0000	0.0000
3-Methyl-1-pentene	0.0000	0.0003	0.0011
t-3-Methyl-2-pentene	0.0077	0.0010	0.0069
c-3-Methyl-2-pentene	0.0077	0.0016	0.0054
2-Ethyl-1-butene	0.0000	0.0005	0.0022
2,3-Dimethyl-1-butene	0.0019	0.0003	0.0017
2,3-Dimethyl-2-butene	0.0046	0.0006	0.0037
3,3-Dimethyl-1-butene	0.0000	0.0000	0.0000
Total C_6 olefins	0.0499	0.0089	0.0331
2,2-Dimethylbutane	0.0000	0.0000	0.0038
2,3-Dimethylbutane	0.0853	0.0283	Feed
2-Methylpentane	Feed	0.2010	0.5360
3-Methylpentane	0.4150	Feed	0.2530
n-Hexane	0.0472	0.0278	0.0282
Total C_6 paraffins	0.5475	0.2571	0.8202

for each of the above-mentioned feed molecules. Isomerization can then proceed one step at a time along the paths indicated in Fig. 1. Since the originating ions are not the same in the various C_6 isomer feeds, it is reasonable to expect that the *steady state* populations of the ions shown in Fig. 1 will not be the same in the cracking of various isomers. This can cause the probability of alternative reactions of the various individual ions to differ from feed to feed, with the result that product selectivities can also vary as the configuration of the feed molecule is changed, as shown in Table 1. The fact that this is so convinces us that the surface ionic species are not in equilibrium.

Figure 2 illustrates the sequence of reaction steps in the cracking of 2MP, 3MP, and 2,3DMB. These contain the species required to explain the formation of all the olefinic products shown in Tables 1 and 2a–2c. Note that species 14, 15, and 16 do not seem to form in any significant amounts, as shown by the observed product distributions, and that species 12 and 13 do not need to be invoked for the formation of the observed products to be explained. In view of their unfavorable configuration it is likely that none of these species is normally present in significant concentration. Moreover, we note that some species, such as species 8, cannot β-crack, explaining, for example, why it is difficult to crack 3MP (6).

Using this general map of the reaction terrain, we can now concentrate on the reactions of C_6 ions which arise when 2MP is the feed.

PROCESS INVOLVING C_6 IONS IN 2-METHYLPENTANE CRACKING

The Originating 2MP Ion

It seems reasonable to assume that the protolytic initiation which generates hydrogen as a primary product (2) in 2MP cracking involves mostly, or even only, the tertiary hydrogen of the feed molecule. The principal originating ion left on the surface is therefore the tertiary or β-2MP ion (species 2 on Fig. 1).

Similarly, chain propagation processes of the type X_{i0} (2) most probably involve the transfer of the tertiary hydrogen of the 2MP molecule to neutralize a surface carbenium ion. Hydride transfers will therefore also result in the formation of β-2MP ions on the surface.

We believe that the formation of these tertiary ions is sufficiently dominant that, for the sake of further discussion, we need not consider the formation of any other *originating* C_6 ions.

We now trace the fate of the originating β-2MP ion in the case of 2MP cracking at 400°C. A subsequent X_{60} process (i.e., the transfer of a hydride ion from the feed to a C_6 carbenium ion on the surface), before skeletal isomerization of the originating ion has taken place, will produce a product with the same configuration as the feed; therefore, no *detectable* product will appear. We note at this point that the addition of deuterium-labeled 2MP to the fully hydrogenated reactant could throw some light on the details of this process, as well as on a number of other events considered in the following discussion.

In the saturated C_6 products we also find both *n*-hexane and 3-methylpentane. We take this as evidence that the originating ion rearranges by a hydride shift to yield species with the charge on the α carbon (species 3) and on the γ carbon (species 1). Those two ions are necessary to allow the formation of γ-*n*-H and β-3MP ions by a subsequent 1–2 methyl shift.

Since it seems reasonable to assume that all the C_6 olefins and most of the C_6 paraffins come from parent carbenium ions on the surface, we must conclude that it is far easier for a C_6 ion to undertake a bimolecular abstraction of a hydride from a feed molecule and desorb as a C_6 paraffin isomer than it is for it to shed a proton and desorb as a C_6 olefin. The total C_6 olefin selectivity is only ~0.05 at 400°C in the pure 2MP feed and drops

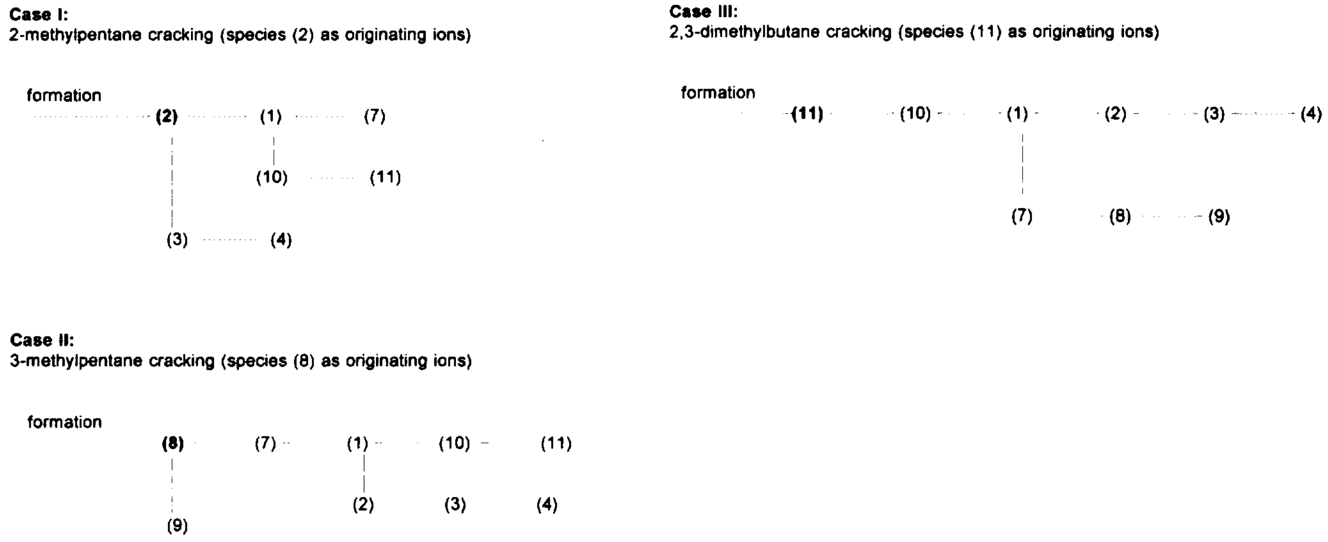


FIG. 2. Subschemes of the reaction of hexyl ions in 2-methylpentane (Case I), 3-methylpentane (Case II), and 2,3-dimethylbutane (Case III) cracking on USHY.

TABLE 2a

Initial Molar Selectivity of C_6 Olefins and Paraffin Isomers Produced in 2-Methylpentane Cracking on USHY at 400°C Using Steam Dilution

	H_2O/Feed ratio (mol/mol)			
	0.00	0.07	0.73	1.46
1-Hexene	0.0000	0.0000	0.0000	0.0000
t-2-Hexene	0.0042	0.0013	0.0009	0.0009
c-2-Hexene	0.0016	0.0012	0.0009	0.0010
t-3-Hexene	0.0015	0.0008	0.0008	0.0006
c-3-Hexene	0.0023	0.0009	0.0011	0.0011
2-Methyl-1-pentene	0.0056	0.0022	0.0022	0.0021
2-Methyl-2-pentene	0.0127	0.0098	0.0092	0.0085
t-4-Methyl-2-pentene	0.0000	0.0000	0.0000	0.0000
c-4-Methyl-2-pentene	0.0000	0.0000	0.0000	0.0000
4-Methyl-1-pentene	0.0000	0.0000	0.0000	0.0000
3-Methyl-1-pentene	0.0000	0.0006	0.0011	0.0012
t-3-Methyl-2-pentene	0.0077	0.0088	0.0084	0.0081
c-3-Methyl-2-pentene	0.0077	0.0094	0.0087	0.0078
2-Ethyl-1-butene	0.0000	0.0042	0.0051	0.0056
2,3-Dimethyl-1-butene	0.0019	0.0016	0.0012	0.0012
2,3-Dimethyl-2-butene	0.0046	0.0036	0.0028	0.0025
3,3-Dimethyl-1-butene	0.0000	0.0000	0.0000	0.0000
Total C_6 olefins	0.0499	0.0443	0.0424	0.0406
2,2-Dimethylbutane	0.0000	0.0057	0.0054	0.0050
2,3-Dimethylbutane	0.0853	0.1830	0.1720	0.1570
3-Methylpentane	0.4150	0.4810	0.4580	0.4390
n-Hexane	0.0472	0.0539	0.0486	0.0445
Total C_6 paraffins	0.5476	0.7226	0.6830	0.6455

TABLE 2b

Initial Molar Selectivity of C_6 Olefins and Paraffin Isomers Produced in 2-Methylpentane Cracking on USHY at 450°C Using Steam Dilution

	H_2O/Feed ratio (mol/mol)			
	0.00	0.07	0.73	1.46
1-Hexene	0.0000	0.0000	0.0000	0.0000
t-2-Hexene	0.0041	0.0017	0.0009	0.0009
c-2-Hexene	0.0020	0.0013	0.0005	0.0004
t-3-Hexene	0.0017	0.0008	0.0006	0.0004
c-3-Hexene	0.0025	0.0013	0.0009	0.0011
2-Methyl-1-pentene	0.0065	0.003	0.0025	0.0020
2-Methyl-2-pentene	0.0091	0.0070	0.0066	0.0063
t-4-Methyl-2-pentene	0.0000	0.0000	0.0000	0.0000
c-4-Methyl-2-pentene	0.0000	0.0000	0.0000	0.0000
4-Methyl-1-pentene	0.0000	0.0000	0.0000	0.0000
3-Methyl-1-pentene	0.0000	0.0006	0.0011	0.0015
t-3-Methyl-2-pentene	0.0058	0.0086	0.0076	0.0054
c-3-Methyl-2-pentene	0.0058	0.0081	0.0064	0.0050
2-Ethyl-1-butene	0.0000	0.0052	0.0051	0.0065
2,3-Dimethyl-1-butene	0.0020	0.0012	0.0011	0.0011
2,3-Dimethyl-2-butene	0.0035	0.0026	0.0024	0.0023
3,3-Dimethyl-1-butene	0.0000	0.0000	0.0000	0.0000
Total C_6 olefins	0.0430	0.0423	0.0358	0.0329
2,2-Dimethylbutane	0.0000	0.0037	0.0048	0.0056
2,3-Dimethylbutane	0.0690	0.1650	0.1490	0.1210
3-Methylpentane	0.3050	0.3520	0.3250	0.3060
n-Hexane	0.0460	0.0476	0.0394	0.0371
Total C_6 paraffins	0.4200	0.5673	0.5192	0.4697

TABLE 2c

Initial Molar Selectivity of C_6 Olefins and Paraffin Isomers Produced in 2-Methylpentane Cracking on USHY at 500°C Using Steam Dilution

	H_2O/Feed ratio (mol/mol)			
	0.00	0.07	0.73	1.46
1-Hexene	0.0012	0.0000	0.0000	0.0000
t-2-Hexene	0.0041	0.0020	0.0023	0.0021
c-2-Hexene	0.0022	0.0009	0.0010	0.0010
t-3-Hexene	0.0017	0.0005	0.0005	0.0002
c-3-Hexene	0.0026	0.0014	0.0011	0.0011
2-Methyl-1-pentene	0.0052	0.0040	0.0032	0.0018
2-Methyl-2-pentene	0.0087	0.0075	0.0072	0.0073
t-4-Methyl-2-pentene	0.0000	0.0000	0.0000	0.0000
c-4-Methyl-2-pentene	0.0000	0.0000	0.0000	0.0000
4-Methyl-1-pentene	0.0000	0.0000	0.0000	0.0000
3-Methyl-1-pentene	0.0000	0.0010	0.0012	0.0013
t-3-Methyl-2-pentene	0.0056	0.0075	0.0072	0.0068
c-3-Methyl-2-pentene	0.0056	0.0071	0.0063	0.0056
2-Ethyl-1-butene	0.0000	0.0047	0.0048	0.0053
2,3-Dimethyl-1-butene	0.0021	0.0011	0.0011	0.0013
2,3-Dimethyl-2-butene	0.0029	0.0025	0.0025	0.0026
3,3-Dimethyl-1-butene	0.0000	0.0000	0.0000	0.0000
Total C_6 olefins	0.0420	0.0402	0.0385	0.0364
2,2-Dimethylbutane	0.0000	0.0036	0.0033	0.0030
2,3-Dimethylbutane	0.0382	0.0523	0.0453	0.0404
3-Methylpentane	0.1210	0.1400	0.1150	0.1020
n-Hexane	0.0210	0.0331	0.0282	0.0243
Total C_6 paraffins	0.1802	0.2290	0.1918	0.1697

to ~0.04 at 1.46 dilution with steam as shown in Tables 2a–2c. At the same time the total C_6 paraffins formed (even ignoring the "invisible" 2MP feed, reformed by the process mentioned above) show a selectivity of ~0.55 for pure feed at 400°C and a maximum of 0.72 at a 0.07 steam dilution ratio.

In other words, the bimolecular hydride transfer is at least 10 times more rapid than proton release. This is so despite the fact that hydride transfer is a bimolecular process, while proton release is monomolecular. This can be seen by writing the ratio of the rates as

$$\frac{\text{rate of proton donation}}{\text{rate of hydride abstraction}} = \frac{k_d[RH^+]}{k_a[RH^+]\,[M]} = \frac{k_d}{k_a[M]} = \frac{0.05}{0.55} \approx 0.1,$$

where k_d is the rate constant for proton release; k_a is the rate constant for hydride abstraction; $[RH^+]$ is the carbenium ion concentration on the surface; and $[M]$ is the feed concentration in the gas phase.

The β-2MP ion can produce both olefins 2M1P and 2M2P. The α ion (species 3) can also produce 2M1P so that we do not know the relative contributions of the two ions to 2M1P formation. No other products are expected from species 3. However, the γ ion (species 1) should be able to produce 4M2P as well as 2M2P, although no 4M2P has been found. Nor has 4M1P been found in the products. It would arise from the δ and ε carbenium ions. We conclude tht the δ (species 13) and ε (species 15) ions are not formed to any significant extent, or are very resistant to proton shedding.

The presence of 3MP in the products indicates that the γ ion (species 1) must be formed. However, its failure to yield 4M2P is puzzling. The alternative fates the γ ion may suffer are

(a) 2M2P formation by desorption;

(b) skeletal rearrangement to a β-3MP (species 7);

(c) skeletal rearrangement to an α-2,3DMB ion (species 10); and

(d) 4M2P formation by desorption.

Of these alternative processes (d) is obviously the slowest. Judging from the abundance of 3MP in the products and the relative scarcity of 2M2P and 2,3DMB, process (b) is dominant. We conclude that on this catalyst 1–2 methyl shifts are easier than the release of a proton to the Brønsted base to yield an olefin by desorption. Moreover, we see that the yield of the paraffin *n*H is less than that of 3MP and interpret this as a greater tendency of the charge to rearrange to the γ carbon rather than the α carbon. This is supported by the excess of 2M2P over 2M1P, as the former is made from the originating ion and its most favored γ isomer. At the same time, it emphasizes the fact that it is the tertiary proton from the γ configuration which is much more likely to be released on desorption.

The γ nH Ion

The isomerization of the originating β-2MP ion into an *n*H ion results from a 1–2 shift of the methyl group to form the α-2MP ion (species 3) and leaves a charge on the γ carbon of the linear hexyl ion.

The fact that both hexene-2 and hexene-3 are formed agrees with the idea that the first and dominant *n*-hexyl ion is the γ ion (species 4). If β ions are subsequently formed, we would have to assume that the primary (i.e., terminal) hydrogens are much more strongly held, so that only hexene-2 is formed from any β *n*-hexyl ions (species 5) which may form. This fact can be correlated with the absence of 4M2P olefins which would be formed by the release of the secondary δ carbon hydrogens as protons. From this behavior of the *n*-hexyl and 2MP ions we can establish the order of facility in which proton detachment takes place at 400°C in the desorption of carbenium ions. Not surprisingly the order is:

tertiary ≫ secondary ≫ primary.

What is surprising is the "much greater" reactivity relationships. These mean that when a tertiary proton is available, secondary protons are not released at all (as in the γ-2MP ion) and when secondary protons are available, primary protons are not released (as in β-*n*H ions).

The β-3MP Ion

In keeping with the above-proposed relative order of proton release, no 3M1P olefins are formed from β-3MP ions (species 7). Instead, the available tertiary proton is released to give 3M2P as the only product olefin. This conclusion will also be true if the γ-3MP ion (species 8) is formed, since the available secondary hydrogens will, in general, preclude the formation of 2E1B which requires the release of a primary proton.

Evidence from cracking 3MP as a pure feed (6), and from the product distribution observed here, indicates that γ-3MP ions are the most stable of the 3MP and 2MP ions and are likely to be the most common ions on the catalyst surface, regardless of the originating ion (and hence of the C_6 feed configuration). The most common product isomer of C_6 is therefore the 3MP paraffin.

INTERPRETING THE PARAFFIN TO OLEFIN RATIO IN THE PRODUCTS

The relative yields of *n*H and 3MP, which arise after a single methyl shift from the originating β-2MP ion, show that the γ-3MP ion configuration yields 10 times more paraffin products than the γ-*n*H configuration. However, this does not mean that there are 10 times as many γ-3MP ions as γ-*n*H ions, as we can see by considering the yields of olefins from the two ions.

The yield of *n*-hexenes is only ~50% smaller than the sum of the 3M pentene yields. We take it that the relative ease with which the two ions undergo either hydride extraction or proton release has a major influence on the P/O ratios of these isomers. If the proton being released is secondary in both molecules, and therefore reacts at similar rates, then the olefin ratio of *n*-hexenes to 3M pentenes indicates that there are only ~50% more 3MP ions than *n*H ions. This value seems low, as it would also reflect the relative likelihood of a methyl shift to the terminal or the γ carbon from a 2MP ion. The other supposition, that in the 3MP ion the proton released is the tertiary proton after rearrangement to a β-3MP configuration, suggests an even smaller difference between the two isomerizations of the originating β-2MP, since in that case the greater yield of 3MP olefins would be partly due to the ease of releasing a tertiary proton compared to the release of one of the secondary protons required for the formation of *n*-hexenes.

We are led to conclude that the relative ease of abstracting a hydride governs the P/O ratio arising from various ions. The 3MP ion, with a P/O ratio of ~26, seems to be more stable to desorption and more active in hydride abstraction than the *n*H ion with a P/O ratio of ~5. It is the greater stability of the tertiary γ-3MP ion that enables it to survive until a hydride transfer can take place, while the secondary γ-*n*H ion, being less stable, tends to shed a proton to achieve stability. In both cases, however, the evidence clearly shows that, on this catalyst at 400°C, hydride transfer from the feed is easier than proton release to the Brønsted base.

The α-2,3DMB Ion

The 2,3DMB ion is the result of shifting the terminal methyl to the same γ carbon of the 2MP ion which most of the time receives the methyl group from the β carbon and forms the β-3MP ion. The formation of α-2,3DMP and β-3MP ions are therefore alternative 1–2 methyl shift processes of the γ-2MP ion. The yields of the corresponding paraffins suggest that the shift to yield the β-3MP ion is preferred. However, Tables 2a–2c show that α-2,3DMB ions desorb relatively more olefins, necessitating a more careful analysis by taking into consideration the fates of all the respective ions.

When we examine the P/O ratio in these two structures (see Tables 2a–2c) we find for the 2,3DMB configuration a P/O ratio of ~13 at 400°C and ~8 at 500°C. For the 3MP configuration the corresponding ratios are ~27 and ~11. Thus 2,3DMB ions form olefins more readily than 3MP ions, presumably because 3MP has to shed a secondary proton from the preferred γ configuration or because it must first rearrange back to the β-3MP configuration before it can shed a tertiary proton. The 2,3DMB ions, whether in their α or β configuration, always have a tertiary proton. The 2,3DMB ions, whether in their α or β configuration, always have a tertiary proton to shed. By examining the total of the 3MP olefins plus paraffins in the products and comparing this number to that for products with the 2,3DMB configuration, we conclude that the 3MP ion is formed more readily than the 2,3DMB ion (see Tables 2a–2c).

We can also see that, after skeletal rearrangement from the 2MP ion, it is the primary α-2,3DMB ion that is formed. This in turn permits the formation of 2,3DM1B as a significant product, without violating the relative order of proton shedding presented above. The terminal ion has a large potential for rearranging to the β configuration; the β ions in turn yield 2,3DM2B in quantities even larger than those of 2,3DM1B obtained from the first-formed α ion. We conclude, therefore, that the 1–2 proton shift is easier than the release of a tertiary proton to create an olefin. Thus our hierarchy of reactions is now:

1–2 proton shift > tertiary proton release ≫ secondary proton release ≫ primary proton release.

THE EFFECT OF STEAM ON THE REACTIONS OF THE C_6 ION

From Tables 2a–2c it is clear that steam reduces the total yield of C_6 olefins and causes a maximum in the yield of C_6 paraffins at low steam/reactant ratios. The first thing which is apparent is therefore the different effect on the two routes of ion desorption caused by the presence of steam. Closer examination shows that yields of all olefinic species, except 3MP olefins, decrease. 3MP olefins go up and stay up within the range of conditions investigated while 3MP paraffins also go up but then go down. The result is that the P/O ratio decreases in the presence of steam dilution, and remains lower than in the case of pure feed. The 3MP ion clearly differs from *n*H and 2,3DMB ions, both of which yield fewer olefins in the presence of steam. The 2,3DMB ion and the *n*H ion show a threefold increase in the P/O ratio as steam is added. Overall, the rise in the P/O ratio of the total C_6 fraction from ~11 to ~17 results in a longer kinetic chain length (*CL*) and attests to an increased activity of hydride ion abstraction in comparison to proton donation.

A possible explanation for these effects is that the Brønsted *base* holding the carbenium ion becomes *weaker* in the presence of water molecules absorbed on the inorganic framework of the catalyst. It is not clear what the exact mechanism of this effect may be; whether, for example, a direct interaction of steam with the active Brønsted sites is involved; or, perhaps some kind of inductive effect is communicated from physically absorbed water elsewhere on the lattice (17). Whatever the specific interaction, we propose that the weakened Brønsted base thus formed is less likely to pull off a proton from an associated carbenium ion. The associated carbenium ion, left with less incentive to shed a proton, stays on the surface until it is released by the easier reaction: a hydride transfer from the feed. The result is that fewer olefins are formed, more paraffins are formed, and a higher P/O ratio is observed. At the same time the overall *initial* rates of reaction are slowed, as confirmed by Table 3. The slowing of initial rates is due to two opposing effects:

—The weaker Brønsted bases cause the reaction to proceed along a path involving longer carbenium ion residence times and higher surface coverage by carbenium ions, hence resulting in lower rates of initiation by protolysis.

—The lower rates of initiation are compensated for to some extent by the longer chain length. However, the chain reactions by and large proceed at a lower rate on the weakened sites. Nonetheless, *higher* rates of propagation are possible and do occur at the lowest temperature investigated (see, for example, R_{32} at 400°C in Table 3).

In the balance the overall initial conversion rate is lower.

The *weaker* charge of the Brønsted bases seems to weaken the ability of the carbenium ions to undergo any reaction. Table 3 shows that rates are generally reduced by the addition of steam. However, since the rate of desorption by proton release is reduced while the population of carbenium ions on the surface is increased, both hydride transfer to carbenium ions and skeletal rearrangement become more likely, relative to desorption, as shown in Table 2.

Evidence for the increased residence time of carbenium ions is found in the tendency to produce more C_6 isomers, and in particular, the "more-difficult-to-form" isomers 2,3DMB and 2,2DMB. The 2,2DMB, we believe, arises mostly by disproportionation reactions; we will discuss its formation later. The 2,3DMB is more likely to be the result of the more frequent formation of γ-2MP ions during the longer 2MP ion residence time on the surface. At the same time, 4MP olefins continue to be absent; we explain this as a result of the reduced extraction activity of the Brønsted bases at which the precursor ions are attached. Secondary protons are difficult to shed even on the strong bases present in the absence of steam; in the presence of steam this becomes even more difficult. In contrast, the formation of 2,3DMB and 3MP is enhanced in the presence of steam.

To understand the increase in the yields of skeletal isomers while the formation of 4MP olefins continues to be suppressed, we note that skeletal isomerization is a monomolecular reaction involving the carbenium ion only. On the other hand, proton shedding to produce any olefin involves a Brønsted base and a carbenium ion in a bimolecular reaction. It seems that the reduced strength of the Brønsted bases which results from the presence of steam makes them too weak to abstract the secondary protons from β-2MP to form 4M2P or 4M1P olefins, despite the increased residence times of precursor ions on the surface. In contrast, the probability of monomolecular skeletal rearrangements which precede the formation of 3MP and 2,3DMB increases as ion residence time increases. In fact, skeletal rearrangement may form 3MP ions so rapidly that the γ-2MP ion required for 4MP olefin production continues to be rare. We conclude that the ability of the carbenium ions to isomerize is less affected by the weakening of the underlying Brønsted bases, and that the reactions most affected are those which require bimolecular interaction of the feed with a Brønsted base.

The Formation of 2-Ethylbutene-1

The formation of 2E1B in amounts corresponding to ~30% of 3M2P in the presence of steam is surprising

TABLE 3

Initial Reaction Rates (IRR) for 2-Methylpentane Cracking on USHY and with Steam Dilution

H_2O/Feed:	0.00	0.07	0.73	1.46	0.00	0.07	0.73	1.46	0.00	0.07	0.73	1.46
T(°C):	400	400	400	400	450	450	450	450	500	500	500	500
IRR[a] (min^{-1})[b]												
r_{0i}												
r_{00}	0.164	0.092	0.008	0.001	5.97	0.731	0.137	0.010	119	9.83	1.52	0.461
r_{01}	0.438	0.061	0.061	0.032	3.44	0.209	0.137	0.103	21.9	4.03	1.29	0.921
r_{02}	0.164	0.061	0.046	0.032	1.15	0.157	0.091	0.052	11.6	1.76	0.759	0.422
r_{03}	4.13	2.46	1.41	0.648	61.1	7.73	3.83	1.92	539	100	31.6	16.4
r_{04}	3.20	1.66	0.967	0.519	26.9	6.37	3.19	1.60	172	40.6	13.3	6.87
$\sum r_{0i}$	8.10	4.33	2.50	1.23	98.5	15.2	7.38	3.69	863	156	48.4	25.1
r_{2i}												
r_{20}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
r_{21}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
r_{22}	0.137	0.215	0.092	0.045	1.15	0.313	0.364	0.155	27.1	2.52	0.683	0.346
r_{23}	2.49	1.17	0.706	0.378	20.7	5.12	2.26	1.10	95.5	26.7	8.73	4.38
$\sum r_{2i}$	2.63	1.38	0.798	0.423	21.8	5.43	2.62	1.25	122	29.2	9.41	4.72
r_{3i}												
r_{30}	0.985	0.000	0.000	0.000	6.66	1.51	0.683	0.341	9.03	0.000	0.835	0.422
r_{31}	0.000	0.092	0.138	0.058	0.000	0.104	0.000	0.000	0.000	0.000	0.000	0.000
r_{32}	0.164	1.32	0.767	0.295	3.44	0.104	0.068	0.072	40.0	6.80	2.20	1.15
$\sum r_{3i}$	1.15	1.41	0.906	0.353	10.1	1.72	0.752	0.413	49.0	6.80	3.04	1.57
r_{4i}												
r_{40}	0.000	1.26	0.645	0.257	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
r_{41}	0.000	0.000	0.000	0.000	0.000	0.000	0.114	0.072	0.000	0.000	0.000	0.000
$\sum r_{4i}$	0.000	1.26	0.645	0.257	0.000	0.000	0.114	0.072	0.000	0.000	0.000	0.000
r_{50}	0.219	0.000	0.000	0.000	1.15	0.000	0.000	0.000	16.8	1.51	0.531	0.499
r_{60}	15.0	22.2	10.5	4.14	96.2	29.6	11.8	4.85	233	57.7	14.6	6.49
$\sum r_{ji}$	19.0	26.3	12.8	5.17	129	36.8	15.3	6.59	422	95.2	27.6	13.3
r_{kc}	0.241	0.194	0.071	0.021	1.84	0.209	0.068	0.021	5.16	0.504	0.110	0.038
r_{b63}	0.000	0.000	0.000	0.000	3.90	0.000	0.000	0.000	90.3	1.51	0.000	0.000

[a] The subscripts *ij* refer to the carbon number of the carbenium ion and the moiety transferred from the feed, respectively (1, 2).

[b] The units are calculated using wt/wt for catalyst/oil and 1 as the density ratio of feed/catalyst.

enough to merit further consideration. We have already seen that primary protons are hard to shed, even on the stronger Brønsted bases present when no steam is added to the feed. Whatever it is that allows 2E1B to become a significant product on the weaker sites in the presence of steam must be connected with the long surface residence time of γ-3MP ions. These ions have the following options:

(a) hydride abstraction to form 3MP;
(b) proton shifts to give β-3MP;
(c) proton shift to give α-EB; and
(d) returning to the γ-2MP configuration.

Of these, option (a) leads to the observed enhanced production of 3MP and (c) leads to 2E1B. We propose that, with the increased surface residence time, the γ-3MP ion will occasionally rearrange, by an internal, monomolecular process, to the α-2EB ion (species 9). The resultant α-2EB ion contains a tertiary proton which it can easily shed to form the olefin 2E1B, which we have found in the products of cracking *only* in the presence of steam. As more steam is added, residence times increase due to the dilution of feed and the consequent reduction in the frequency of bimolecular reactions and, while the other olefin yields decrease, 2E1B and 3M1P—the "difficult-to-form" olefins—increase as a *fraction of the C_6 product mix*. It is not clear why 3M1P is formed while 4M1P and 4M2P are not.

The action of H_2O, and perhaps that of other additives such as CO_2 and CO, is therefore one in which there are two causes and a variety of effects. The causes are the weakening of the bases corresponding to the acid sites on the lattice and the dilution of the feed stream. The effects are:

—carbenium ions have a longer surface residence time;
—initiating reactions are slowed due to a reduction in the concentration of pristine sites;
—propagating reactions are slowed less than the initiation reactions;
—kinetic chain length is increased;

—hard-to-form skeletal isomers form;
—hard-to-form paraffins are produced;
—the overall reaction rate is decreased;
—the selectivity for coke formation is decreased; and
—the rate of decay is decreased.

These effects interact in such a way that, at low steam additions, a maximum occurs in the kinetic chain length and in feed isomerization selectivity.

THE MODIFICATION OF CATALYST SELECTIVITY BY DILUENTS

From work with CO_2 and CO dilution (13) we have seen that the maximum in isomerization is a function of the nature of the diluent and its concentration. There is no clear guideline as to which diluents will be effective as promoters of isomerization, or in what amounts. Previous work has shown that truly inert molecules, such as N_2 and H_2 (12, 13), cause selectivity changes which can be totally ascribed to gas phase dilution effects. More complex, polarizable molecules such as CO, CO_2, and H_2O, show effects like those described here. Of these, CO shows the least effect, CO_2 comes next, and H_2O has the most pronounced effect.

If all these "chemical" effects are indeed due to a weakening and redistribution of site energies by a subtle delocalization of the charge on the lattice-attached Brønsted base, a whole panorama of cracking process modifications opens up: Other diluents, for example, NH_3 or H_2S, may give still other product distributions by altering site strength and distribution in new ways. Commercial cracking selectivities may be alterable by appropriate feed preparation, for example adding or removing constituents of the feed to improve product selectivity via the adsorption of various fractions. Finally, it should be possible to find solid additives which will change the site energy distribution in the solid catalysts. These may have to be deposited on the catalyst after solidification, or periodically added during cracking operations. We expect that catalysts designed with these concepts in mind will start with highly modified versions of today's best formulations. A match will have to be found between the modifying adsorbent and the underlying matrix in order to optimize the desired effects.

THE FORMATION OF 2,2-DIMETHYLBUTANE

In pure 2MP cracking, it is unlikely that 2,2DMB paraffins are formed by the sequence of isomerizations starting from 2MP ions. To form 2,2DMB in that way one would have to propose that besides hydrogen shifts, two methyl shifts take place: the second after the originating β-2MP ion has rearranged to a β-2,3DMB ion. The β-2,3DMB species could then form a γ-2,2DMB ion (species 14).

TABLE 4

Activation Energies for the Formation of C_6 Olefins in 2-Methylpentane Cracking on USHY (kJ/mol)

Product names	Species number[a]	Proton release modes[b]	H_2O/Feed ratio 0.00	0.07	0.73	1.46
t-2H	4	S	155.77	103.05	103.11	107.13
c-2H	4	S	169.70	73.83	77.37	72.67
t-3H	4	S	161.84	66.42	70.12	70.70
c-3H	4	S	161.74	62.83	64.95	72.67
2M1P	2	P	153.73	89.51	80.19	66.40
2M2P	2	S	141.36	70.59	59.05	62.42
3M1P	7	P	—[c]	106.31	68.49	75.93
t-3M2P	8	S	143.80	79.03	58.68	65.56
c-3M2P	8	S	143.80	74.05	51.83	59.20
2E1B	8	P	—[c]	90.11	62.49	70.43
2,3DM1B	11	P	160.82	70.29	61.42	75.93
2,3DM2B	11	T	137.99	66.63	60.35	74.26

[a] The most common species.

[b] P, primary proton release; S, secondary proton release; and T, tertiary proton release.

[c] Undetectable.

From the lack of 3,3DM1B olefins in the product we suspect that γ-2,2DMB ions do not form in significant numbers, even in the presence of steam. We believe the major part, or even all, of the 2,2DMB is formed via the X_{51} and perhaps the X_{42} disproportionation processes (10). The isobutyl ions required for the X_{41} reaction are formed by protolysis of the feed and are always in the form of the β-2M propyl ion. The C_5^+ species required for the X_{51} process could be either a β-*n*-pentyl or an α-2MB species. Any β-*n*-pentyl ions formed will readily rearrange to the more stable β-2MB configuration and accumulate in this form on weak sites. The 2,2DMB would then form by the transfer of a methyl group from the feed to a β-2MB ion or (reaction 51), of an ethyl group to a β-2M propyl ion (reaction 42). The RPPs for these processes are not reported here as they are inseparable from the RPP for reaction 60 by the methods described to date. We will elaborate on this issue in a future publication.

THE EFFECT OF TEMPERATURE

The most obvious effect of increased temperature on C_6 products is a decrease in paraffin yield. The P/O ratio of the 2,3DMB configuration decreases by a factor of 1.7, that of the 3MP configuration decreases by 2.5, while that of *n*H goes down by 2.8 over the range from 400 to 500°C. This decrease is largely due to a decrease in C_6 paraffin selectivity rather than any increase in C_6 olefin selectivity. In fact, olefin selectivity for C_6 decreases over this temperature range in most species.

TABLE 5

C_6 Olefins and their Precursor C_6^+ Carbenium Ions

Groups	Names of C_6 olefins	C_6^+ Carbenium Ions	
		Names	No.
A	1-Hexene	α or β-hexyl	5, 6
	t-2-Hexene	β or γ hexyl	4, 5
	c-2-Hexene	β or γ hexyl	4, 5
	t-3-Hexene	γ hexyl	4
	c-3-Hexene	γ hexyl	4
B	2-Methyl-1-pentene	α or β 2-methylpentyl	2, 3
	2-Methyl-2-pentene	β or γ 2-methylpentyl	1, 2
	t-4-Methyl-2-pentene	γ or δ 2-methylpentyl	1, 13
	c-4-Methyl-2-pentene	γ or δ 2-methylpentyl	1, 13
	4-Methyl-1-pentene	δ or ε 2-methylpentyl	13, 15
C	3-Methyl-1-pentene	α or β 3-methylpentyl	7, 12
	t-3-Methyl-2-pentene	β or γ 3-methylpentyl	7, 8
	c-3-Methyl-2-pentene	β or γ 3-methylpentyl	7, 8
	2-Ethyl-1-butene	α 2-ethylbutyl	9
		γ 3-methylpentyl	8
D	2,3-Dimethyl-1-butene	α or β 2,3-dimethylbutyl	10,11
	2,3-Dimethyl-2-butene	β 2,3-dimethylbutyl	11
E	3,3-Dimethyl-1-butene	γ or δ 3,3-dimethylbutyl	14, 16

TABLE 6

Activation Energies of Various Reactions Involving the Originating 2-Methylpentyl Ions in the Temperature Range 400–500°C (kJ/mol)

Path	Detectable products from the path indicated and shown in Fig. 3.	H_2O/Feed ratio (mol/mol)			
		0.00	0.07	0.73	1.46
I	2,3DMB isomer and olefins	126.06	56.53	43.69	44.40
II	*n*H isomer and olefins	134.39	68.19	48.54	51.70
III	3MP isomer and olefins	108.69	53.60	39.73	42.57
IV	2MP olefins	145.56	83.80	61.23	66.43

Among the C_6 olefins only *n*-hexene selectivity increases. We interpret this as being due to the larger activation energy required to achieve an α-2MP configuration from the β-2MP originating ion, as compared to the alternative γ-2MP configuration. On the strong bases present in the undiluted reaction, this first leads to γ-*n*H ions which then undergo enough proton shifting to allow even the formation of 1-hexene at the highest temperature studied, 500°C. By the time small amounts of steam are added, *n*H olefin production has dropped by a factor of two and the sites are too weak to allow 1-hexene formation, even at 500°C.

The two optional skeletal shifts, that to a 3MP or to a 2,3DMB ion configuration from the γ-2MP ion, show the same degree of change, as evidenced by olefin product yields. When we also consider the paraffin yields we see that there must be an increase in 2,3DMB configurations on the surface since the ratio of total 2,3DMB to total 3MP product increases slightly. This suggests that the formation of 2,3DMB ions requires a higher activation energy than the formation 3MP ions from γ-2MP.

Table 4 gives the temperature coefficients for the forma-

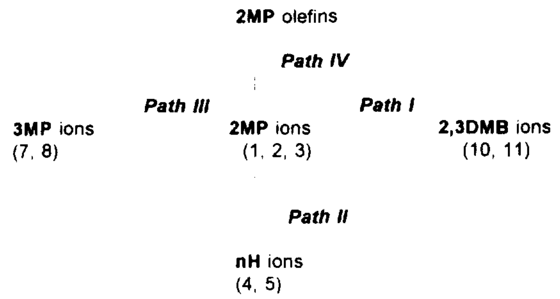


FIG. 3. Reaction paths involving the originating 2-methylpentyl ions. Numbers in brackets correspond to species numbers possible for that skeletal configuration as shown in Fig. 1.

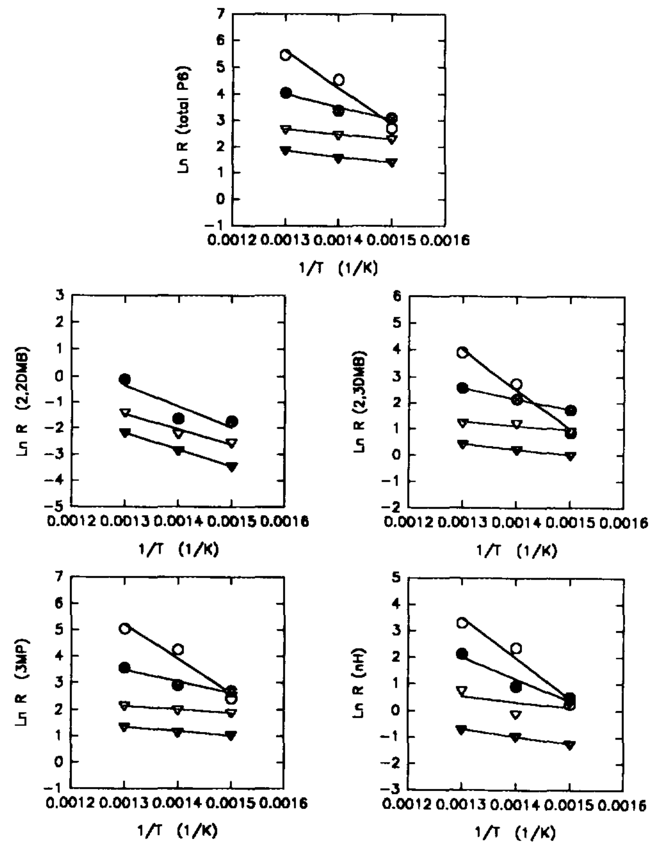
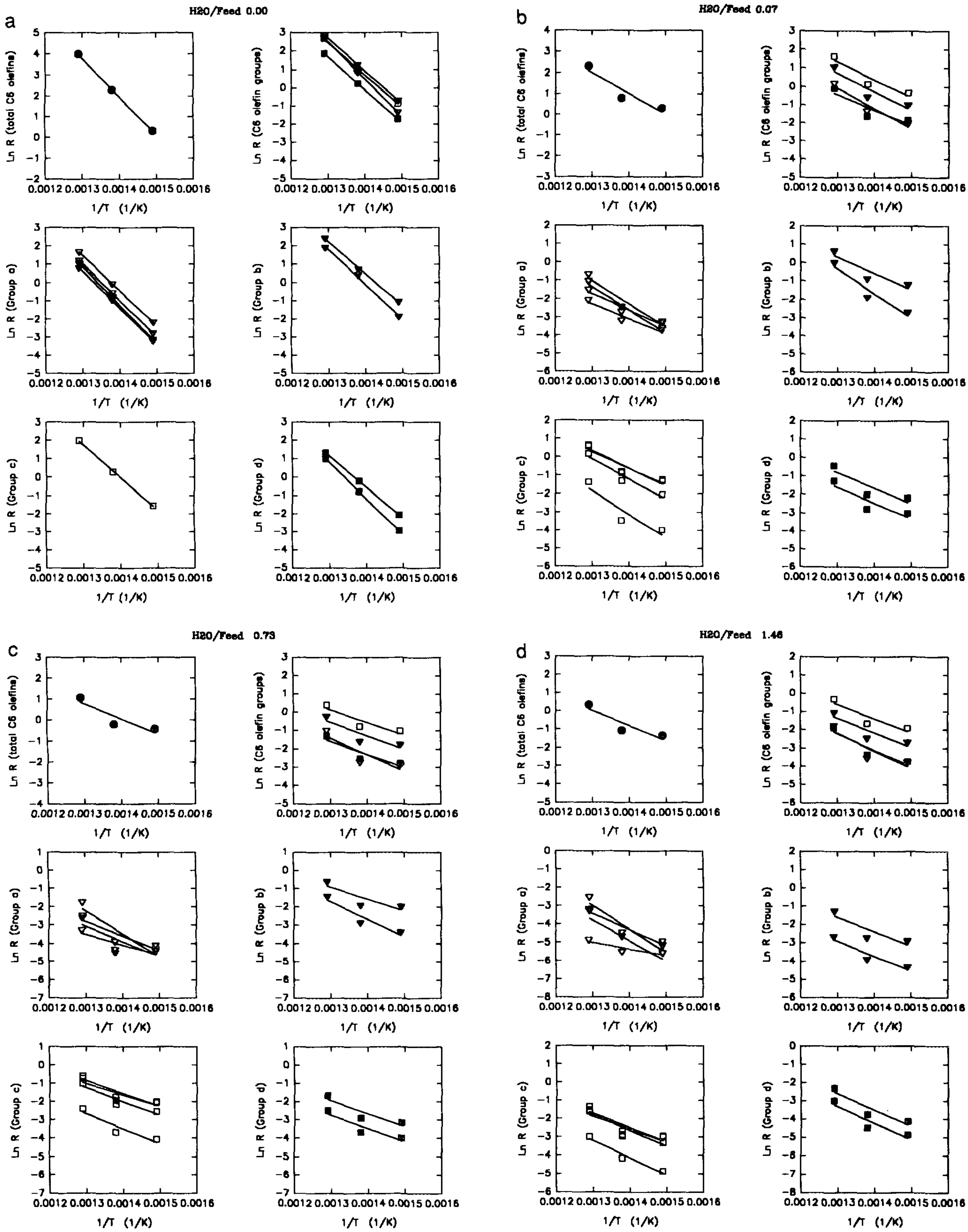


FIG. 4. Arrhenius plots for the formation of C_6 isomers in 2-methylpentane cracking on USHY with steam dilution. H_2O/Feed ratios (mol/mol): (○) 0.00; (●) 0.07; (▽) 0.73; (▼) 1.46.


a
H2O/Feed 0.00
b
H2O/Feed 0.07
c
H2O/Feed 0.73
d
H2O/Feed 1.46
Ln R (total C6 olefins)
Ln R (C6 olefin groups)
Ln R (Group a)
Ln R (Group b)
Ln R (Group c)
Ln R (Group d)
0.0012 0.0013 0.0014 0.0015 0.0016
1/T (1/K)

tion of each olefin product shown in Table 2, at each dilution ratio. The values in Table 4 are not activation energies since in each case temperature-dependent concentration terms are included in the temperature coefficients. For example, the molar selectivity for any olefin is:

$$\mathcal{F}_i = \left[\frac{\text{moles of olefin } i}{\Sigma \text{ moles of products}}\right] \text{initial}$$

$$= \left[\frac{\text{rate of formation of olefin } i}{\Sigma \text{ rate of formation of products}}\right] \text{initial.}$$

The rate of formation of each product olefin is in turn

$$r_i = k_i[I_i]$$

while the production of paraffins by protolysis is

$$r_j = k_j[M][BH]$$

and by chain propagation is

$$r_l = k_l[M][I_l]$$

In the above, each of the surface species concentrations $[I_i]$, and $[BH]$ is a temperature-dependent function of the steady states involving that concentration. Thus the concentration terms in both the numerator and the denominator have temperature dependencies. As the denominator is a sum of such dependencies the function $\mathcal{F}_i$ need not have an Arrhenius dependence on temperature. However, when we take a ratio of two $\mathcal{F}_i$ functions, the denominators cancel and, if the functions are properly selected, the concentration dependence in the numerators may cancel as well. In those ratios the temperature coefficient is the difference between the activation energies of the two processes involved. Using Table 5 we can see where such ratios may be appropriate.

A better-defined set of activation energies may be calculated if we take sums of products formed by individual isomerizing processes starting with the originating ion from 2-methylpentane. Figure 3 shows the ion structures which can arise from this originating ion together with the species-numbers for ions which can arise by hydride shifts. Table 6 shows the activation energies for the formation of products arising from each shift in turn. The effects of dilution with steam are also given.

At zero dilution the shedding of protons to yield 2MP olefins requires the highest activation energy, in agreement with previous discussion. Next comes the shift of the methyl group to the terminal carbon to produce *n*-hexyl products; a sum of both olefins and paraffins. This is followed by the shift of the terminal methyl group to form 2,3DMB configurations and finally the shift to yield the 3MP configurations, which is the easiest process of these four. None of this is unexpected; what is nice to have is a method for quantifying these properties and comparing them from system to system as a quantitative measure of the changes between systems.

IS STEAM SIMPLY A "MITIGATOR" OF CATALYST ACTIVITY?

An interesting example of the use of the quantitative information provided by the calculated RPPs is provided by an examination of the effects of steam dilution on the activation energy. Table 6 shows that the order of ease of isomerization is not changed by the presence of steam. What is radically changed is the size of the activation energies and the relative differences between the activation energies for the various isomerizations. Whereas, in the absence of steam, Path III required 75% of the activation energy of Path IV, in the presence of a 0.07 dilution ratio with steam it requires only 65% as much. Moreover, the activation energies in both cases are down by factors of two.

To appreciate the changes in activation energies due to the addition of steam, we look at Figs. 4 and 5. In all cases there is a remarkable drop in activation energy upon the addition of the smallest amount of steam. The lower activation energy persists, essentially unchanged by further additions of steam. One could well come to the conclusion that steam *strengthens* the active sites and thereby reduces the activation energy for the pertinent reactions. Such a conclusion is refuted in Figs. 4 and 5 and in Table 3 by the fact that *rates* generally *decrease* upon the addition of steam.

We propose the following explanation instead. The steam adsorbs on the catalyst lattice at the active centers, or elsewhere. Its adsorption causes some form of electronic rearrangement in the lattice which leads to a weakening of the catalytically active Brønsted bases. Reactions which proceed on these bases are therefore slowed. The effect of this electronic rearrangement in the lattice is greater at higher temperatures, with the result that the effect of adding a given amount of steam is greater at high temperatures, and the reaction rates are reduced therein to a greater extent. The consequence is an *apparent* de-

FIG. 5. Arrhenius plots for the formation of C_6 olefins in 2-methylpentane cracking on USHY (a) without steam dilution; (b) with steam dilution at the H_2O/Feed ratio of 0.07; (c) with steam dilution at the H_2O/Feed ratio of 0.73; and (d) with steam dilution at the H_2O/Feed ratio of 1.46. Symbols: (▽) hexenes; (▼) 2-methylpentenes; (□) 3-methylpentenes; and (■) 2,3-dimethylbutenes.

crease in the activation energy of the reactions involved. It is not, however, an activation energy of an elementary reaction we observe but a combination of the temperature effect on the elementary reactions of the ions and on the modification of site properties by steam.

It also seems that steam addition, beyond some point at molar ratios of 0.07 or less, results in no more than the dilution of the feed. Further modification of site properties does not seem to take place. As a consequence, the lines on an Arrhenius plot fall lower as steam is added but maintain the slope appropriate to the behavior of the fully altered sites formed at the lowest levels of steam addition studied here. The steam ratio at which this "fully mitigated" condition is reached in this system lies at a molar ratio of 0.07 or lower for this combination of feed and catalyst. Similar behavior has been observed in the "inhibition" of gas phase pyrolysis of hydrocarbons (18–20). In that case nitric oxide was the inhibitor of choice, but other molecules were also capable of leading to inhibition. The characteristic behavior in that case, which led to a protracted debate lasting some 30 years, was the appearance of a "limiting" reaction rate with no change in product distribution. This limiting rate was attained at fairly low inhibitor concentrations for some inhibitors and did not change with further additions of inhibitor. Now we find that CO, CO_2 (13), and H_2O are active as mitigators in catalytic cracking and also show limiting behavior, with the added complication that they change the selectivity of the catalyst.

The nature of the self-limiting process at work in catalytic cracking "mitigation" remains to be seen; hopefully it will not take the length of time it did to understand the "inhibition" of thermal cracking (19, 20).

CONCLUSIONS

Examination of C_6 product selectivities, including the selectivities of C_6 paraffin isomers in 2-methylpentane cracking, has revealed a number of important features concerning the reactions of C_6 carbenium ions on the active sites of USHY cracking catalyst. Quantification of the associated reaction parameters has led us to propose some ideas regarding the control of selectivity in catalytic cracking.

We find that hydride ion transfer from the 2MP molecule to a C_6 carbenium ion is easier than the release of a proton from a C_6 ion to form a C_6 olefin and reconstitute the Brønsted acid site. However, proton release has a higher activation energy, with the result that, as temperature is increased, the paraffin-to-olefin ratio of products from each type of C_6 ion decreases. The result is that, at low temperatures, USHY causes 10 times as much isomerization to C_6 paraffins as dehydrogenation to C_6 olefins.

We also find that the order of facility of the surface reactions of C_6 carbenium ions is such that skeletal proton migration is easier than the shedding of a tertiary proton, which in turn is much easier than the shedding of a secondary proton, which is much easier than the shedding of a primary proton.

The addition of steam to the reaction appears to weaken the lattice-resident bases on which the carbenium ions reside. This causes the population of carbenium ions on the surface to increase since they have more difficulty in shedding a proton on the weakened base. The result is that, while catalyst activity is decreased, the reactions of carbenium ions are facilitated. One consequence of this is that selectivity for C_6 isomerization is increased in the presence of steam. At relatively low levels of steam addition and low temperatures, USHY is essentially an isomerization catalyst with 70% of the products consisting of paraffinic C_6 isomers. At the same time, olefin formation is somewhat suppressed.

Steam appears to act as a "mitigator" of site activity. That is to say, it changes the activity of sites to a new and constant lower value. This new value is not changed by further additions of steam once a "limiting" activity is achieved. From previous work with CO and CO_2 it appears that various molecules lead to various types of mitigation resulting in selectivities which are diluent-specific.

These insights into the chemistry which underlies product formation on acid catalysts can obviously be applied to the development of additives which enhance and control catalyst selectivity.

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