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Cracking of Long-Chain Alkyl Aromatics on USY Zeolite Catalysts

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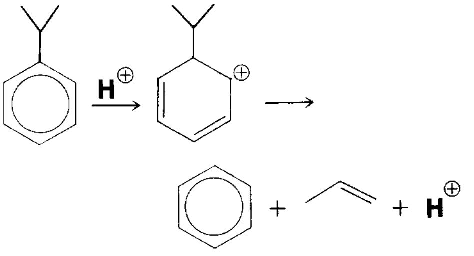
Long-chain alkyl aromatics are important precursors for FCC gasoline. It is well known that for short-chain alkyl aromatics like cumene the dominant cracking process is simple alkyl aryl cleavage. In contrast we have found that for long-chain alkyl aromatics like 1-phenylheptane, cracking over *in situ* USY catalysts is much more complex. Cracking in a long alkyl side chain results in a carbenium ion that isomerizes easily and gives self-alkylation of the aromatic ring. Self-alkylation produces coke precursors and heavy gasoline aromatics. Product selectivities vary with zeolite unit cell size in ways that are rationalized on the basis of decreasing acid site density and zeolite adsorption properties. © 1992 Academic Press, Inc.

INTRODUCTION

Long-chain alkyl aromatics are important constituents of fluid catalytic cracking (FCC) unit feedstocks (*1*). Acid-catalyzed cracking of alkyl aromatics often is assumed to occur by complete cleavage of the side chain from the aromatic ring (*2*) (Eq. (1)). This belief is based on studies of short-chain alkyl aromatics. For example, cumene gives propene and benzene; t-butylbenzene cracks to isobutene and benzene (*3*):



(1)

However, not much literature actually exists on the cracking of long-chain alkyl aromatics (*4, 5*). Most pure hydrocarbon model reactions have been done on paraffins, olefins, and short-chain alkyl aromatics such as cumene (*3*). Unfortunately, short-chain alkyl aromatics are not appropriate model compounds for longer chain analogs because the number of reaction pathways for short-chain alkyl aromatics like cumene is limited, especially under FCC conditions. While this simplicity makes cumene a good test reactant, the chemistry of longer chain alkyl aromatics may be more complex. It seems reasonable that long-chain alkyl aromatics could react by a number of alternate pathways and that a study of their cracking chemistry could lead to insights about their reactivity and help in understanding the process of aromatics formation in cracking.

The aromatics content of gasoline is an important issue for refiners that are concerned about gasoline octane and reformulated gasolines. Since FCC units are the largest contributor to the gasoline pool, aromatics formation in cracking is an important and timely topic.

In this work we have studied the reaction of 1-phenylheptane over a series of *in situ* cracking catalysts containing ultrastable Y (USY) zeolite with a range of unit cell sizes. Product selectivities were obtained and the influence of the cracking catalyst on product distribution and reaction patterns was determined. The long alkyl chain on 1-phenylheptane results in several different cracking

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modes. For example, the alkyl chain can support a carbenium ion which results in self-alkylation of the benzene ring and bicyclic aromatic reaction products.

EXPERIMENTAL

Materials

1-Phenylheptane (>99%) was purchased from Aldrich and used without further purification.

Zeolite Y was grown in calcined clay microspheres by a published procedure (*6*). Ammonium exchange and zeolite unit cell size (UCS, reported in angstroms) reduction to give Catalyst I (UCS = 24.60) and Catalyst II (UCS = 24.39) were done by standard methods (*6*). Catalyst III (UCS = 24.26) was prepared by steaming Catalyst II in a fluidized bed of 100% steam at 1 bar for 4 h at 788°C. Catalyst IV (UCS = 24.24) was prepared by steaming Catalyst II at 816°C for 4 h in 100% steam. Table 1 lists relevant physical and chemical properties.

TABLE 1

Physical and Chemical Properties of the Catalysts

Catalysts	I	II	III	IV
SiO_2 (wt%)	38.4	39.3	39.3	39.3
Al_2O_3 (wt%)	57.7	60.2	60.2	60.2
Na_2O (wt%)	0.41	0.33	0.33	0.33
UCS[a]	24.60	24.39	24.26	24.24
Surface area (m^2/g)	434	372	282	230
%Zeolite Y	41	33	25	19

[a] Zeolite Y unit cell size (UCS) in angstroms as measured by X ray.

Catalysis

Catalytic experiments were done in a fixed-bed continuous-flow glass tubular reactor with a 16 mm internal diameter and 0.3 m length. All experiments were done at 773 K and 1 bar. The catalyst to oil ratio was varied between 5.3×10^{-3} and 500×10^{-3} g/g by changing the amount of catalyst and feeding a constant weight, 2.00 g, of phenylheptane in all cases. At each catalyst to oil ratio the times on stream studied were 51, 127, 254, 507, and 1267 s. After the reaction was complete, the reactor was stripped with nitrogen for 10 min and then the catalyst was regenerated at 780 K in a 20 cm^3/min flow of air for 45 h.

Blank experiments to assess the extent of thermal reactions were done using ground glass in place of the catalyst at the above conditions. Additional control experiments were done to approximate the contribution from matrix cracking. *In situ* growth of zeolite onto clay means that the matrix and zeolite are coupled. Cracking experiments were done where the same calcined clay microspheres on which the zeolite was grown were used in place of the catalyst. The weight of microspheres charged to the reactor was equal to the amount of matrix present when the catalyst (zeolite plus matrix) was used. Two different times on stream (50.7 s and 21 min) were run. After correcting for thermal reactions in both cases, the "matrix conversion" is about 4–7% of the catalyst conversion. This contribution is an upper limit because the zeolite lines the catalyst pores, thus, in practice, the zeolite covers up or masks a significant portion of the matrix. Therefore, the results reported here reflect essentially zeolitic cracking.

Yields and Selectivities

Yield is defined as moles of product X obtained per 100 moles of 1-phenylheptane fed. Product selectivity is moles of product X obtained for each mole of phenylheptane converted. Reaction selectivity is moles of reactant transformed through a specific reaction per mole of reactant converted.

Initial product selectivities were obtained using optimum performance envelope techniques (*3*). Initial selectivities for each primary product were determined from the initial slope of a plot of (% molar) yield for that product vs 1-phenylheptane conversion. The shape of this plot determines whether the product is primary or secondary, stable or unstable (*3*).

Analysis

Gaseous products (C_1–C_4) were analyzed by gas chromatography using a 2-m silica gel plus Poropak Q column. Liquid products were analyzed using a 100-m Supelco Petrocol DH capillary column. Product identification was done using gc-mass spectrometry.

RESULTS AND DISCUSSION

Thermal Cracking

Thermal products were determined by passing 1-phenylheptane over ground glass at reaction conditions. Yields of products vs conversion are plotted in Fig. 1. Clearly 1-phenylheptane fractures relatively easily. Products formed are those expected from thermal reactions such as methane, ethane, and ethene. Significant amounts of styrene, toluene, and hexenes are also formed. Therefore at FCC reaction conditions, thermal cracking of long-chain alkyl aromatics can be significant. For this reason, in order to analyze the acid catalysis, thermal yields over ground glass were subtracted from yields using catalysts. In some cases, e.g., styrene, negative values result. This is probably due to the saturation of reactive species such as styrene by hydride transfer on the catalyst surface.

Initial Selectivities

The initial product selectivities for 1-phenylheptane cracking over Catalysts I–IV are listed in Table 2. Plots of yield vs conversion of 1-phenylheptane are shown in Fig. 2 for Catalyst IV. These plots are qualitatively similar for Catalysts I–IV. From the product distribution it is clear that long-chain aromatics cracking is complex and very different from short-chain aromatics cracking (e.g., cumene or t-butylbenzene). For molecules like 1-phenylheptane, cracking in the alkyl chain (C_3, C_4, $C_{7\text{-}n}$Ph products) is as important as the dealkylation reaction (benzene).

In order to establish a reaction network, the initial selectivities for complementary reaction products were compared (Table 3). For example, C_4s are compared to propylbenzenes; i.e., the sum of the carbons in complementary products totals 13, the number of carbons in phenylheptane. If initial products undergo no further transformations before desorption from the catalyst, the molar selectivities of complementary products should be the same. This comparison shows that the initial selectivities for methane, C_2, and C_6 are very close to the values for C_6Ph, C_5Ph, and toluene, respectively. However, for other complementary pairs the selectivities are not equivalent, i.e., C_2Ph $>$ C_5, $C_3 \gg C_4$Ph, $C_4 \gg C_3$Ph, benzene $\ggg C_7$. This indicates that some products formed during the first cracking event can recrack before desorption. These recracked products thus appear as primary initial products. As a starting point, the simplest hypothesis for most of the observed discrepancies between complementary products is that C_{7-n}Ph products do not recrack extensively at very low conversion and that excess C_3 and C_4 alkyl products and excess benzene arise from recracking of the dealkylated C_7^+ ion before desorption. This decreases the C_7 yield vs benzene and increases the apparent yield of C_3 and C_4s vs C_4Ph and C_3Ph, respectively. The assumption that recracking of C_{7-n}Ph species at low levels of conversion must be small is reasonable because plots of C_3Ph, C_5Ph, and C_4Ph yields vs conversion (Fig. 2) do not show instability until $>20\%$ conversion. However, there may be some contribution from recracking of C_6Ph.

Table 4 compiles reaction selectivities (moles of reactant transformed through a particular reaction per mole of reactant converted). Reaction selectivities were determined by taking into account Tables 2 and 3 and the proposed reaction pathways discussed above. Therefore, the reaction selectivity for reactions 1, 2, and 6 in Table 4 coincides with the initial selectivity to either one of the reaction products for a particular reaction. For reactions 3, 4, 5, and 7 we have assumed that the initial selectivity for

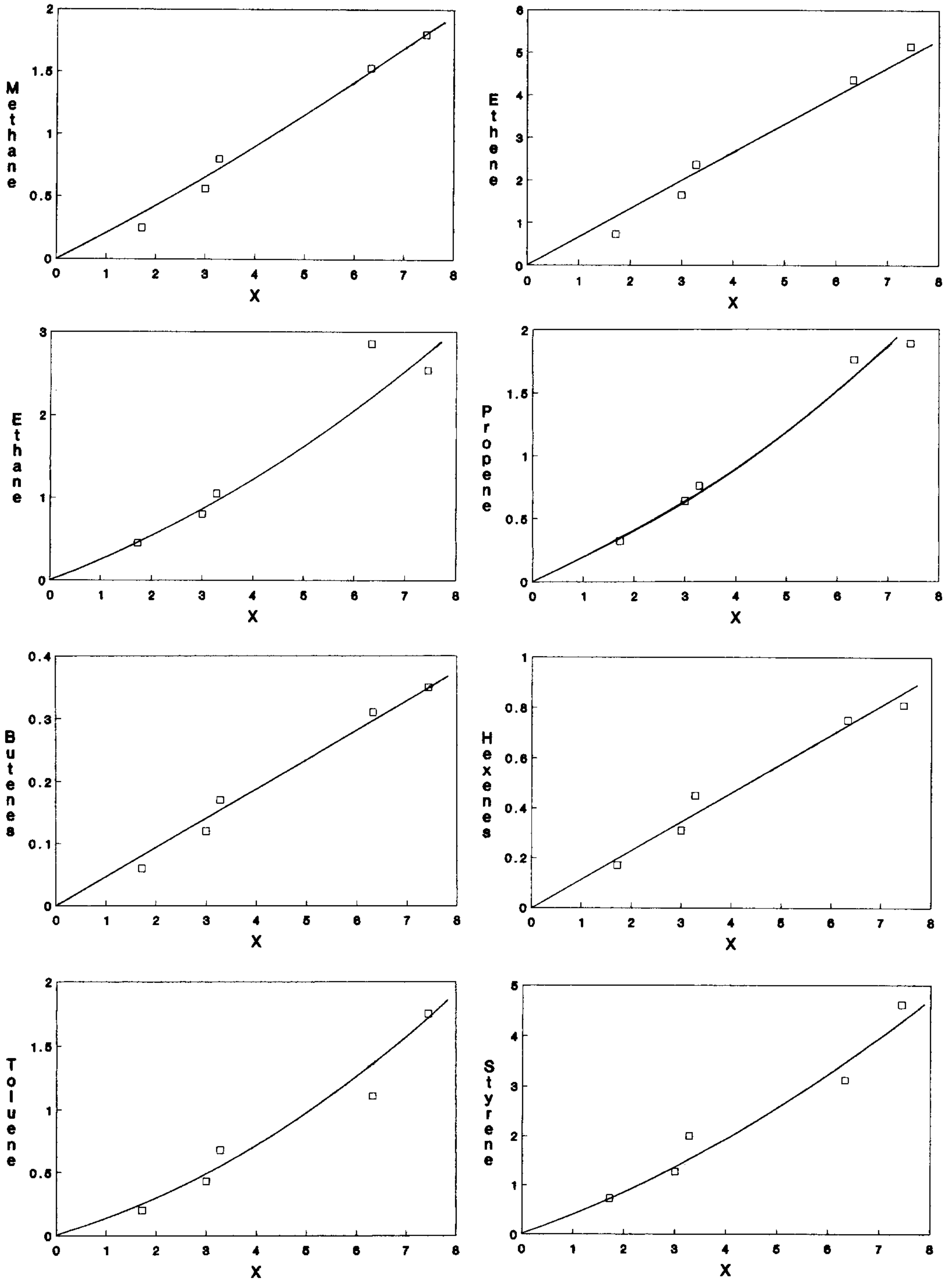


FIG. 1. Yields (% molar) vs conversion for selected products from 1-phenylheptane thermal cracking. Lines are dotted to show expected behavior of yield curve.

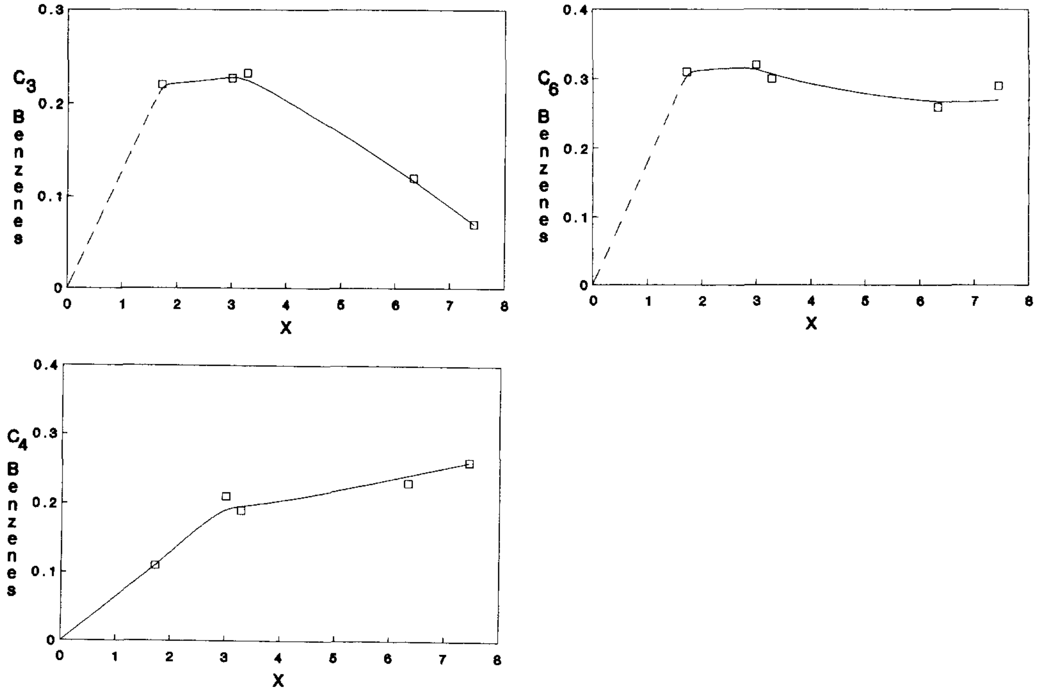


FIG. 1—*Continued*

the least abundant reaction product defines the reaction selectivity. So, for example, the reaction selectivity for reaction 4 is defined by the initial selectivity to C_3Ph, not by the initial selectivity to C_4s. In addition, reaction 8, where feed is transformed to other C_{13} compounds, is included.

If only reactions 1–9 occurred and if excess C_3 and C_4 products arise only from scission of C_7^+, the initial selectivity (IS) to benzene would be given by either Eq. (2) or (3) where the second and third terms correct for the excess of C_3 and C_4 from the dealkylated C_7 fragment:

$$\text{IS Benzene} = \text{IS } C_7 + \text{IS } C_3 - \text{IS } C_4Ph \quad (2)$$

$$\text{IS Benzene} = \text{IS } C_7 + \text{IS } C_4 - \text{IS } C_3Ph. \quad (3)$$

However, the initial selectivities for benzene calculated from Eq. (2) and (3) are significantly lower than those observed (Table 3). Therefore the situation is more complicated and additional reactions that produce benzene must be occurring. One possibility (7) is that C_3 and C_4 olefins can give aromatics from a process of oligomerization, cyclization, and hydride transfer. Alternatively, benzene can also result from disproportionation of 1-heptylbenzene. In addition, disproportionation could be used to rationalize the formation of C_8Ph and $C_{10}Ph$ as primary products. Formally this can be written as Eq. (4) and (5) (reactions 10 and 11 in Table 4):

$$2C_7Ph \rightarrow C_{10}Ph + C_6H_6 + C_4 \quad (4)$$

$$2C_7Ph \rightarrow C_8Ph + C_6H_6 + 2C_3. \quad (5)$$

We can include these reactions in our analysis and approximate the reaction selectivities for reactions 10 and 11 in Table 4 as two times the initial selectivity to $C_{10}Ph$ and C_8Ph. Then the reaction selectivity for reaction 9 of Table 4 must be modified to account for the C_3 and C_4s produced in Eq. (4) and

TABLE 2

Initial Molar Selectivities and Product Type for 1-Phenylheptane Cracking

Product	Type	Catalyst			
		I	II	III	IV
Methane	1 + 2S	—	0.002	0.008	0.010
Ethane	1 + 2S	0.023	0.013	0.047	0.043
Ethene	1 + 2S	0.026	0.033	0.035	0.037
Propane	1 + 2S	0.117	0.140	0.045	0.053
Propene	1U	0.293	0.250	0.282	0.277
Isobutane	1 + 2S	0.150	0.130	0.105	0.101
n-Butane	1 + 2S	0.046	0.047	0.025	0.018
Butenes	1U	0.128	0.125	0.205	0.161
Isopentane	1U	0.023	0.035	0.021	0.023
n-Pentane	1U	0.001	0.005	0.005	0.002
Pentenes	1U	0.006	0.003	0.014	0.011
n-Hexane	1U	0.008	0.014	0.018	0.007
Branched hexanes	1 + 2U	0.075	0.085	0.068	0.071
n-Heptane	1U	0.012	0.008	0.015	0.015
Monobranched heptanes	1U	0.141	0.160	0.138	0.140
Dibranched heptanes	1U	0.031	0.035	0.031	0.030
Heptenes	1U	0.007	0.006	0.015	0.010
Benzene	1S	0.503	0.490	0.510	0.480
Toluene	1 + 2S	0.090	0.093	0.084	0.077
C_2 Benzenes	1 + 2U	0.055	0.065	0.059	0.058
Ethylbenzene	1 + 2U	0.092	0.076	0.139	0.125
Styrene		−0.037	−0.011	−0.080	−0.067
C_3 Benzenes	1 + 2U	0.113	0.115	0.125	0.130
Cumeme + propylbenzene	1 + 2U	0.028	0.016	0.034	0.037
Propenyl benzene	1U	0.085	0.099	0.091	0.093
C_4 Benzenes	1U	0.161	0.162	0.110	0.134
Butylbenzenes	1U	0.010	0.013	0.007	0.009
Butenylbenzenes	1U	0.022	0.026	0.032	0.035
Tetralin	1 + 2S	0.024	0.030	0.027	0.030
Naphthalene	1S	0.086	0.075	0.024	0.031
1-Methylindan	1S	0.019	0.018	0.020	0.029
C_5 Benzenes	1U	0.051	0.053	0.095	0.091
Pentenylbenzenes	1U	0.003	0.003	0.004	0.003
1-Methylnaphthalene	1S	0.034	0.032	0.021	0.033
1,3-Dimethylindan	1U	0.016	0.018	0.070	0.055
C_6 Benzenes	1U	—	0.002	0.007	0.009
C_7 Benzenes	1U	0.026	0.019	0.047	0.031
2-Heptenylbenzene	—	−0.002	−0.010	−0.019	−0.034
2-Phenylbicyclo-[2.2.1]hept-2-ene	1U	0.12	0.12	0.046	0.035
1,4,6-Trimethylnaphthalene	1U	0.016	0.017	0.020	0.030
C_8 Benzenes	1U	0.006	0.003	0.009	0.011
C_{10} Benzenes	1U	0.021	0.023	0.018	0.023

Note. 1, primary; 2, secondary; S, stable; U, unstable.

(5). Thus the reaction selectivity for reaction 9 of Table 4 can be approximated as (IS C_3 − IS C_4Ph—reaction selectivity for reaction 11). Finally, one can account for the formation of excess C_2Ph compared to C_5, formally, by reaction 12 in Table 4.

TABLE 3

Initial Selectivities of Complementary Fragments

Fragment	Catalyst			
	I	II	III	IV
C_1	—	0.002	0.008	0.010
C_6Ph	—	0.002	0.007	0.009
C_2	0.049	0.046	0.082	0.080
C_5Ph	0.051	0.048	0.095	0.091
C_3	0.410	0.390	0.330	0.330
C_4Ph	0.160	0.168	0.110	0.160
C_4	0.330	0.300	0.340	0.280
C_3Ph	0.110	0.115	0.125	0.130
C_5	0.030	0.043	0.040	0.036
C_2Ph	0.055	0.065	0.059	0.058
C_6	0.083	0.099	0.086	0.078
Toluene	0.090	0.093	0.084	0.077
C_7	0.190	0.209	0.200	0.200
Benzene	0.500	0.490	0.510	0.480

From this analysis it is clear that only 35–45% of the cracking of 1-phenylheptane proceeds via dealkylation.

Cracking Mechanisms

Short-chain alkyl aromatics, such as cumene, crack by a monomolecular mechanism involving attack by zeolitic protons on the benzene ring (3). However, for long-chain alkyl aromatics, such as heptylbenzene, cracking also can occur along the alkyl chain. Therefore, two cracking mechanisms can be operative: a monomolecular mechanism, involving proton attack either on the benzene ring or on a sigma C–C bond in the alkyl chain (protolytic cracking); or a bimolecular mechanism involving carbenium ions, chain transfer via hydride transfer and β-scission (*2*).

Monomolecular reaction involving proton attack on the benzene ring gives benzene and an alkyl carbenium ion. The alkyl ion can react in several ways: by desorbing as an olefin by proton elimination; by isomerizing and then cracking to give an olefin and a smaller carbenium ion; or by hydride transfer with another molecule (e.g., 1-phenylheptane) to give an alkane and a new carbenium ion. Protolytic cracking of the alkyl chain generates either a short-chain alkane and an alkylphenyl carbenium ion or a C_{7-n} alkyl aromatic and an alkyl carbenium ion. Bimolecular reactions, which involve generation of a phenylalkyl carbenium ion via hydride transfer and β-scission, produce either an olefin and a smaller phenylalkyl carbenium ion or a short-chain phenylalkene and

TABLE 4

Initial Reaction Selectivities for 1-Phenylheptane Cracking

	Reactant	Products	Catalysts			
			I	II	III	IV
1.	C_7Ph	$C_1 + C_6Ph$	—	0.002	0.008	0.010
2.	C_7Ph	$C_2 + C_5Ph$	0.052	0.046	0.095	0.091
3.	C_7Ph	$C_3 + C_4Ph$	0.160	0.168	0.110	0.160
4.	C_7Ph	$C_4 + C_3Ph$	0.110	0.115	0.125	0.130
5.	C_7Ph	$C_5 + C_2Ph$	0.030	0.043	0.040	0.036
6.	C_7Ph	C_6 + Toluene	0.090	0.093	0.084	0.078
7.	C_7Ph	C_7 + Benzene	0.190	0.209	0.200	0.200
8.	C_7Ph	C_7Ph	0.026	0.019	0.047	0.031
9.	C_7Ph	$C_3 + C_4 + C_6H_6$	0.239	0.216	0.202	0.148
10.	$2C_7Ph$	$C_{10}Ph + C_6H_6 + C_4$	0.042	0.046	0.036	0.046
11.	$2C_7Ph$	$C_8Ph + C_6H_6 + 2C_3$	0.011	0.006	0.018	0.022
12.	$2C_7Ph$	$3C_6H_6 + C_2Ph$	0.050	0.044	0.038	0.044
			1.000	1.008	1.003	0.996

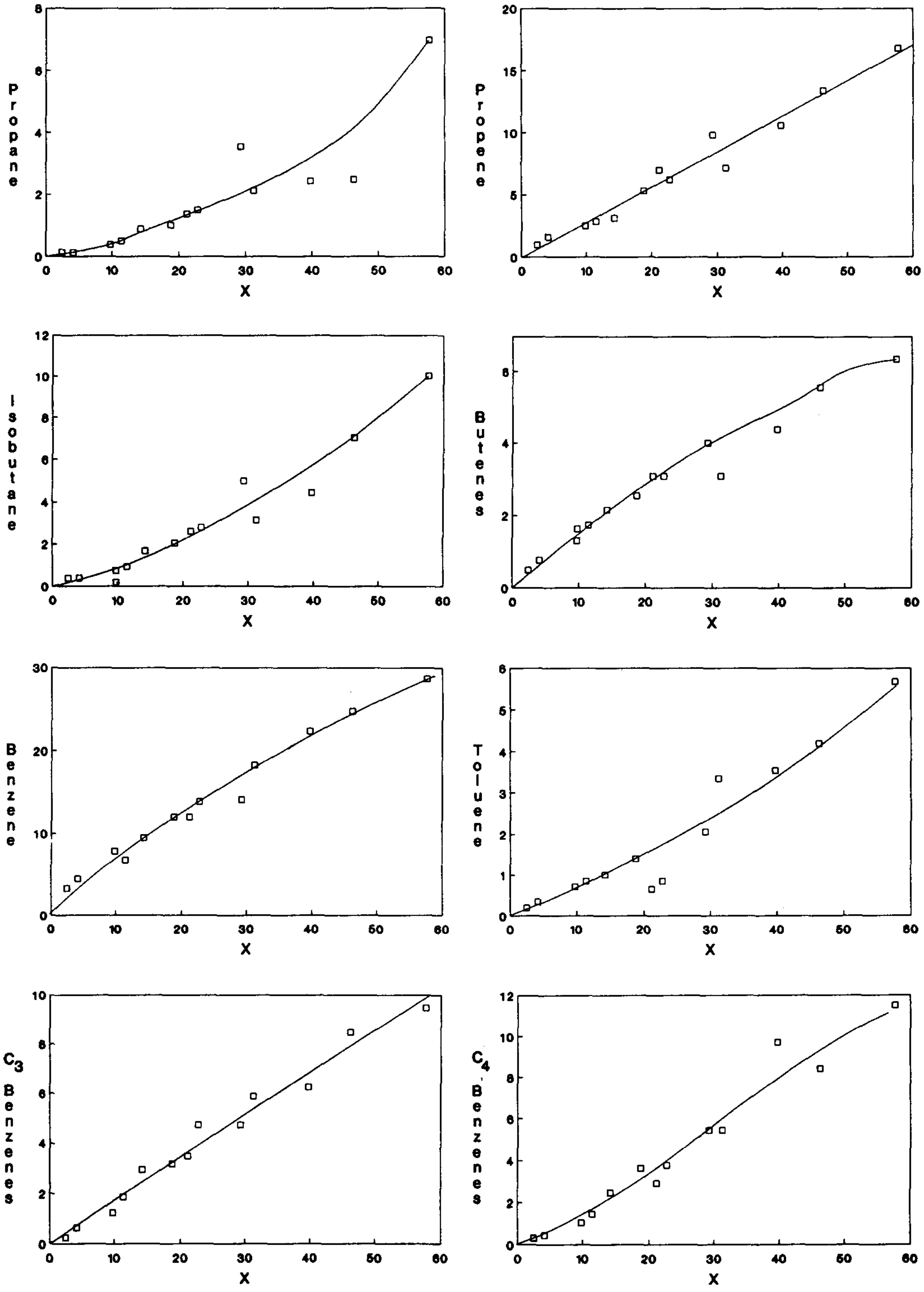


FIG. 2. Yield (% molar) vs conversion for selected products from acid catalyzed cracking of 1-phenylheptane over Catalyst IV.

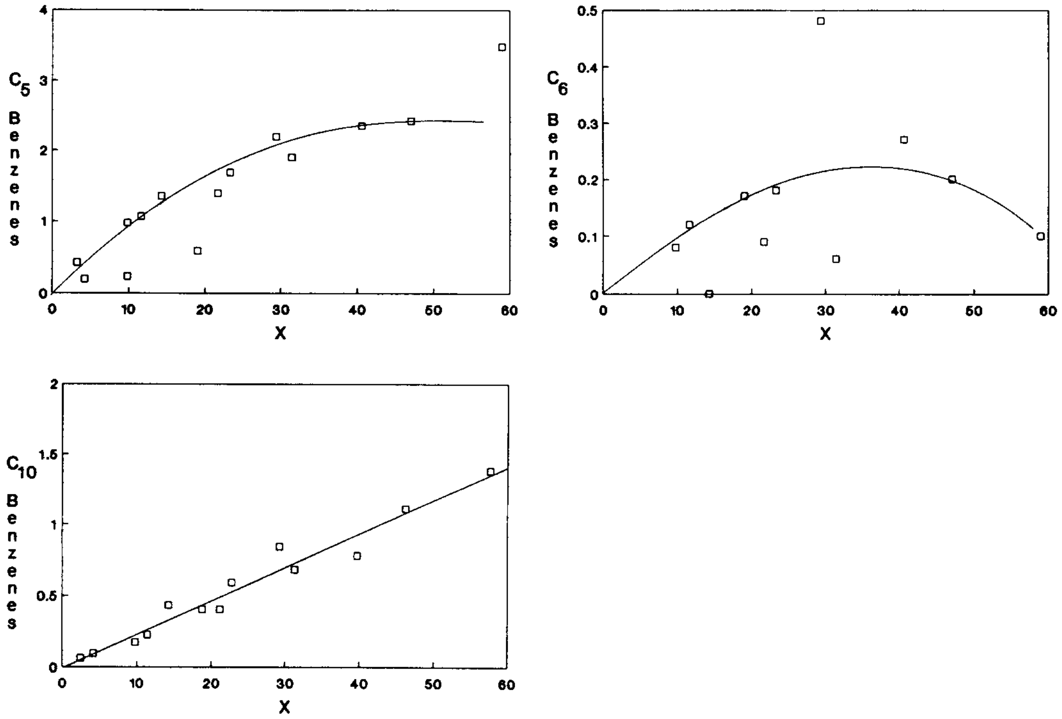


FIG. 2—*Continued*

an alkyl carbenium ion. All these processes are illustrated in Table 5. By comparing the products predicted by these processes and their permutations to the observed products one can see that it is likely that heptylbenzene cracking takes place by both mono- and bimolecular cracking mechanisms.

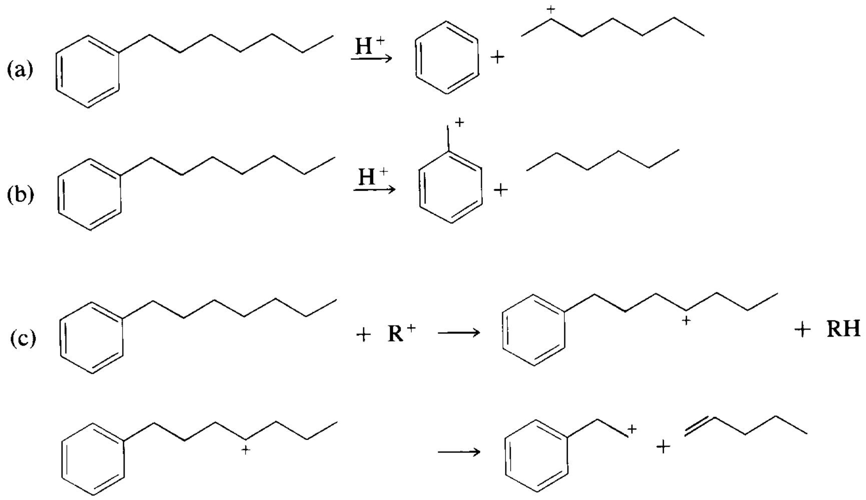
Branched Products

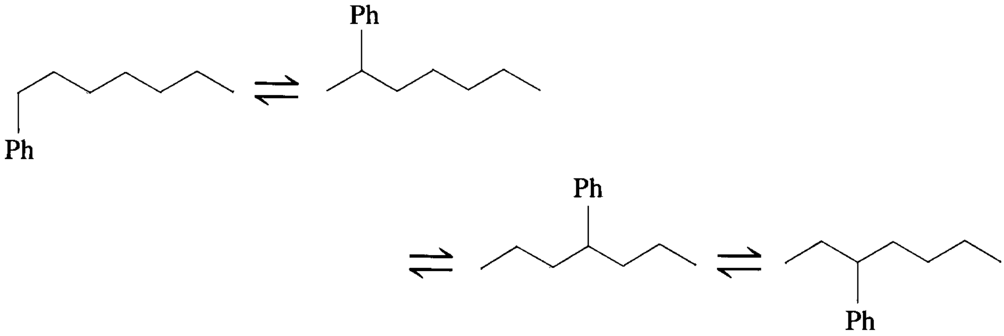
The products of phenylheptane cracking suggest that cracking of the C_7 alkyl chain is analogous to cracking pure *n*-heptane (*5*). This implies that the mechanism and transition states should be similar. Nevertheless there are important differences. For example, the ratio of branched to unbranched products in the C_4, C_5, and C_6 fraction (Table 6) are higher from 1-phenylheptane than from *n*-heptane.

We speculate that these differences may result from the presence of the phenyl group which facilitates isomerization of the alkyl side chain. It is well known that carbocation rearrangements often involve 1, 2 shifts of hydrides, alkyl groups, and phenyl groups (*8*, *9*). In β-phenylethyl cations the phenyl group migrates faster than a hydride and leads to stable ethylenebenzenium ions (*8*). Thus phenyl migration can be very facile. It is likely that phenyl migration occurs rapidly for 1-phenylheptane in the presence of zeolite acid sites to give three additional positional isomers: 2-, 3-, or 4-phenylheptane (e.g., Eq. (6)). This phenyl migration followed by alkyl migration leads to a variety of branched alkyl chain isomers (e.g., Eq. (7)). In addition, the phenyl group can stabilize certain product ions. For heptane certain cracking modes would result in unstable primary ions (Eq. (8) and (9)). In contrast, the phenyl group of heptylbenzene stabilizes analogous reaction modes in heptylbenzene cracking (Eq. (10) and (11)):

TABLE 5

Examples of Cracking Mechanisms for 1-Phenylheptane





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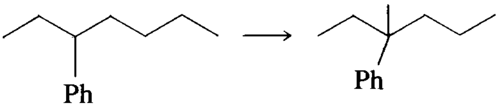

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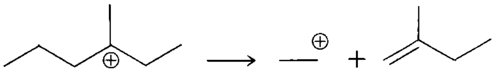

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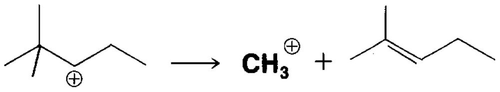

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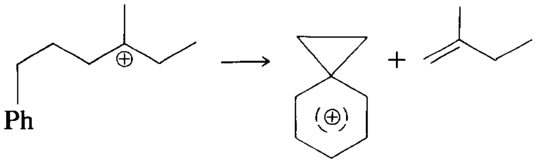
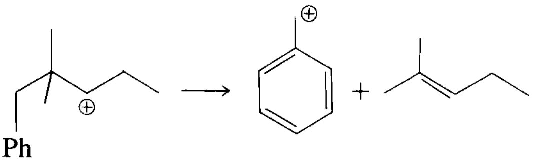


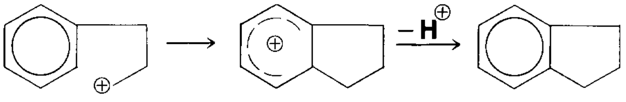
(10)



(11)

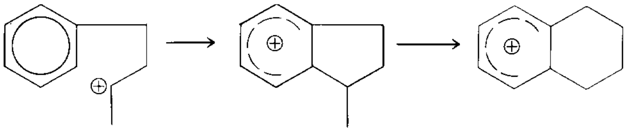
Bicyclic Products

It is interesting that initial selectivities to bicyclic products are significant since these compounds are important precursors for coke (*10, 11*) and heavy gasoline aromatics. Bicyclic compounds can arise from self-alkylation of the aromatic ring. When alkyl chain cracking leaves an alkyl aromatic carbenium ion with 2, 3, or 4 carbons in the chain, recracking becomes unfavorable because it would involve unstable primary carbenium ions. However, an alternate reaction pathway, self-alkylation, is possible. For this to occur, a secondary carbenium ion in the chain must be formed. This ion will alkylate the benzene ring if a five- or six-member ring results. This requires at least 4 carbons in the side chain. Table 7 gives the possible products from self-alkylation through secondary carbenium ions. We believe indane does not form even though it is stable because it requires a primary carbenium ion:



(12)

In contrast 2,3-dihydro-1-methyl-1*H* indene is formed apparently from self-alkylation of a secondary carbenium ion of butylbenzene. In addition, 1,2,3-tetrahydronaphthalene is observed in the C_4Ph fraction indicating that ring expansion occurred:



(13)

Thus clearly long-chain alkyl aromatics do not crack simply by aryl alkyl cleavage. In addition these molecules can give rise to bicyclic aromatics via self-alkylation. These multiring aromatics can ring expand/contract. Moreover, the presence of significant amounts of naphthalene indicates that these species can rapidly transfer hydrogen to give polyaromatic compounds.

These models compound results have important implications for gas oil cracking. Our phenylheptane cracking results suggest that cracking of long-chain alkyl aromatics

TABLE 6

Comparison of Branched to Unbranched Ratios for C_4, C_5, and C_6 Products from the Cracking[a] of *n*-Heptane and 1-Phenylheptane

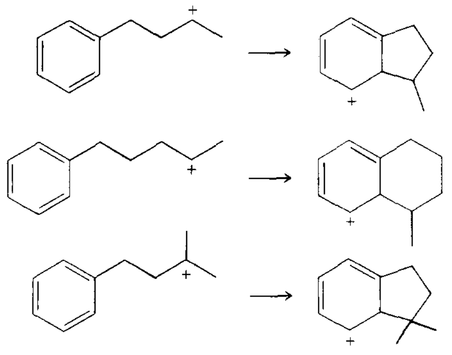
Ratio	1-Phenylheptane	Heptane[b]
iC_4/nC_4	2.8	1.8
iC_5/nC_5	7.0	1.7
iC_6/nC_6	6.1	2.3

[a] Cracking conditions: 500°C; USY catalyst UCS = 24.39 Å.

[b] From A. V. Orchilles, D. Th., Universitat de Valencia, 1984.

TABLE 7

Possible Intermediates Leading to Products Formed by Self-Alkylation of Stable Alkyl Aromatic Carbenium Ions in the C_4Ph and C_5Ph Fractions



(with either one, two, or three aromatic rings) in gas oil involves much more than simple dealkylation reactions. The alkyl chain can also crack in the middle and the resultant products can self-alkylate and transfer hydrogen to give very efficiently, coke precursors and heavy gasoline aromatics. The relative rate of chain dealkylation and cracking and the rate of self-alkylation and hydrogen transfer should be strongly dependent on the reaction conditions and the catalyst characteristics.

Influence of Zeolite Unit Cell Size on Product Distribution

In general, zeolite cracking chemistry is a function of the pore size, pore structure, acid site density, acid site strength, and adsorption properties of the zeolite (*12*). All these factors generally have a direct impact on cracking reaction selectivity.

In zeolite Y, the unit cell size is an important parameter that has been used to explain a variety of important catalytic properties (*13*). UCS is directly proportional to the number of framework acid sites in the zeolite (*14*). Thus as the number of framework aluminum atoms decreases, UCS also decreases. For this reason the UCS also reflects the strength and density of the zeolitic acid sites and is related to the adsorption properties of the zeolite. If the number of framework sites (and thus UCS) is decreased by steaming, Lewis acidity also results. The ratio of Brønsted to Lewis acid sites is dependent on the dealumination conditions (*15*).

For the Y zeolite catalysts studied here, Fig. 3 shows that when the framework aluminum content decreases (UCS decreases) the ratio of dealkylation to cracking in the chain decreases. This suggests as a first approximation that the presence of strong acid

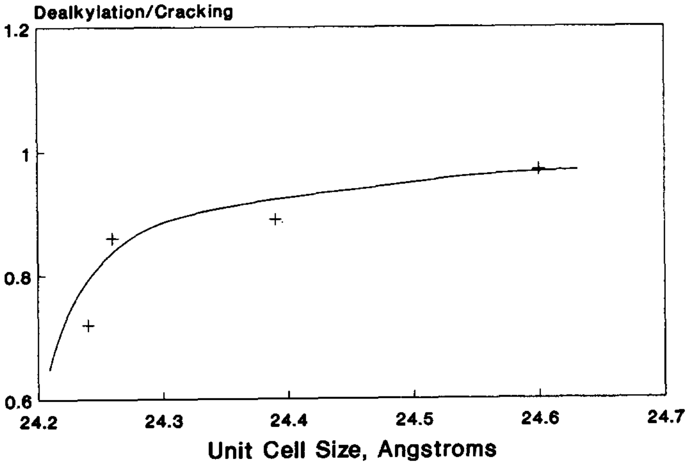


FIG. 3. Dealkylation/chain cracking ratio for 1-phenylheptane cracking.

sites in highly dealuminated Y zeolites would be responsible for chain rupture. This seems quite reasonable from the point of view of electrophilic attack on the molecule by a proton. The most available electron density is associated with the pi electrons of the aromatic ring. Protonation of the ring leads to dealkylation (Eq. (1)). Stronger acids would be necessary to protonate C–C bonds in the alkyl chain. Therefore it seems reasonable that dealkylation is favored by weaker Brønsted acids while stronger acids can also catalyze cracking along the alkyl chain.

Acid strength in dealuminated Y zeolites remains approximately constant below a unit cell size of 24.40 Å (*16*). Therefore if acid strength is the determining factor for the ratio of side chain cracking to dealkylation, samples below 24.40 Å UCS should give equivalent results. However, Fig. 3 suggests that other factors such as adsorption also play a role.

For long-chain alkyl aromatics, adsorption can occur through either the aromatic ring or the alkyl chain. To determine the influence of zeolite UCS on these two adsorption modes, we have studied the adsorption of xylenes and *n*-butane for a series of steam dealuminated Y zeolites. Figure 4 shows that for the xylenes a strong decrease in adsorption capacity occurs for samples

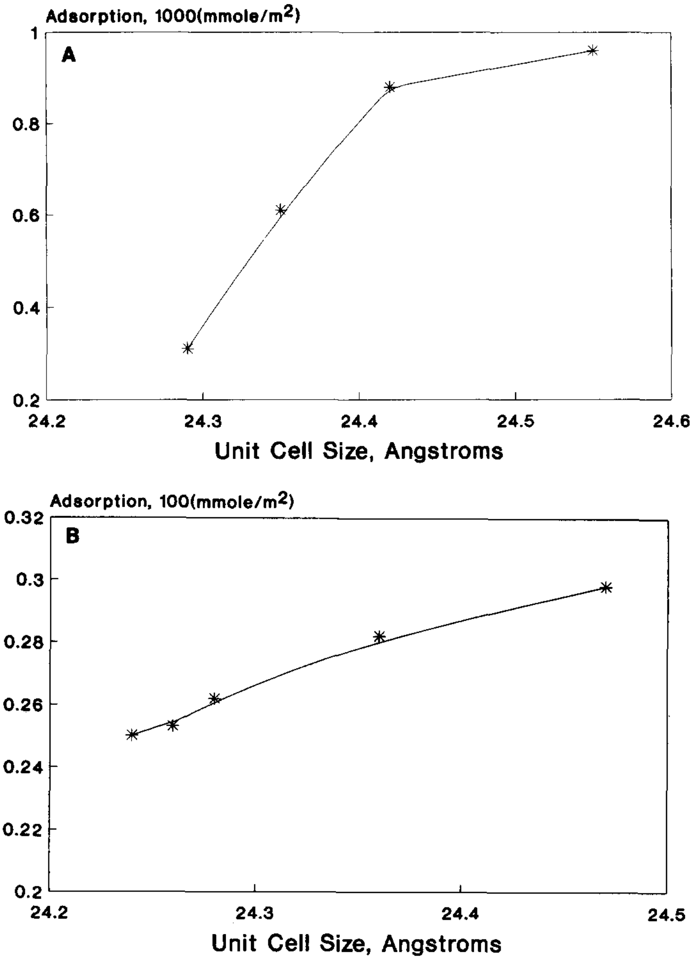


FIG. 4. Adsorption of xylenes (A) and *n*-butane (B) on USY zeolites.

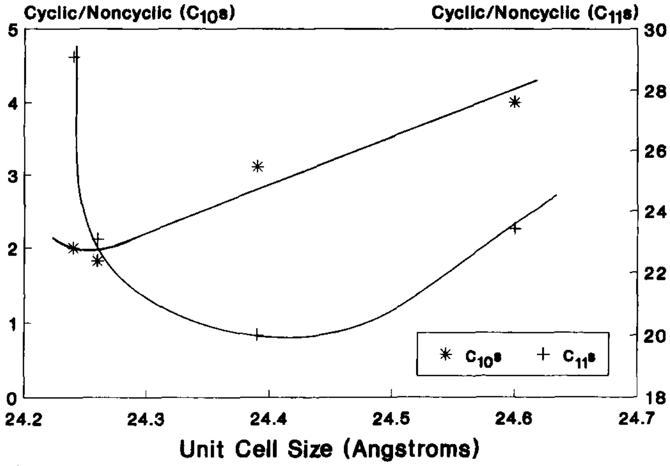


FIG. 5. Cyclic/noncyclic ratio for C_{10} and C_{11} Products in 1-phenylheptane cracking.

with UCS less than 24.40 Å. The relative magnitude of the decrease is much less for *n*-butane. This suggests that as zeolite dealumination increases, the adsorption of the alkyl chain of 1-heptylbenzene would become more likely. This could lead to an increase in selectivity to alkyl chain cracking compared to dealkylation.

What effect does UCS have on the bicyclic products that are formed? As discussed above, precursors of bicyclic products are butyl and pentyl alkylaryl carbenium ions formed from cracked 1-phenylheptane. These ions can attack the aromatic ring and self-alkylate to give bicyclic products or alternatively they can desorb as saturated or unsaturated open chain alkyl aromatics. Figure 5 shows that for C_5Ph (C_{11}) products, the ratio of cyclic to noncyclic products first decreases with UCS and then sharply increases. Thus at low and high UCS a high portion of bicyclic products relative to open chain alkyl aromatics will be formed. The cyclic to noncyclic ratio also initially decreases with UCS for C_4Ph (C_{10}). Thus UCS does not seem to control bicyclic product formation. However, in this analysis products from both unimolecular and bimolecular reactions are lumped together. If instead we compare the products that are from unimolecular reactions i.e., cycloalkenyl aromatics and alkenyl aromatics, to those products involving at least one bimolecular reaction (H transfer) step, i.e., alkyl aromatics, cycloalkyl aromatics, and bicyclic aromatics, then the picture is more straightforward (Fig. 6). As UCS decreases, unimolecular reactions increase relative to bimolecular reactions. This result is consistent with a decreasing acid site density (*13*) and changes in the adsorption properties of the zeolite that arise from changes in aluminum site density (*17*).

CONCLUSIONS

Using 1-phenylheptane as a model compound, we have demonstrated that cracking of long-chain alkyl aromatics involves much more than simple dealkylation reactions. Cracking in the side chain is just as important as aryl alkyl cleavage.

The side chain can support a carbenium ion. This leads to isomerization of the alkyl skeleton as well as self-alkylation of the aromatic ring. Self-alkylation gives bicyclic aromatic compounds that can efficiently produce coke precursors or heavy gasoline aromatics.

Paraffins and olefins from alkyl aromatics are more branched than cracking products

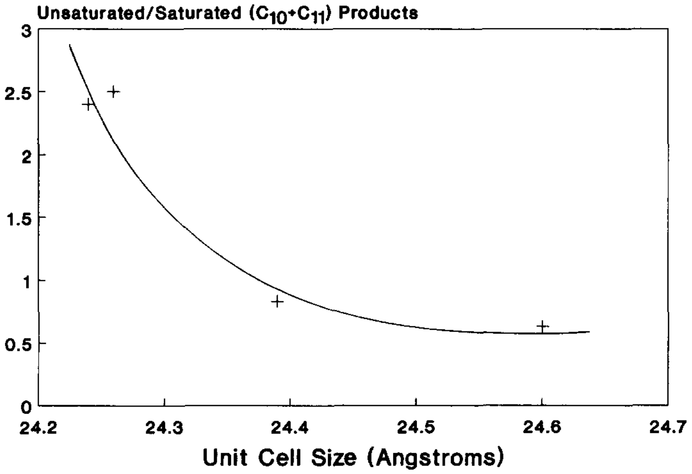


FIG. 6. Ratio of Unimolecular/Bimolecular Reactions in C_{10} and C_{11} Products.

from the analogous paraffins. The presence of a phenyl group on the chain may facilitate isomerization.

Changing zeolite unit cell size results in selectivity effects that can be explained on the basis of decreasing acid site density and zeolite adsorption properties.

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