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On Identifying the Primary and Secondary Products of the Catalytic Cracking of Cumene

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A thorough and fundamental study of the cumene cracking reaction has been carried out using a tubular packed bed reactor and a highly active lanthanum exchanged Y type zeolite catalyst. Over 60 reaction products have been observed and the selectivity behavior of the major ones has been examined using the concept of "optimum performance envelopes" in order to identify which products are primary and which are secondary. In this way benzene, ethyl benzene, *n*-propyl benzene, cymene, *m*- and *p*-diisopropyl benzene as well as propylene, *i*-butene and butene have been found to be primary products of the cumene reaction; whereas methane, ethylene, ethane, toluene, ethyl toluene, diethyl benzene and *i*- and *n*-butane are identified as the major secondary products. Based on these observations, a reaction network for the cumene cracking reaction is constructed. Chemical mechanisms by which the primary products arise are postulated on the basis of various considerations presented here and elsewhere in the literature. Of particular interest here is the competing influence of Brönsted and Lewis acids and the observation that at 360°C cumene dealkylation accounts for only 64% of the total cumene converted under initial conditions.

INTRODUCTION

In most previous studies benzene and propylene have been reported to be the only products of cumene cracking under a variety of conditions (*3*, *9*) encouraging the belief that here we have a simple example of a cracking reaction. Despite this reputed simplicity there is a great lack of uniformity in the way the kinetics of the cracking reaction are interpreted in the various studies. Not only are there several methods of measuring conversion but there are also a number of kinetic rate expressions used to interpret the experimental data. The use of various mathematical approaches to account for catalyst decay during the reaction compounds these difficulties. To make matters worse some workers (*22*, *23*, *25*) have reported an apparent "deficiency" of propylene in the reaction products as well as the presence of various minor products. We are therefore apparently faced not only with a system containing a decaying catalyst but also with one where the formation of numerous minor products may play an important role.

THEORY

One of the first theoretical discussions of selectivity behavior in an aging catalyst was attempted by Froment and Bischoff (*7*, *8*) who discussed the effect of catalyst decay on various types of selectivity patterns in fixed bed reactors. More recent attempts to describe catalyst selectivity with concomitant decay have been carried out by Sagara *et al.* (*28*) as well as by

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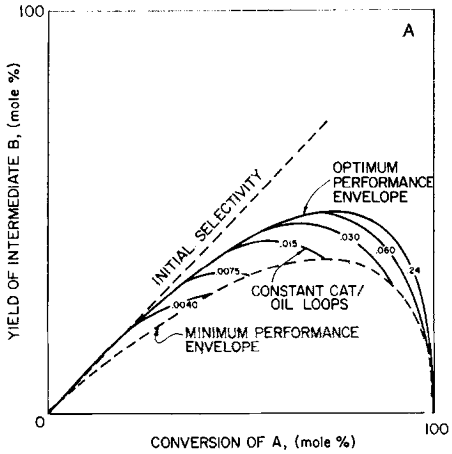

Fig. 1a. Catalyst selectivity plot for the mechanism A → B → C. The system shown exhibits Class II aging characteristics.

Riekert and Wei (*26*). Campbell and Wojciechowski (*4*) and Pachovsky *et al.* (*21*) developed a more general method of treating the selectivity behavior in gas oil cracking using a versatile *m*th order decay expression. This latter approach appears to have wide applicability and is used in this work to analyze the selectivity behavior in the cumene cracking reaction.

According to the technique of Cambell and Wojciechowski (*4*), the selectivity bebehavior of aging catalysts in a packed bed reactor is best seen by plotting time averaged yield against the time averaged conversion, with the cat/oil ratio as a parameter. In this way a system of constant cat/oil loops is generated as illustrated in Fig. 1a for Class II aging and in Fig. 1b and c for Class I and III decay.

For all classes of decay, the system of loops can be enveloped by a single curve called the optimum performance envelope (OPE) which represents the selectivity pattern for the same system in the absence of decay, or equivalently it represents the instantaneous selectivity for that product in the presence of decay. This OPE can be constructed as the curve obtained at a cat/oil ratio approaching infinity, but in practice it is approximated by the data from runs at short times on stream for which the effects of catalyst decay are small.

The curves shown (Fig. 1) represent typical selectivity patterns for a *primary unstable* reaction product. However, primary products can display two other basic behaviors as well and the OPE's for these are illustrated in Fig. 2. If an observed reaction product is a *stable primary* product, the OPE of the yield of that product will be a linear function of conversion as shown in Fig. 2. If the primary product is unstable, the shape will be that shown by the broken line which is also the OPE shown previously in Fig. 1. For both curves in Fig. 2a, the slope at the origin is nonzero and the degree of nonlinearity for the unstable product will depend on the rate of secondary reactions. The slope at the origin represents the ratio of the rate of formation of that primary product to the total rate of conversion of the feed.

The morphology of the secondary prod-

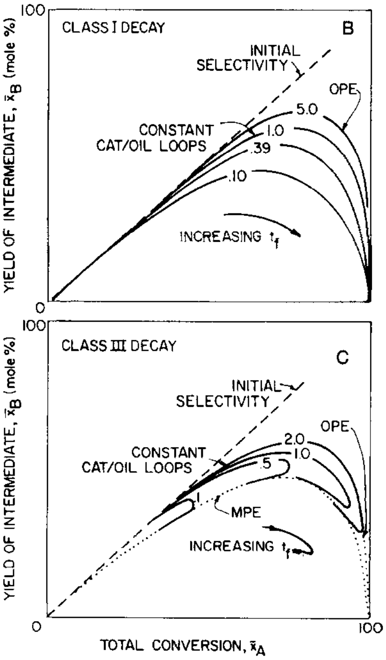

Fig. 1b and c. Catalyst selectivity for Class I and III decay for the mechanism A → B → C.

ucts is illustrated in Fig. 2b. Again, two cases might be expected: *stable secondary* products characterized by an increasing product yield with increasing conversion, and *unstable secondary* products which exhibit a decrease in yield after an initial increase. Unlike the OPE's of primary products those of secondary reaction products show a zero slope at the origin. A product which arises from both primary and secondary reactions and is stable will have an OPE such as that shown by the dotted line in Fig. 2a. For our present purposes these are all the types of OPE's we need to consider.

EXPERIMENTAL METHODS

The apparatus used in this work consisted of a fixed bed reactor shown schematically in Fig. 3. Cumene was charged to the top of the reactor by means of a positive displacement pump and was vaporized in the preheater section which contained alumina berl saddles. Below the saddles and located near the middle of the tube was the catalyst section. The catalyst in this zone was diluted to a constant volume of 15 cm^3 using ground glass of the same mesh size as the catalyst. The liquid products from the reaction were trapped in a pot located at the outlet of the reactor while the gaseous products passed through this pot and into gas burettes where they were trapped by the downward displacement of water.

In a typical run, the reactor was initially purged for 30 min with nitrogen. Following this, a measured volume of liquid cumene was pumped through the reactor at a constant rate [constant space time (τ)] over a given weight of catalyst [constant cat/oil ratio (P)] for a specified time t_f. This produced one point on the $\bar{x}$ vs t_f curve. Additional data were obtained at a constant P value by changing the rate at which the same quantity of cumene was pumped through the reactor. Various cat/oil loops were obtained by repeating the process with different weights of catalyst in the reactor.

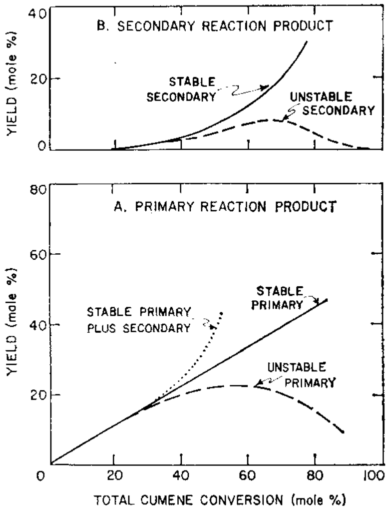

FIG. 2. Typical selectivity plots for primary and secondary reaction products.

The total liquid products collected during a run were analyzed chromatographically with a Chromosorb W column while a Poropak Q column was used to separate the gaseous products. In this manner mass balances in the order of 100% were obtained in all runs. In addition to the mass balance, an aromatic ring mole balance, side chain carbon mole balance, total carbon mole balance and total hydrogen mole balance were performed to ensure that all inputs were accounted for in the products. Conversion was defined as the moles of cumene reacted per mole of cumene fed and yield was defined as the moles of product observed per mole of cumene in the feed.

High boiling trace components were also analyzed by gas chromatography after being concentrated by distilling approximately 2 liters of reaction products under vacuum. The recovered residue amounted to approximately 5 cm^3 of which 70% was composed of diisopropyl benzenes together with a wide variety of minor constituents.

The catalyst used in this study was a LaY zeolite made by exchanging, calcining, and reexchanging a Linde SK40 molecular sieve in a $LaCl_3$ solution until no additional Na^+ could be exchanged. This material was

TABLE 1

Cumene Feed Composition[a]

Compound	Quantity in cumene
Benzene	0.0586
Toluene	0.0703
Ethyl benzene	0.186
Styrene	0.476
Cumene	100
n-Propyl benzene	0.0375
Ethyl toluene	0.0684
Cymene	0.0
m-Diisopropyl benzene	0.0370
p-Diisopropyl benzene	0.0081

[a] Mole% per mole of cumene.

pelletized and steamed for 24 hr, then crushed and sieved to yield the various mesh sizes used in this work. The cumene was supplied by Aldrich Co. and had the composition shown in Table 1.

RESULTS

In this study a total of 67 components have been isolated in the reaction products. Twenty-eight of these have been found to be light hydrocarbons up to a boiling point of 80°C and include most isomers of C_4, C_5, and C_6. The remaining fractions contain phenyl compounds, 29 of which have higher boiling points than dipropyl benzene and comprise less than 0.1% of the total liquid products. Positive identification of most of these compounds could not be made, but with the aid of a mass spectrometer the molecular weights were found to range up to 214.

Of major interest to us are those products which appear in concentrations of 0.01% or more. Eleven of these have been identified in the liquid products: benzene, toluene, ethyl benzene, styrene, cumene, *n*-propyl benzene, ethyl toluene, diethyl benzene, cymene, *m*-diisopropyl benzene and *p*-diisopropyl benzene. In the gases, we have found methane, ethane, ethylene, propylene, *i*-butane, *n*-butane, *i*-butene and butene.[3] Unfortunately, the propylene is present in such abundance that it could not be separated from any propane which may also be present in the products. For purposes of illustration the product composition from a typical run is shown in Table 2.

It was noted earlier that selectivity behavior for a given product can be characterized by the shape of the OPE and in this way one can determine whether the reaction product is primary or secondary, stable or unstable. Theoretical morphologies of such OPE curves are illustrated in Figs. 1 and 2. Examples of experimentally determined OPE curves for products which appear in amounts greater than 0.01 mole% are shown as the solid lines in Figs. 4a to g. The broken lines in these figures appear where necessary to distinguish the various cat/oil loops. Notice that the "origin" of these plots is taken to be the initial concentration of that compound in the feed.

The data reported in Fig. 4 have been obtained at a constant reaction temperature of 430°C using a 100/140 mesh catalyst. The initial selectivities of the primary products for reaction temperatures of 360, 430, and 500°C are listed in Table 3. As mentioned above, these were determined from the initial slopes of the appropriate selectivity plots.

DISCUSSION

Primary Product Analysis

The instantaneous conversion in a fixed bed reactor containing a catalyst which is subject to decay is obviously dependent on the catalyst activity at each moment during the run. The first differential segment of feed which meets the fresh catalyst is converted to some degree but each subsequent segment is cracked to a lesser extent on a less active catalyst. As a result the con-

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[3] In this context, butene refers to 1-butene, and 2-butene, both *cis* and *trans* since we have not examined this fraction in detail.

TABLE 2

Major Products Detected in the Catalytic Cracking of Cumene[a]

Product	Product type	Yield
Liquid[b]		
Benzene	Stable primary	43.2
Toluene	Secondary	0.26
Ethyl benzene	Stable primary	1.04
Styrene	Unstable impurity	0.0
(Cumene)		52.5
n-Propyl benzene	Stable primary and secondary	0.36
Ethyl toluene	Unstable primary	0.16
Cymene	Primary stable	0.16
Diethyl benzene	Unstable secondary	0.09
m-Diisopropyl benzene	Unstable primary	1.00
p-Diisopropyl benzene	Unstable primary	0.49
Gaseous[b]		
Methane	Secondary	0.10
Ethylene	Secondary	0.07
Ethane	Secondary	0.04
Propylene	Primary stable	41.4
i-Butene	Primary	0.38
Butene	Primary	0.28
n-Butane	Secondary	0.16
Butane	Secondary	0.14
Coke		
Wt% coke per g catalyst		11.9
Wt% coke per g of feed		0.39
Hydrogen/carbon mole ratio		0.382
Recovery		
Aromatic (mole%)		98.7
Side chain carbon (mole%)		100.7
Total carbon (mole%)		99.2
Total hydrogen (mole%)		99.3
Total mass (%) recovery		98.9

[a] Experimental data shown are for 100/140 mesh LaY at 430°C, cat/oil of 0.033 and time on stream of 85.5 sec.

[b] Mole %/mole of pure cumene in feed.

version from the reactor after some time t_f is an averaged value and dependent on t_f. Similarly the average selectivity is also a function of catalyst time on stream. In previous discussion it was noted that the difference between the instantaneous yield and average yield is small at short on stream times when catalyst decay is not significant. Therefore, data obtained under these conditions can be used to approximate the optimum performance envelopes.

We have discussed above the fact that if the OPE for a given product has a nonzero initial slope then that reaction product is primary. In this way, nine primary reaction products have been identified in concentrations of 0.01% or greater and are listed in Table 3 with their initial selectivities for the three reaction temperatures used in this work. Also shown in Table 3 is a more detailed classification of these products. As noted earlier, primary products can be further categorized as being stable primary, unstable primary or stable primary plus secondary depending on the morphology of the selectivity plots shown in Figs. 4a to g.

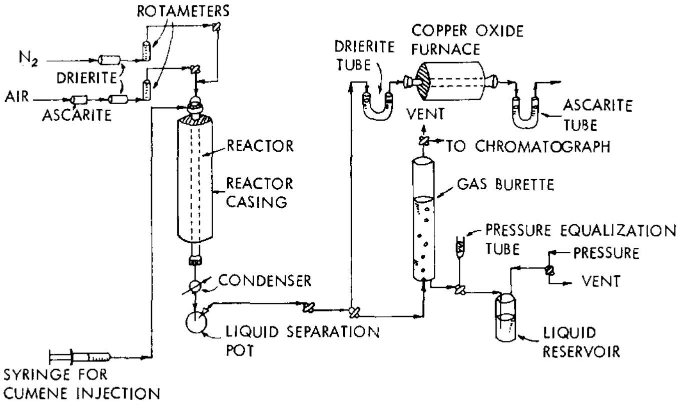

FIG. 3. Schematic diagram of apparatus.

Complete data for all reaction temperatures and also for the various mesh sizes of catalyst appear elsewhere (*1*).

That benzene and propylene have been found to be primary is not surprising. Greensfelder *et al.* (*10*) studied the cracking behavior of a number of selected hydrocarbons and reported that, for the dealkylation of aromatics, the prominent gaseous components corresponded exactly in structure to the original alkyl group on the benzene ring. Their data and that of others (*22*, *31*) encouraged the belief that the reaction is almost exclusively a severence of the entire alkyl group from the benzene ring. Both Thomas (*31*) and Greensfelder *et al.* (*10*) have proposed theories to account for this phenomenon but it is generally accepted that the mechanism is a Friedel-Crafts type of dealkylation and involves the steps illustrated in Fig. 5. At high temperatures equilibrium is shifted to the right and dealkylation predominates over alkylation. The selectivities for the formation of benzene or propylene in Table 3 bear this out. However, as the temperature decreases, disproportationation becomes more significant and at the lowest temperature studied only 64% of the cumene (based on propylene yield) dealkylates directly to benzene and propylene. Consequently, the total disappearance of cumene is not a good measure of the extent of the cracking reaction and serious errors will occur if such data are used to determine the corresponding reaction kinetics. This will also be the case if

TABLE 3

Initial Slopes of the Primary Reaction Products of the Cumene Cracking Reaction

Product	Type	Initial selectivity		
		500°C	430°C	360°C
Benzene	Primary stable	0.952	0.904	0.786
n-Propyl benzene	Primary + secondary	0.0030	0.0031	0.0028
Cymene	Primary stable	0.0028	0.0033	0.0130
m-Diisopropyl benzene	Primary unstable	0.0135	0.0335	0.0850
p-Diisopropyl benzene	Primary unstable	0.0070	0.0199	0.058
Propylene	Primary stable	0.930	0.870	0.640
i-Butene	Primary + secondary	0.0020	0.0040	0.0095
Butene	Primary + secondary	0.0038	0.0048	0.0072

the rate of production of benzene is used as a measure of the rate of reaction of cumene. It is shown below that benzene is formed in significant amounts through primary disproportionation reactions as well as the main dealkylation reaction.

The reversible nature of the mechanism for benzene formation and the existence of a propyl ion that can isomerize to the *n*-propyl form suggests that *n*-propyl benzene can be formed as a secondary reaction product. As shown in Fig. 4c this is the case. It is also apparent from Fig. 4c that *n*-propyl benzene is produced as a primary reaction product. Such isomerization of isopropyl benzene to the *n*-propyl form has been reported by Neitzescu *et al.* (*19*, *20*) and others (*6*, *27*) during the heating of isopropyl benzene with $AlCl_3$ at 100°C. In the opinion of Neitzescu, the isomerization of the side chain is caused by the removal of a hydride ion from the molecule, resulting in the formation of a carbonium ion which then undergoes rearrangement as shown in Fig. 6. Notice in this figure that a hydride shift as well as a methyl shift is involved. A similar mechanism was proposed by Douglas and Roberts (*6*), however, in this proposal far less movement is involved since a phenonium ion intermediate is postulated as shown in Fig. 7. We prefer this mechanism because of its obvious simplicity.

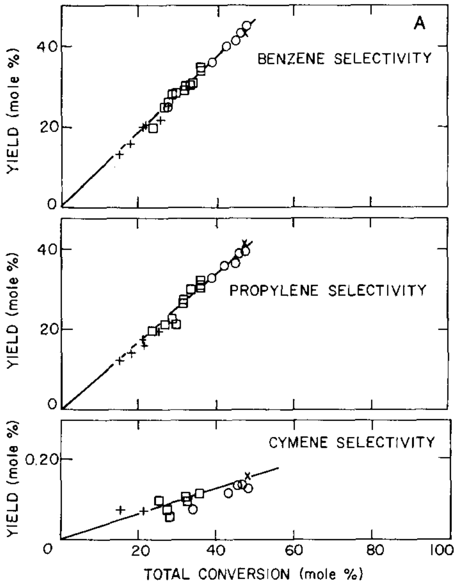

FIG. 4a. Selectivity plots for benzene, propylene and cymene at 430°C on 100/140 LaY catalyst. The symbols represent the following cat/oil ratios: (+) 0.004; (□) 0.008; (○) 0.016; (×) 0.033.

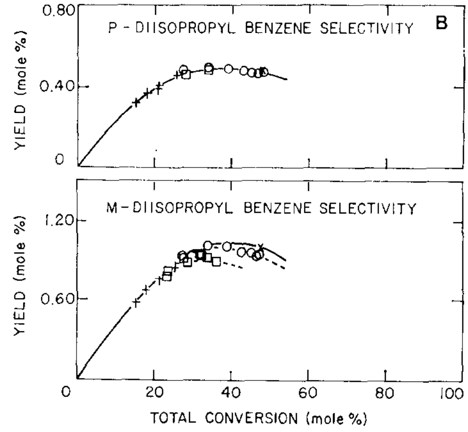

FIG. 4b. Selectivity plot for *p*- and *m*-diisopropyl benzene at 430°C on the 100/140 mesh LaY catalyst. The symbols represent the following cat/oil ratios: (+) 0.004; (□) 0.008; (○) 0.016; (×) 0.033.

Both mechanisms require initiation through hydride ion extraction which can be provided by the Lewis acid centers on the zeolite. Both mechanisms also allow for the production of either 1-phenyl-1-propylene or 3-phenyl-1-propylene. It is unlikely, however, that these products will be observed. At the reaction temperatures used in this study, the equilibrium is almost completely on the side of the saturated alkyl product which results from the replacement of the originally abstracted hydride ion and hence, in a way, is the reverse of the first step in the reaction.

From Table 3 it can be seen that *m*- and *p*-diisopropyl benzene are also primary products of the reaction in which case the diisopropyl benzenes must result from a disproportionation reaction of cumene, and not an alkylation of cumene with propylene. This is in complete agreement with the observations of Murakami *et al.* (*18*) who have

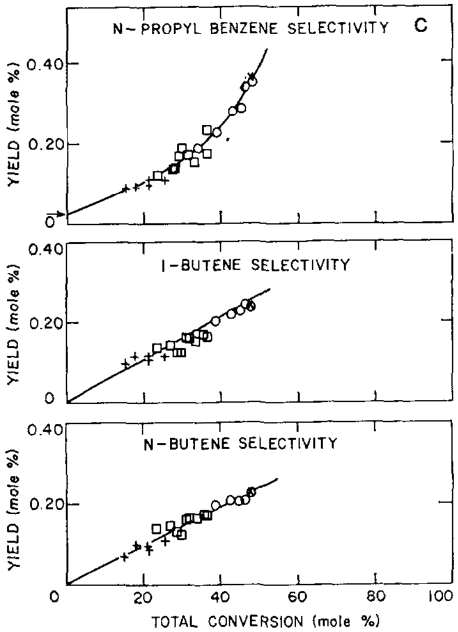

FIG. 4c. Selectivity plots for *n*-propyl benzene, *i*-butene and butene at 430°C on 100/140 mesh LaY catalyst. The symbols represent the following cat/oil ratios: (+) 0.004; (□) 0.008; (○) 0.016; (×) 0.033.

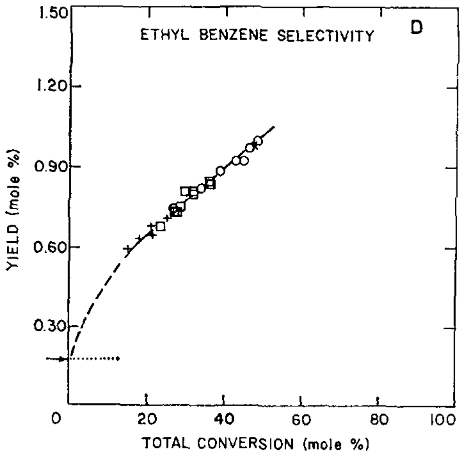

FIG. 4d. Selectivity plot for ethyl benzene at 430°C on 100/140 mesh LaY catalyst. The symbols represent the following cat/oil ratios: (+) 0.004; (□) 0.008; (○) 0.016; (×) 0.033.

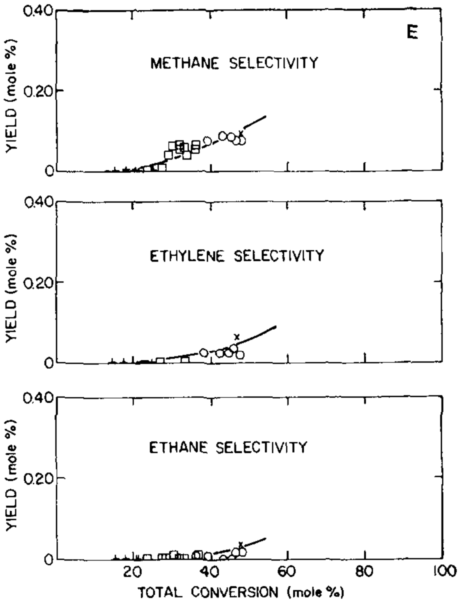

FIG. 4e. Selectivity plots for methane, ethylene and ethane at 430°C on 100/140 mesh LaY catalyst. The symbols represent the following cat/oil ratios: (+) 0.004; (□) 0.008; (○) 0.016; (×) 0.033.

found that propylene was not involved in the production of the dialkyl product. Shine (*29*) noted that the ease of the disproportionation increases with increasing ability of the alkyl group to support a positive charge. However, it appears from our results that it is not necessary for the alkyl group to become free of the aromatic ring prior to its transfer. In fact, Shine himself reviews evidence to show that with the possible exception of *t*-alkyl groups, the side chain remains associated with the aromatic nucleus at all stages of the transfer. To account for this McCaulay and Lien (*15*) have proposed the mechanism illustrated in Fig. 8. According to this mechanism initiation is through proton addition, but before the dealkylation reaction occurs there is an attack by a benzene ring at the alpha carbon of the alkyl group to form a partial bond. Evidence for this comes from the fact that neopentyl benzene is inert under conditions that cause rapid disproportionation of ethyl benzene (*15*). With neopentyl benzene it is thought that the *t*-butyl portion of the neopentyl group blocks the backside approach of the attacking benzene ring.

The ratio of the diisopropyl benzene isomers was found in this study to be approximately 2:1 *meta* to *para*. Some *ortho* was also observed but in such small amounts that it could not be measured accurately. Such a predominance of the meta isomer is an interesting observation as the alkyl group of the attacking species is normally *ortho–para* directing. Consequently, one would anticipate the major product in the diisopropyl benzene fraction to be the *para* form as observed by Melpolder *et al.* (*16*). These workers found that the dialkyl benzene fraction obtained from the isopropylation of benzene in the presence of phosphoric acid supported on kieselguhr consisted of 6% *o*-, 36% *m*-, and 42% *p*-diisopropyl benzene. Obviously then the problem of orientation of the alkyl groups is a complex one, and is the result not only of the directing effect of the side chain but also of the steric constraints involved in the reaction. In addition, the severity of the reaction conditions, i.e., the strength, type of catalyst, and reaction temperature may also have some influence (*14*). It should also be pointed out that at the lowest temperature of 360°C the average *m*/*p* ratio is somewhat less than 2 in our study. This supports the hypothesis that something other than a random attack at the *m*- or *p*-positions occurs.

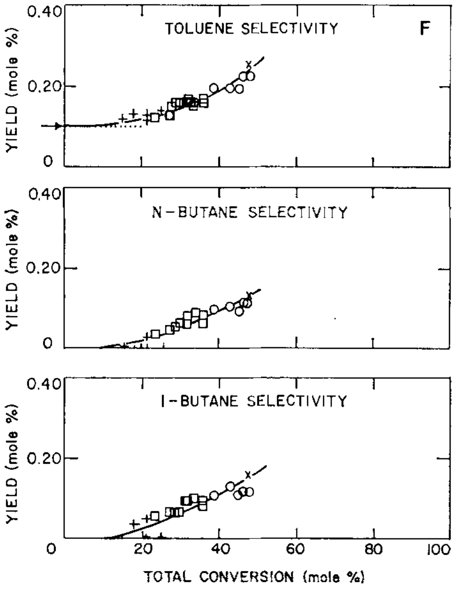

Fig. 4f. Selectivity plot for toluene, *n*- and *i*-butane at 430°C on the 100/140 mesh LaY catalyst. The symbols represent the following cat/oil ratios: (+) 0.004; (□) 0.008; (○) 0.016; (×) 0.033.

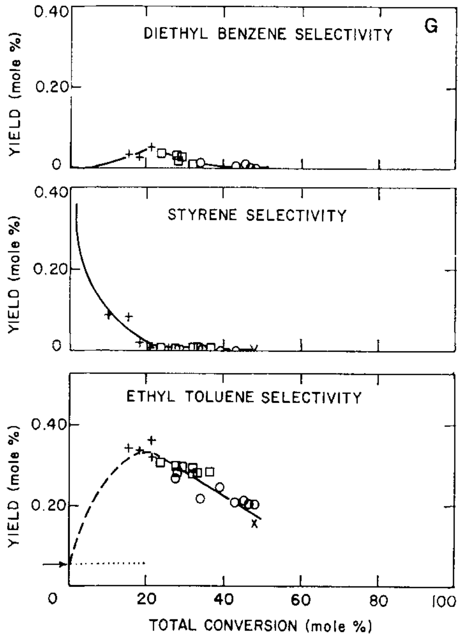

Fig. 4g. Selectivity plot for diethyl benzene, styrene and ethyl toluene at 430°C on the 100/140 mesh catalyst. The symbols represent the following cat/oil ratios: (+) 0.004; (□) 0.008; (○) 0.016; (×) 0.033.

One final question concerning the dialkyl benzene product is whether the product is diisopropyl benzene or a combination of the normal and iso forms. There is no experimental evidence in this work to indicate that the disproportionation product is entirely the diiso-form. However, Kinney and Hamilton (*13*) and others (*29*) showed that the disproportionation as well as the reverse transfer of the alkyl group to benzene is not accompanied by isomeric changes of the aliphatic chain. Consequently, the reaction products for disproportionation are expected to be largely the iso form.

The other primary products observed in this study are butene, isobutene, cymene and ethyl benzene. The last two compounds

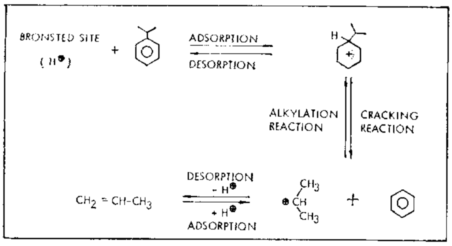

FIG. 5. Mechanism for the dealkylation of cumene.

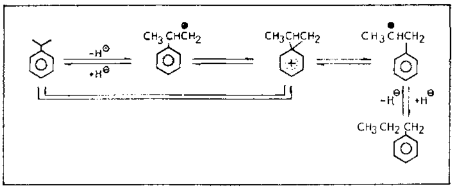

FIG. 7. Mechanism for cumene isomerization using a phenonium ion intermediate (*6*).

are also thought to be the result of a hydride extraction as illustrated in Fig. 9. In the second step of this mechanism the attack of the nucleophilic benzene ring must occur before a hydride shift takes place on the alkyl group, in which case diisopropyl benzene could be produced. (It is unlikely that diisopropyl benzene will form via this route, however, as the resulting ion would be a phenonium ion.) In the last step, proton elimination could occur with the subsequent formation of styrene. However, this product is thermodynamically unstable (see Fig. 4g) and the addition of the hydride ion from the adsorption site seems to be the favored reaction.

Butene has been reported as a primary product for gas oil cracking (*11*), but its presence as a primary product for cumene cracking was a great surprise to us. The mechanism which explains its appearance as a primary product evolved from the following considerations. If a cumene carbonium ion is formed by a hydride extraction from the alkyl group, then an attack by the benzene ring of a second cumene molecule will produce ethyl benzene/cymene as previously discussed. We postulate here that a C_4 olefin is formed if the attack by the second cumene molecule takes place via the alkyl group instead of the benzene ring. Such a mechanism is shown in Fig. 10. If the initial hydride extraction occurs from the α carbon of the side chain, then *i*-butene will be formed from the unstable intermediate *t*-butyl benzene. On the other hand if the hydride ion is removed from a β carbon, butene will be formed.

Notice that in this mechanism and also in the mechanism for diisopropyl benzene formation, benzene is formed as a primary reaction product. Consequently the total benzene yield and therefore the initial selectivity for benzene shown in Table 3 consists of three components: those from the two types of disproportionation reactions and that from the dealkylation reaction. The latter quantity can be estimated by subtracting from the total benzene yield the amount formed through the various disproportionations. When this "corrected" benzene yield is plotted against propylene yield in Fig. 11 it can be seen that, within experimental accuracy, the two yields are equal. Therefore, what many workers (*5*,

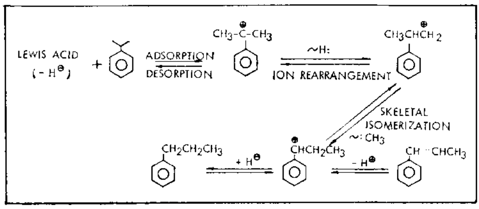

FIG. 6. Neitzescu's mechanism for the isomerization of isopropyl benzene to *n*-propyl benzene (*20*).

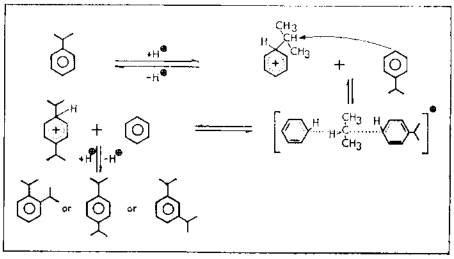

FIG. 8. Mechanism for diisopropyl benzene formation from cumene (*15*).

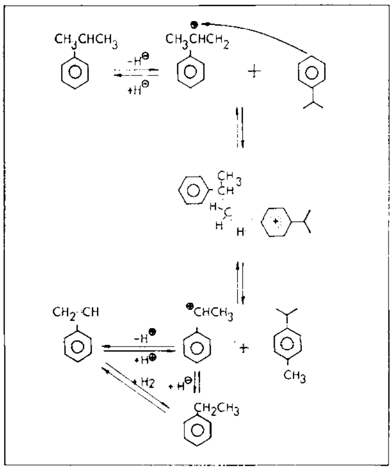

FIG. 9. Mechanism for the formation of cymene and ethyl benzene.

22) call a "deficiency of propylene" in fact is an "excess of benzene" which results from the two side reactions discussed above.

Effect of Regeneration Temperature on Primary Product Yield

It is well established (*30*) that both Brönsted and Lewis acid sites can be present in Y type zeolites. If the former are responsible for reactions initiated by proton addition while the latter are involved in the hydride extraction reactions, then any procedure which would preferentially reduce either of these site densities would be an important test of the above mechanistic postulates.

With this objective in mind we have made use of the well-known fact that the Lewis acid site concentration increases with increasing catalyst calcination temperature, whereas the concentration of Brönsted sites remains constant between 400 and 500°C before decreasing. Consequently, if hydride extraction occurs in our system and if Lewis sites are responsible, one should observe an increase in the yield of products formed via hydride extraction reactions as the catalyst pretreatment temperature is increased. Conversely the yield of products initiated through proton addition would decrease with increasing calcination temperature. Therefore, to test if and where Lewis and Brönsted sites are involved in the above mechanisms, the effect of regeneration temperature on product selectivity was studied and the results are reported in Fig. 12.

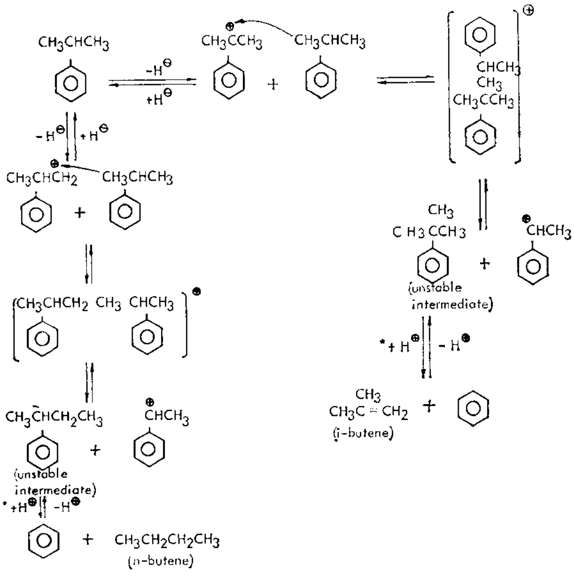

FIG. 10. Mechanism for butene and isobutene formation. (The steps marked by the asterisk indicate cracking via the mechanism illustrated in Fig. 5.)

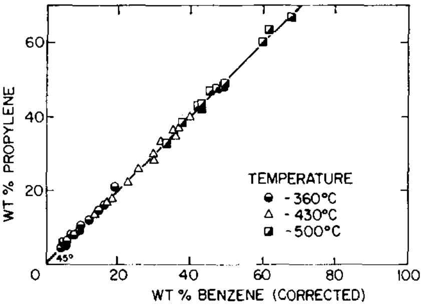

FIG. 11. Corrected benzene yield plotted against the total propylene yield for the 100/140 mesh data at all reaction temperatures studied.

TABLE 4

Secondary Reaction Products from Cumene Cracking Reaction

Product	Type
Toluene	Secondary stable
Methane	Secondary stable
Ethane	Secondary stable
Ethylene	Secondary stable
i-Butane	Secondary stable
n-Butane	Secondary stable
Ethyl toluene	Secondary unstable
Diethyl benzene	Secondary unstable

As shown in Fig. 12 the yield of *n*-propyl benzene and cymene does indeed increase over some range of temperatures with increasing calcination temperature. Recall that in both these cases initiation was postulated to be through hydride extraction. The analogous behavior demonstrated by coke strongly suggests that it may result from hydride extraction as well. On the other hand, the yields of benzene, propylene and the diisopropyl benzenes, which are thought to be initiated by proton addition, decrease. The behavior of isobutene and butene is also consistent with the previously postulated mechanisms for their formation. In both these cases, initiation is thought to be by hydride extraction but a proton addition is also postulated in the subsequent dealkylation of the unstable intermediate butyl benzene. These two processes would tend to compensate each other as the regeneration temperature is increased with the result that the butene yields would be expected to be almost independent of regeneration temperature as shown in Fig. 12. The yields of cymene, coke and *n*-propyl benzene are also seen to decline at calcination temperatures above 480°C. Such behavior is not completely clear to us and consequently no attempt is made at this time to explain this observation. This last set of results is clearly very sketchy and is included here only to show how a study of

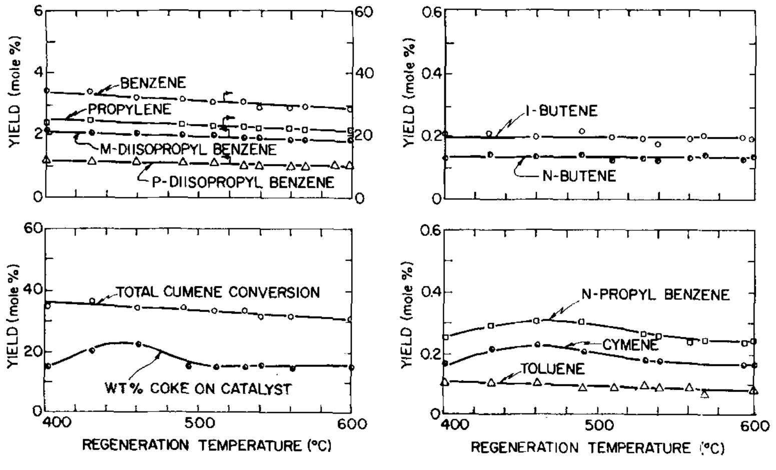

FIG. 12. Effect of regeneration temperature on product selectivity. In all cases, regeneration was carried out for 5 hr.

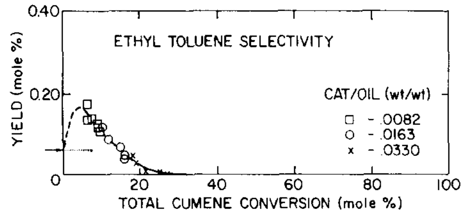

FIG. 13. Selectivity data for ethyl toluene for 100/140 mesh catalyst at 360°C.

catalyst acidity may be undertaken using a kinetic approach to this problem.

Secondary Product Analysis

Up to this point, the discussion has been concerned with primary reaction products and the possible mechanisms by which these are produced. A number of other products have been observed that show zero slope at the origin of the selectivity plot and consequently have been classified as secondary in Table 4. Unfortunately since several mechanisms could be written to describe the formation of most of these products, they provide little insight into cumene cracking. They, and the trace components, do however, confirm the complexity of the reaction. As indicated previously, a total of 47 products in trace quantities have been observed including many of molecular weight greater than diisopropyl benzene.

TABLE 5

A Summary of the Primary Reaction Products to Indicate Whether they Result from Hydride Extraction (Lewis Acid) or Proton Addition (Brönsted Acid)

Product	Initiation
Benzene	Proton addition
Propylene	Proton addition
m-, *p*-Diisopropyl benzene	Proton addition
n-Propyl benzene	Hydride extraction
Cymene	Hydride extraction
Ethyl benzene	Hydride extraction
(Coke)[a]	Hydride extraction
Butene, *i*-butene	Hydride extraction followed by proton addition

[a] Secondary product but included for reference.

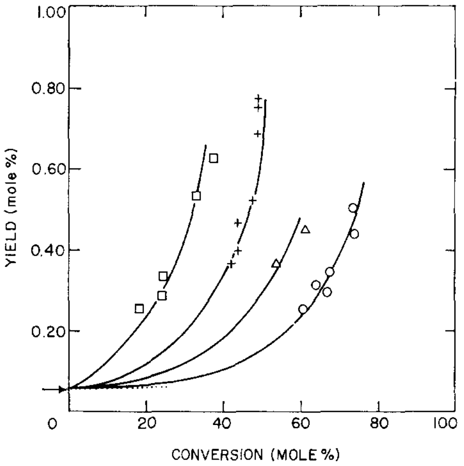

FIG. 14. Selectivity data for ethyl toluene for the 100/140 mesh catalyst at 500°C. The symbols on the plots represent the following cat/oil ratios: (□) 0.004; (+) 0.008; (△) 0.016; (○) 0.033.

Nearly all the secondary products of the reaction display selectivity patterns typical of the theoretical morphologies discussed above. Ethyl toluene, however, seems to be an exception. Selectivity data for this compound at 430 and 360°C are illustrated in Figs. 4g and 13, respectively, and it is obvious from these figures that this compound is consumed during the course of a reaction. It is equally apparent that the initial slope of these data is nonzero, thereby indicating that ethyl toluene is in fact a primary product. On the other hand in Fig. 14 obvious secondary characteristics are observed at a reaction temperature of 500°C. This apparent inconsistency can be explained if the following reaction is postulated for the formation of ethyl toluene:

ethyl benzene + cumene →
ethyl toluene + ethyl benzene.
↓
decomposition
products

If a significant portion of the ethyl benzene reactant comes from the hydrogenation of styrene impurity (a thermodynamic analy-

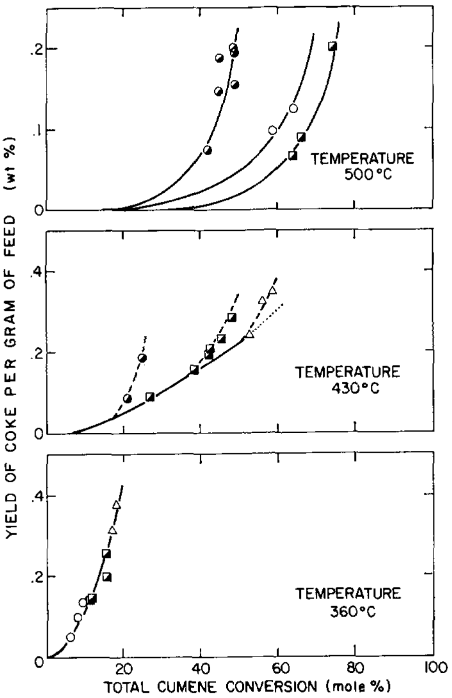

FIG. 15. Selectivity plot for coke at 500, 430, and 360°C. The catalyst was the 100/140 mesh LaY and the symbols on the plots represent the following cat/oil ratios: (◐) 0.004; (○) 0.008; (◪) 0.016; (△) 0.033.

sis indicates that nearly complete reduction of styrene will occur under the conditions studied here), then the ethyl toluene formed from such ethyl benzene would give the appearance of being a primary product, particularly at low cumene conversions. To test if styrene has such an effect on ethyl toluene production one can see if an increase in initial styrene contaminant will result in an increase in the yields of both ethyl benzene and ethyl toluene. This in fact has been found to be the case as shown in Fig. 17. Thus it seems that ethyl toluene is in fact a secondary product of the reaction.

It is also of some interest to consider here the selectivity pattern for the coke formed during the reaction. There appears to be no clear definition of coke but in this work it denotes the hydrogen deficient carbonaceous material remaining on the catalyst after postreaction stripping by N_2 for 30 min at 500°C. From Fig. 15 it can be seen that this material demonstrates secondary selectivity behavior not unlike that observed by John *et al.* (*12*) for gas oil cracking on a zeolite catalyst. This behavior might have been anticipated in view of the work by Blue and Engle (*2*) and others which suggest that the presence of olefins in the reacting medium is essential for coke formation. Moreover, all the postulated mechanisms for coke formation involve reactions of olefins, which are not present in the cumene feed.

Effect of Adding Styrene to the Feed

As mentioned above, some styrene was present in the feed and it was necessary to consider how this may affect the product distribution. To determine the influence of styrene experiments were carried out with cumene which contained various amounts of added styrene and which was cracked at 430°C and 283 sec time on stream. The results are plotted in Figs. 16 and 17.

The effects of styrene contaminant on the

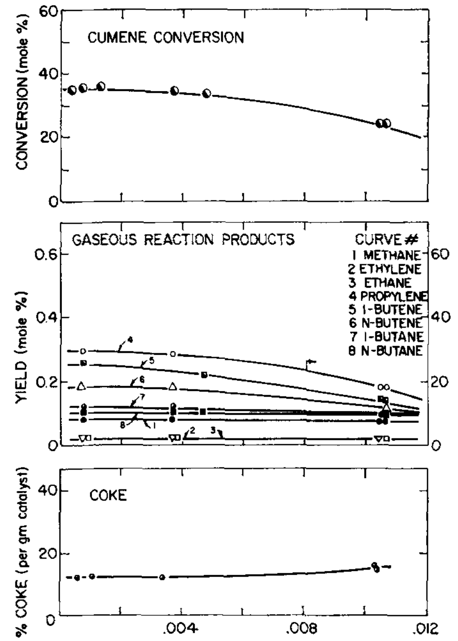

FIG. 16. Effect of styrene on cumene conversion, yield of gaseous reaction products and coke.

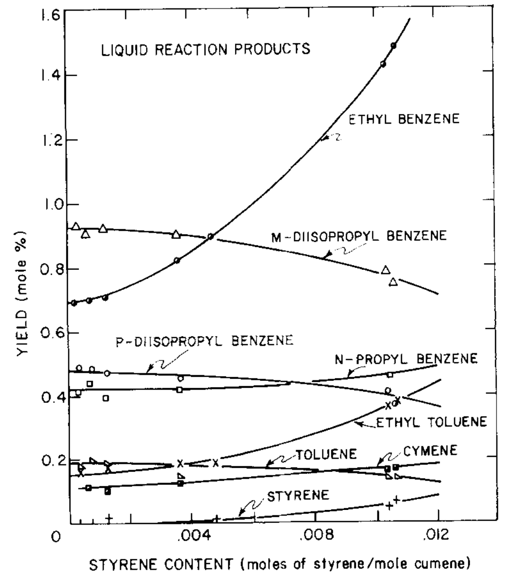

FIG. 17. Effect of styrene on yield of liquid products in a standard run.

yields of the various reaction products are consistent with all previous considerations. For example, it can be seen that increasing the styrene content of the feed results in a significant increase in ethyl benzene and ethyl toluene yield in spite of the inhibiting effect it has on the overall reaction. Cymene and *n*-propyl benzene, which are thought to be the result of a hydride extraction, show a slight increase as well. This is thought to be a consequence of an increase in the concentration of ethyl benzene carbonium ions acting as hydride extractors, and is not unlike the results reported by Miale and Weisz (*17*). In cracking *n*-butane at 250°C these workers found that conversion could be increased from 0 to 17% by the addition of trace quantities of an olefin to the charge. A similar increase in the yield of butene and *i*-butene should also be observed with increasing styrene contaminant but is not. One explanation for this might be that any increase in yield was negated by a simultaneous decrease that results from a decrease in conversion alone. Such behavior is confounded by the fact that butenes are not formed solely by hydride extraction but require a proton addition step as well. The remaining products appear unaffected by styrene and increase or decrease in a fashion consistent with that expected to be caused by changing conversion.

In Fig. 16 it can be seen that increasing styrene concentration in the feed results in a decrease in cumene conversion; hence it can be reasonably argued that large quantities of styrene act as an inhibitor in the cumene cracking reaction. Moreover, one might suspect that the reduction of styrene

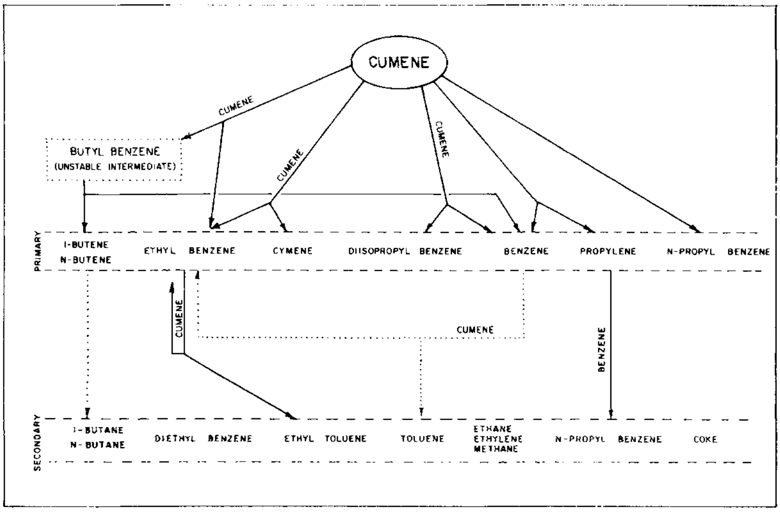

FIG. 18. A reaction network for the cumene cracking reaction.

consumes Brönsted acid hydrogens, resulting in a decrease in the rate of cumene dealkylation which is the dominant reaction on such sites.

As there is little increase in coke yield with increasing styrene contamination, it appears that the coke does not result from the strong adsorption of this inhibitor; in other words, that styrene is not a precursor to coke. This contradicts the results of Plank and Nace (*23*) and Prater and Lago (*24*). Both groups of workers studied the effects of various inhibitors on coke yield in the cumene cracking reaction and concluded that these inhibitors are the sole source of coke.

CONCLUSION

We have shown that a selectivity study based on optimum performance envelopes can be used to interpret the nature of the reaction products from the catalytic cracking of cumene on an aging catalyst. Two main categories exist: primary products and secondary products. Included in the first are benzene, ethyl benzene, *n*-propyl benzene, cymene, *m*- and *p*-diisopropyl benzene, propylene, *i*-butene and butene. In the secondary category we observe toluene, ethyl toluene, diethyl benzene, methane, ethane, ethylene, *i*-butane and *n*-butane. Based on these observations, a reaction network has been developed for the cumene reaction and is presented in Fig. 18.

It is obvious from Fig. 18 that the reaction of cumene on a LaY zeolite catalyst is by no means a simple reaction. Of particular interest to the chemist is the postulated occurrence of competing hydride extraction and proton addition reactions which are summarized in Table 5. If our postulates are correct then it appears that one can alter the selectivity behavior of the catalyst simply by changing the proportions of the active sites on the catalyst and that LaY can therefore be considered a bifunctional catalyst.

Finally, we have shown why the kinetics of the dealkylation reaction cannot be studied by measuring the total disappearance of cumene. Instead, the preferred technique is to use the yield of benzene which has been corrected for any benzene formed in other primary reactions. A simpler alternative consists of using the yield of propylene without corrections.

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