



Alumina activated with anhydrous hydrogen fluoride as a dealkylation catalyst for aromatic hydrocarbons  
by Emil O Kindschy

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering  
Montana State University  
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**Abstract:**

The purpose of this investigation was to evaluate anhydrous hydrogen fluoride activated alumina as a dealkylation catalyst for aromatic hydrocarbons.

Toluene, ethyl benzene, xylenes, isopropyl benzene, diethyl, benzenes, monoamyl benzene, diamyl benzene, and triamyl benzene Were the aromatic hydrocarbons investigated.

The average run charged about 600 cc. of aromatic hydrocarbon over 900 cc. of catalyst at a space velocity of approximately 0.5 volume per volume of catalyst per hour, and at atmospheric pressure. The temperature that yielded the most dealkylated and the least alkylated products was found for xylene and monoamyl benzene and this temperature used throughout the balance of the investigation.

Runs were made using alumina unactivated with anhydrous hydrogen fluoride to obtain a standard of comparison for those runs with hydrogen fluoride treated alumina.

All the aromatic hydrocarbons used except toluene were successfully dealkylated. Isopropyl benzene and the amyl benzenes were, dealkylated practically quantitatively. Alkylation took place with the xylenes and ethyl benzene.

Benzene was found to be the ultimate dealkylation product of every aromatic hydrocarbon with two or more carbon atoms in every branch chain, while toluene was the ultimate dealkylation product of any aromatic hydrocarbon that contained only one carbon atom in any of its branch chains.

The data obtained also showed that as the temperature increased, other conditions being held constant, dealkylation increased and alkylation decreased. 'All aromatic dealkylation products were the result of carbon-carbon fission at the benzene ring.

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AS A DEALKYLATION CATALYST FOR AROMATIC  
HYDROCARBONS

by

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## ABSTRACT

The purpose of this investigation was to evaluate anhydrous hydrogen fluoride activated alumina as a dealkylation catalyst for aromatic hydrocarbons.

Toluene, ethyl benzene, xylenes, isopropyl benzene, diethyl benzenes, monoamyl benzene, diamyl benzene, and triamyl benzene were the aromatic hydrocarbons investigated.

The average run charged about 600 cc. of aromatic hydrocarbon over 900 cc. of catalyst at a space velocity of approximately 0.5 volume per volume of catalyst per hour and at atmospheric pressure. The temperature that yielded the most dealkylated and the least alkylated products was found for xylene and monoamyl benzene and this temperature used throughout the balance of the investigation.

Runs were made using alumina unactivated with anhydrous hydrogen fluoride to obtain a standard of comparison for those runs with hydrogen fluoride treated alumina.

All the aromatic hydrocarbons used except toluene were successfully dealkylated. Isopropyl benzene and the amyl benzenes were dealkylated practically quantitatively. Alkylation took place with the xylenes and ethyl benzene.

Benzene was found to be the ultimate dealkylation product of every aromatic hydrocarbon with two or more carbon atoms in every branch chain, while toluene was the ultimate dealkylation product of any aromatic hydrocarbon that contained only one carbon atom in any of its branch chains. The data obtained also showed that as the temperature increased, other conditions being held constant, dealkylation increased and alkylation decreased. All aromatic dealkylation products were the result of carbon-carbon fission at the benzene ring.

## I INTRODUCTION

The purpose of this investigation is to evaluate hydrogen fluoride activated alumina as a dealkylation catalyst for aromatic hydrocarbons.

Hydrogen fluoride activated alumina was selected as a catalyst because hydrogen fluoride has been used as a dealkylating as well as an alkylating catalyst for aromatic hydrocarbons. Brandt et al (2) used liquid anhydrous hydrogen fluoride as a catalyst in the dealkylation of xylenes to toluene. Their investigation also showed that trimethyl benzene is formed concurrently by alkylation of the xylene. Frey (5) dealkylated polyethyl benzenes in the presence of an excess of benzene and a catalyst of anhydrous liquid hydrogen fluoride to form ethyl benzene.

Alumina impregnated with aqueous zinc chloride was used to dealkylate xylenes and other polymethyl benzenes to toluene and also polyethyl benzenes to ethyl benzene (14). An alumina and silica catalyst was used to dealkylate dialkyl benzenes (9). Mattox (12) used a catalyst of alumina and other metal oxides in the "dealkylation" of diethyl benzene to xylene.

That alkylation as well as dealkylation could take place might be expected from previous uses of hydrogen fluoride as an alkylating catalyst. Frey (4)(5) alkylated benzene using light olefins as the alkylating agents and substantially anhydrous liquid hydrogen fluoride as the catalyst. Koch (8)

alkylated the products of "Kogasin" synthesis (hydrocarbons from the Fischer-Tropsch process) in the presence of anhydrous hydrogen fluoride and converted them into high-octane fuels similar to isooctane. A number of other investigations have reported hydrogen fluoride to be an alkylating catalyst (3), (10), (11), (13), (15).

Alumina has been used as a catalyst in the alkylation of aromatic hydrocarbons. Ipatieff and Monroe (6) used oxides of aluminum in the alkylation of benzene to toluene, and alumina with magnesium chloride was used to alkylate aromatic hydrocarbons in another investigation (7).

Because of the alkylating effect of hydrogen fluoride and alumina when used separately, part of this investigation was concerned with the alkylation effect of the alumina when activated with anhydrous hydrogen fluoride. This investigation is primarily, however, a study of the dealkylation reaction.

Data were not available in the literature on the dealkylation effect of alumina alone under the reaction conditions employed in this investigation. It was necessary, therefore, to make several runs with alumina unactivated by hydrogen fluoride in order to obtain a standard of comparison for those runs with hydrogen fluoride treated alumina.

This study was not concerned with the determination of the optimum conditions of space velocity and pressure in the

dealkylation system. All runs were conducted at essentially atmospheric pressure and the liquid space velocity was held in the neighborhood of 0.5 vol. per vol. of catalyst per hour. The optimum temperature at this pressure and space velocity, however, was readily determined.

As it was not feasible to attempt the dealkylation of all the known aromatic hydrocarbons, a representative group was selected. Toluene, xylenes, ethyl benzene, diethyl benzenes, isopropyl benzene, monoamyl benzene, diamyl benzenes, and triamyl benzenes were chosen to be the dealkylated reagents. These compounds are all available commercially in a fairly pure state and were, therefore, not subjected to further purification.

The boiling temperatures of compounds used or formed in this investigation were not corrected to standard pressure since no precise method is available to make this conversion. The average barometric pressure during this study was approximately 635 mm. Hg.



## II EQUIPMENT, METHODS, AND MATERIALS

## A. Equipment

The equipment used in this investigation consisted of the reaction system shown in Figure 1, iron-constantan thermocouples, a potentiometer, a precision rectification column, a graduated water-cooled receiver for the column, a vacuum system, three glass stem mercury thermometers, a Claisson type distillation flask with condenser, a ceramic heater, a one liter distillation flask, a Harvard type triple beam balance, a refractometer, and four autotransformers.

The reactor was made from a piece of three inch standard mild steel pipe 24 inches long. Black pipe was used instead of galvanized to avoid vaporization of the zinc at the elevated temperatures of the reactions. The pipe was threaded at both ends with the bottom end capped and the top end fitted with a flanged head for easy removal. The thermowells were made from pieces of 1/8 inch standard steel pipe 4-3/4 inches long and sealed at one end. The lower thermowell was placed two inches from the bottom of the reactor. The middle and upper thermowells were spaced at four inch intervals above the lower one. The catalyst bed extended from just below the bottom thermowell to within 1/2 inch of the top thermowell. Holes, 13/32 inch in diameter, were drilled in the reactor at these points and the thermowells, when welded to the reactor wall, extended into the exact

center of the catalyst space. The iron-constantan thermocouples were connected to a Brown potentiometer. This potentiometer was calibrated in millivolts and could be used to record temperatures up to  $1200^{\circ}\text{C}$ . The millivolt readings were converted into degrees Centigrade using a standard conversion table for iron-constantan thermocouples with the reference junction at  $0^{\circ}\text{C}$ .

Two  $3/8$  inch low carbon steel rods were welded onto the reactor on the opposite side from the thermowells to act as supports for the reactor chamber. These rods were eleven inches long.

The reactor was wrapped with asbestos tape. Over this tape, 75 feet of nichrome wire with a resistance of 1.079 ohms per foot was wound. This winding drew 2.95 amperes from a 220 volt autotransformer. The winding was covered with asbestos tape and another resistance winding 33 feet long placed over it. The second winding was connected to a 110 volt autotransformer and drew about seven amperes. This second winding was covered with asbestos tape and then a one inch layer of magnesia was placed over all the windings and tape.

The malleable iron caps at the top and bottom of the reactor were drilled and tapped to take  $1/2$  inch short nipples. The upper one was fitted with a  $1/2$  inch malleable iron cross and reduced to  $1/8$  inch, while the bottom one was reduced

directly to 1/8 inch.

Feed was admitted to the top of the reactor from a 1000 ml. graduated separatory funnel through a Merkle-Korff type bellows pump operating on 110 volt A. C. and connected to the reactor by 1/8 inch copper tubing.

To the bottom outlet, a 1/8 inch flexible copper tube was fitted. The tube led to a glass bulb type water cooled condenser 20 inches long and a dry ice condenser connected in series as shown in Figure 1.

The gas meter following the dry ice trap was a three liter "Precision " Wet Test Meter.

The rectification column was constructed of three concentric glass tubes. The innermost tube was 33 mm. inside diameter and was packed with 1/8 inch Fenske stainless steel helices. A thermometer was fastened to the outside surface of the inner tube about halfway between top and bottom. The second or middle tube was wrapped with nichrome resistance wire which was connected to a 110 volt autotransformer to provide heat to the column. The third or outer tube served as a protector and insulator. The column was 48 inches high and calibrated about 30 theoretical plates at total reflux. The top of the column was fitted with an adjustable reflux head with a cold finger condenser and a thermometer to record vapor temperatures. A graduated water-cooled receiver was attached to the outlet from the distilling head.

The vacuum system used consisted of a Cenco Megavac pump connected through two surge tanks to the distillation system. The pump, operated on 220 volts A. C., was capable of taking the first surge tank down to about one mm. Hg. absolute. The first surge tank connected to the second through a Solenoid valve. This valve was controlled by a mercury switch and an electronic relay to give the desired pressure upon the system. The second surge tank was connected to the distillation system with a tee to a mercury filled manometer. For the purpose of consistency in this investigation all vacuum distillations were made at 85 mm. Hg. absolute.

The heater used for the distillation flask had a ceramic base supporting nichrome coils in a concave depression in which the distillation flask was placed. These coils were connected to a 110 volt autotransformer.

The one liter distillation flask used was equipped with a 35/25 spherical joint.

The Abbe type Valentine refractometer was capable of reading to six significant figures. All refractive indices were read at  $20 \pm 0.1$  °C.

The autotransformers were Superior Electric Company Powerstats. The 110 volt powerstats had a voltage range of 0 to 135 volts and were fused at seven amperes. The 220 volt powerstats had a voltage range of 0 to 260 volts and were fused at three amperes.

## B. Methods

### 1. Preparation of the catalyst:

The reactor was filled with Berl saddles to a point about 1/4 inch below the bottom thermocouple. Nine hundred cc. of Harshaw 1/8 inch activated alumina pellets were placed in the reactor over the Berl saddles. The reactor was then completely filled with additional Berl saddles. These saddles acted as a preheat section.

The manner of catalyst activation was similar to that outlined by Berg et al (1). The catalyst was dried at 250°C. for two hours after being placed in the reactor. After cooling to room temperature, anhydrous hydrogen fluoride was passed through for another hour with the catalyst at room temperature. With the hydrogen fluoride still passing through, the temperature was increased to 400°C. in one hour. The catalyst was then purged with nitrogen gas for about fifteen minutes to sweep out the excess hydrogen fluoride. During the catalyst activation, the excess hydrogen fluoride was bubbled through kerosene and out a blow down line.

### 2. Making the reaction runs:

The reactor was heated until the center thermocouple gave a reading slightly below the desired temperature. Dry ice was placed in the dry ice trap using a liquid such as acetone or "Tromex" to give a better cooling medium. The density of the aromatic hydrocarbon being used was measured

by weighing a 1000 cc. sample on the Harvard triple beam balance. A charge, usually about 700 cc., was placed in the separatory funnel and the pump started to fill completely all connecting tubing to the reactor. If necessary, air was swept from the reactor by using a fifteen minute nitrogen purge. After the reactor was completely purged of air, the feed system was connected. Readings from all three thermocouples, the gas meter, and the volume of feed in the separatory funnel were noted before the run was started and continued at ten minute intervals throughout the duration of the run. Upon completion of the run, the reactor was purged of all hydrocarbon vapors by passing nitrogen through for fifteen minutes. During this purge, the gas meter was taken out of the system and all condensable hydrocarbons were retained in the receiver. The receiver was placed in a refrigerator maintained at  $-40^{\circ}\text{C}$ . to minimize evaporation of the reaction product prior to distillation. The same procedure was used in runs with both activated and unactivated catalyst.

### 3. Distillation of reaction products:

Each charge was placed in the distillation flask with about 100 grams of a suitable chaser. The chasers used for all runs are tabulated in Tables I-V. Heat flows to the column and distillation flask were adjusted by means of the autotransformers in such a manner as to allow the column to flood and insure complete wetting of the packing. The heat

flows were then reduced sufficiently to stop the flooding and the column permitted to operate at total reflux for one hour. After the column had attained equilibrium, the reflux ratio was set at about 5/1 and overhead cuts taken. During this time a dry ice condenser was kept in series with the water condenser to retain any light hydrocarbon vapors passing through the latter.

Vapor temperatures were taken at the beginning and end of each cut. The size of the cuts taken depended upon the rate of increase of the vapor temperature. When the breaks or mid-fractions were reached, smaller cuts were taken better to define the distillation curve.

Distillation was continued until all the charge was distilled or until atmospheric distillation had to be abandoned in favor of vacuum distillation. If vacuum distillation had to be used, the charge was allowed to cool, the system placed under vacuum, and distillation recommenced.

When vacuum distilling the products of the triamyl benzene runs, a Claisson type distilling flask was used instead of the rectification column because of excessive foaming.

Refractive indices were taken whenever the rate of increase of the vapor temperature indicated that a plateau was reached on the distillation curve.

#### 4. Catalyst burn-off and reactivation:

As the catalyst was used, a deposit of carbonaceous

material was laid down upon the catalyst surface, reducing its activity and necessitating periodic burn-offs. The catalyst was burned off at the end of every third run when dealkylating materials such as the xylenes, toluene, or ethyl benzene and at the end of every run when the reactant was diethyl benzene, isopropyl benzene, monoamyl benzene, diamyl benzene, and triamyl benzene.

Burning off was accomplished by passing air through the reactor while maintaining the burn-off temperature below the sintering point of the catalyst, about 600°C. The burn off was done immediately after the completion of the run before the catalyst bed had time to cool.

The catalyst was reactivated after the burn-off whenever hydrogen fluoride was detected in appreciable amounts in either the products from the reactor or in the exhaust gases from the burn-off. Reactivation was accomplished by cooling the catalyst to room temperature and treating as described above.

5. Plotting the data obtained from distillation:

The data were plotted as vapor temperature vs. weight per cent distilled. Whenever the water condenser was incapable of condensing all the vapors, an allowance was made on the distillation curves for the material retained in the dry ice trap. This is indicated on the distillation curves whenever the first plotted point is not at the zero per cent



distilled abscissa.

Whenever vacuum distillations were made, the vapor temperatures were plotted on the same scale as the atmospheric distillation temperatures.

All data for yields and conversions were taken from these distillation curves.

## C. Materials

No attempt was made to purify any of the reagents used.

<u>Compound</u>	<u>Grade</u>	<u>Source</u>
Meta and Para Xylene	Analytical	Mallinckrodt Chemical Works
Ortho Xylene		Eastman Kodak Company
Toluene		Dow Chemical Company
Ethyl Benzene		Dow Chemical Company
Diethyl Benzene		Dow Chemical Company
Isopropyl Benzene		Dow Chemical Company
Amyl Benzene	Technical	Sharples Chemical Co.
Diamyl Benzene	Technical	Sharples Chemical Co.
Triamyl Benzene	Technical	Sharples Chemical Co.
n-Tetradecane		The Connecticut Hard Rubber Company
Anhydrous Hydrogen Fluoride		The Matheson Company
Activated Alumina Pellets, 1/8 inch diameter		Harshaw Chemical Company

## III SAMPLE CALCULATIONS

The sample calculations of conversions and space velocity were based on Run #15 using activated catalyst and triamyl benzene as the reagent. This run was chosen because it yielded the most complex reaction products. In this run, however, the conversions and the yields were the same. Therefore, the sample calculations of yields were based upon Run #3 using activated catalyst and a meta and para xylene mixture.

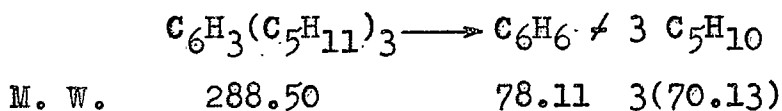
## A. Determination of per cent liquid product:

These data were taken from Figure 5, the distillation curve for the activated triamyl benzene run. The division lines between compounds on this curve were located at the arithmetic mean of the temperatures of the adjacent plateaus. The quantity of the distillation charge between the zero per cent distilled point and the first point on the distillation curve represents that fraction of the distillation charge which passed through the water condenser and was retained in the dry ice trap placed in series with the column condenser. This fraction of the distillation charge contained  $C_3$ ,  $C_4$ , and  $C_5$  hydrocarbons. Thus, for a distillation charge of 530.2 grams:

<u>Compound</u>	<u>Grams</u>	<u>Weight Per Cent</u>
C <sub>3</sub> , C <sub>4</sub> , and C <sub>5</sub>	118.0	22.3
Pentenenes	88.5	16.7
Benzene	72.6	13.7
Amyl Benzene	150.3	28.3
Diamyl Benzene	71.6	13.5
Triamyl Benzene	0.0	0.0
Distillation Losses	<u>29.2</u>	<u>5.5</u>
	530.2	100.0

B. Calculation of per cent of theoretical yield converted per pass:

For benzene:



Based upon the amount of triamyl benzene charged to the reactor, 689 grams:

$$\text{Theor. Yield; } \frac{689 \times 78.11}{288.50} = 186 \text{ grams}$$

$$\text{Actual Conversion; } \frac{72.6}{186} \times 100 = 39.0\%$$

In like manner, it can be determined that:

<u>Compound</u>	<u>Conversion, per cent</u>
Amyl Benzene	42.3
Diamyl Benzene	13.7
and Benzene	<u>39.0</u>
	95.0

## C. Calculation of liquid space velocity:

In Run #15, 760 cc. of triamyl benzene were charged to the reactor in 1.75 hours. Since the reactor contained 900 cc. of catalyst, it was determined that:

$$\text{Space Velocity} = \frac{760}{1.75 \times 900} = 0.482$$

## D. Calculation of yields:

In Figure 2, charging xylene over activated catalyst, 60.5 per cent of the distillation charge was unreacted xylene. Since the distillation charge was 400.1 grams,

$$(400.1)(0.605) = 242 \text{ grams of unconverted xylene.}$$

From the original charge to the reactor, 431 grams,

$431 - 242 = 189$  grams of xylene were consumed or held up by the reactor. This represents 43.9 per cent of the total charge. The yield of toluene calculated by the method given in these sample calculations was 16.0 per cent of the theoretical. If 43.9 per cent of the xylene made 16.0 per cent of the theoretical yield of toluene, then 100 per cent of the xylene would make

$$\frac{16.0 \times 100}{43.9} = 36.4 \text{ per cent of theoretical}$$

yield of toluene.

## IV RESULTS

## Xylenes:

Table I in the appendix tabulates the conditions and results of the xylene runs. Runs 1-4 were made using a meta-para xylene mixture as the reactor charge and the activated catalyst. Run 1, at 401°C., produced neither alkylation nor dealkylation products of xylene. At 440°C., Run 2, the liquid product from the reactor contained 18.5 per cent trimethyl benzene and 12 per cent toluene, while at 510°C., Run 3, the yield of trimethyl benzene decreased to 16 per cent of the liquid product and the yield of toluene increased to 15 per cent of the liquid product. In Run 4, the temperature was increased to 542°C. and an analysis of the products showed only 13 per cent trimethyl benzene while the yield of toluene was increased to 19.1 per cent of the product. At 542°C., however, an inspection of the catalyst after the run showed that part of the catalyst had sintered.

These results showed that as the temperature increased, the amounts of dealkylated products also increased, while the amounts of alkylated products decreased. Since this investigation was primarily interested in the dealkylation reaction, 500°C. was chosen the optimum temperature for dealkylating xylenes without sintering the catalyst.

The meta-para xylene mixture was partially separated into its components by freezing. The para-rich xylene mixture gave

slightly lower yields than the mixture used in Runs 1-4, but the yields of both the alkylated and the dealkylated products were considerably lower for the meta-rich xylene mixture.

Run 7, made with ortho xylene on the activated catalyst, gave essentially the same yield of toluene, 14.7 per cent of the liquid product, as the meta-para xylene mixture but gave a slightly higher alkylation to trimethyl benzene than did the meta-para xylene mixture.

At 504°C. and essentially the same conditions of space velocity and pressure, the unactivated catalyst was inactive towards either the alkylation or the dealkylation reaction.

No benzene was detected in the dealkylation products of any of the xylenes nor was benzene detected when an attempt was made to dealkylate toluene itself (Run 17).

From the fact that alkylation did take place in these runs, it was presumed that part of the toluene formed was alkylated back to xylene, while at the same time, some of the trimethyl benzene formed by alkylation of xylene was dealkylated back to xylene.

Traces of ortho xylene were detected in the products of the meta-para xylene runs. Whether this was due to the isomerization effect of the catalyst, the alkylation of toluene to ortho xylene, or the dealkylation of trimethyl benzene was not determined.

#### Monoamyl Benzene:

At 427°C., 75.5 per cent of the theoretical yield of benzene was detected in the reaction products. At 504°C., Run 10, this conversion was increased to 84 per cent. Run 11, duplicated the results of Run 10 after the catalyst was burned off and reactivated. The conditions and results of these runs are tabulated in Table II. Only 16.8 per cent of the theoretical benzene was formed, however, when monoamyl benzene was passed over the unactivated alumina catalyst at 503°C.

No appreciable amounts of alkylated products were detected in any of the monoamyl benzene runs, nor were any aromatic dealkylated products other than benzene found.

#### Diamyl Benzene and Triamyl Benzene:

Table III tabulates the conditions and results of the dealkylation of diamyl benzene and triamyl benzene. At 498°C. with the activated catalyst, diamyl benzene formed 63.3 per cent of the theoretical yield of benzene, 26.4 per cent of the theoretical yield of monoamyl benzene, and no unreacted diamyl benzene. Over the unactivated catalyst, however, at the same conditions of temperature, pressure, and liquid space velocity, the reaction products contained no benzene and 38.8 per cent of the theoretical monoamyl benzene.

Triamyl benzene with the activated catalyst at 499°C.



formed 39.0 per cent of the theoretical benzene, 42.3 per cent monoamyl benzene, 13.7 per cent diamyl benzene, and no unreacted triamyl benzene remained. At 500°C. and with the unactivated catalyst, only a trace of benzene or monoamyl benzene was formed, but 41.1 per cent of the theoretical yield of diamyl benzene was detected.

The presence of the intermediate products of the dealkylation of these polyamyl benzenes to benzene, indicated that the contact time was too short for the dealkylation reaction to be complete.

As in the dealkylation of monoamyl benzene, the polyamyl benzenes did not form alkylation products, nor did any dealkylation occur except at the benzene ring.

#### Toluene:

Table IV gives the conditions and results of the dealkylation of toluene, diethyl benzene, and isopropyl benzene.

The dealkylation of toluene, as mentioned previously, formed no appreciable amount of benzene. Even though no alkylation products of toluene were apparent, it cannot be stated that alkylation of toluene would not take place with the catalyst under the conditions used. Since any alkylation would depend upon a product of dealkylation for the alkylating reagent, and since no dealkylation took place, no alkylation of toluene could occur even though the catalyst was active

with respect to alkylation.

#### Diethyl Benzene:

At 500°C. with the activated catalyst, 38.6 per cent of the theoretical yield of ethyl benzene was formed by dealkylation of diethyl benzene. No appreciable amounts of benzene nor alkylated products of diethyl benzene were found. The unactivated catalyst was inactive towards diethyl benzene at 499°C.

#### Isopropyl Benzene:

Eighty-six per cent of the theoretical yield of benzene was produced when isopropyl benzene was passed over the activated catalyst at 505°C. At 500°C., the unactivated catalyst formed only 2.9 per cent of the theoretical amount of benzene. In neither of these runs was any liquid reaction product found other than benzene.

#### Ethyl Benzene:

Ethyl benzene was reacted under four different stages of the catalyst cycle. Table V shows the conditions and results of these runs. Run 22, made with activated catalyst, showed that ethyl benzene formed 17.4 per cent of the theoretical benzene and 4.9 per cent of the theoretical yield of diethyl benzene.

Under the same conditions of temperature, pressure, and

space velocity, the activated catalyst, when fouled with carbon, was inactive for either alkylation or dealkylation. This is shown in the results of Run 23.

When the carboned catalyst was burned off, the conversion to benzene was 7.2 per cent of theoretical and the conversion to diethyl benzene was 4.6 per cent. This shows that the catalyst had part of its former activity restored by the carbon burn-off but that it needed reactivation with anhydrous hydrogen fluoride to recover all of its previous activity. The unactivated alumina gave approximately the same results as the carboned catalyst.

Figure 10 shows the distillation curves for the ethyl benzene runs under all these conditions of the catalyst cycle.

It is important to note that for none of the hydrocarbons used, was any liquid dealkylation product detected other than those that resulted from cleavage at the benzene ring.

## V CONCLUSIONS

The following conclusions may be drawn concerning both alkylation and dealkylation with the hydrogen fluoride activated alumina catalyst:

1. Benzene is the ultimate dealkylation product for all aromatic hydrocarbons that contain two or more carbon atoms in every branch chain.
2. Toluene is unaffected by the catalyst under the conditions used in this investigation and will probably be the ultimate dealkylation product of any aromatic hydrocarbon that contains only one carbon atom in any of its branch chains.
3. Pressure and space velocity being constant, dealkylation will increase as the temperature increases and alkylation will decrease as the temperature increases.
4. The rate of dealkylation increases with the length of the side chains on any aromatic hydrocarbon.
5. Alkylation probably takes place whenever dealkylation occurs but when the molecules are large, (diethyl benzene or larger) the alkylated products are so readily dealkylated that none appear in the final product.
6. Dealkylation with this catalyst and at the conditions used always takes place at the benzene ring.

## VI ACKNOWLEDGMENT

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He also acknowledges with thanks the courtesy of the Sharples Chemical Company who furnished the mono-, di-, and triamyl benzene used in this research.

## VII LITERATURE CITED AND CONSULTED

- (1) Berg, L., Sumner, G. L., and Montgomery, C. W., (To Gulf Research and Development Co.); U. S. Patent 2,397,639 (April 2, 1946)
- (2) Brandt, P. L., Lee, R. J., Radford, H. D., Klemm, L. H., and Drennan, P. S.: Paper presented before the Division of Petroleum Chemistry of the Am. Chem. Soc., April, 1947
- (3) Burk, R. E., and Hughes, E. C., (To Standard Oil Co. of Ohio); U. S. Patent 2,399,662 (May 7, 1946)
- (4) Frey, F. E., (To Phillips Petroleum Co.); U. S. Patent 2,372,320 (March 27, 1945)
- (5) Frey, F. E., (To Phillips Petroleum Co.); U. S. Patent 2,394,905 (Feb. 12, 1946)
- (6) Ipatieff, V. N., and Monroe, G. S., (To Universal Oil Products Co.); U. S. Patent 2,352,199 (June 27, 1944)
- (7) Ipatieff, V. N., and Schmerling, L., (To Universal Oil Products Co.); U. S. Patent 2,329,858 (Sept. 21, 1943)
- (8) Koch, H; Reichsamt Wirtschaftsbaus, Prof-Nr. 102 (PB52004), 49-57 (1940)
- (9) Kutz, W. M., and Corson, B. P.; Ind. Eng. Chem. 38, 761-4 (1946)
- (10) Linn, C. B., (To Universal Oil Products Co.); U. S. Patent 2,372,505 (March 27, 1945)
- (11) Linn, C. B., (To Universal Oil Products Co.); U. S. Patent 2,373,580 (April 10, 1945)
- (12) Mattox, W. J., (To Universal Oil Products Co.); U. S. Patent 2,386,969 (Oct. 16, 1945)
- (13) O'Kelly, A. A., Meadow, J. R., and Woodward, R. E., (To Socony-Vacuum Oil Co., Inc.); U. S. Patent 2,414,271 (Jan. 14, 1947)
- (14) Schmerling, L., and Ipatieff, V. N., (To Universal Oil Products Co.): U. S. Patent 2,349,834 (May 30, 1944)

- (15) Woodward, R. E., Hawthorne, W. P., and Meadow, J. R.,  
(To Socony-Vacuum Oil Co., Inc.); U. S. Patent  
2,409,090 (Oct. 8, 1946)

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