

- P_R^* = pseudo reduced pressure, atmospheres
 P_f = correction factor for critical pressure to get P_R^*
 z = compressibility factor, PV/RT
 z_c = compressibility factor at the critical state, $P_c V_c / RT_c$
 α = $(RT/P) - v$ (deviation from perfect gas law)

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CONVERSION OF AROMATICS

Alkyl Group Transfer in the Presence of Silica-Alumina Catalysts

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The conversion of alkylaromatic hydrocarbons in the presence of a typical petroleum cracking catalyst under conditions similar to those encountered in commercial catalytic cracking and reforming operations has been studied. Xylene is converted to toluene and trimethylbenzenes by disproportionation of methyl groups. Trimethylbenzenes are converted to toluene, xylene, and polymethylbenzenes, and methylnaphthalene is converted to naphthalene and polymethylnaphthalenes by the same mechanism. Diethylbenzene is converted to ethylbenzene and ethylene; no triethylbenzenes are detected in the products. In the presence of benzene, alkyl groups from alkylbenzenes are transferred to this hydrocarbon with the formation of higher yields of monoalkylbenzene than in the disproportionation reaction. Methyl groups are not, however, transferred from methylnaphthalene to benzene.

THE reactions of alkylaromatic hydrocarbons in the presence of various catalysts, particularly those of the Friedel-Crafts type, have been the subject of many investigations during the past sixty years. The primary interest in some of these investigations has been the conversion of polyalkylbenzenes to monoalkylbenzenes, as exemplified in the conversion of xylene to toluene.

The first commercial interest in this type of conversion was aroused during World War I, when the demands for larger quantities of toluene than could be obtained directly from coal carbonization forced attention to the problem of converting polymethylbenzenes to toluene. Many years prior, however, considerable work had been reported on the reactions of xylene, pseudocumene, mesitylene, and other polyalkylbenzenes in the presence of aluminum chloride. Thus, Anschütz (1) reported that *m*-xylene can be converted to toluene in yields as high as 25%, with the simultaneous formation of trimethylbenzenes, by refluxing with about 30% aluminum chloride for 2-3 hours. Pseudocumene was reported to yield about 20% each of xylene and toluene. The reaction of polyalkylbenzenes to form monoalkylbenzenes (or alkyl

benzenes having a smaller number of corresponding alkyl groups) with the simultaneous formation of more highly alkylated benzenes is an excellent example of the type of reaction commonly termed "disproportionation".

Jacobsen (5) reported fair yields of toluene from xylene and of toluene and xylene from pseudocumene, through the displacement of one or more methyl groups as methyl chloride, on passing anhydrous hydrogen chloride into the refluxing polyalkylbenzene in the presence of aluminum chloride. This type of reaction is not one of disproportionation in the true sense.

Later efforts toward possible commercial conversion of polymethylbenzenes to toluene were directed mainly to the thermal cracking reaction at very high temperatures and to the transfer of methyl groups to benzene in the presence of aluminum chloride. The results reported on the latter reaction were generally negative. Boedtke and Halse (2) found no toluene in the reaction of xylene with benzene in the presence of aluminum chloride at the reflux temperature after 6 hours. Fischer and Niggemann (4) reported that the results of their investigation on this reaction were inconclusive. However, these investigators did report yields of toluene up to 12% from xylene by decomposition (undoubtedly disproportionation) at the reflux temperature in the presence of 3-4% aluminum chloride.

A high-temperature noncatalytic cracking process for the conversion of coal-tar solvent naphtha to 13-14% toluene and 8% benzene was described by Egloff (3).

A comprehensive review of the literature on the action of aluminum halides on alkylbenzenes, including alkylation and dealkylation reactions and intermolecular and intramolecular rearrangements, was compiled by Nightingale (7). More recently Pitzer and Scott (8) published a notable contribution on the thermodynamics and structure of benzene, toluene, and xylene. They reported equilibrium measurements on the reaction of two moles of toluene to give a mole of benzene and a mole of xylenes at 50° C., the catalyst being aluminum bromide promoted with anhydrous hydrogen bromide. Calculated equilibrium values for this reaction at 298.16° to 1500° K. are also reported in their paper.

Related to the present investigation are the results published by Thomas, Hoekstra, and Pinkston (10), who investigated the removal of side chains from aromatics with catalysts of substantially the same type as that used here. Natanson and Kagan (6) also used this type of catalyst in an investigation of the reaction of toluene to produce benzene and xylenes.

While the production of toluene from xylene and other polymethylbenzenes no longer represents a problem of great commercial interest, due to the availability of toluene from other hydrocarbon conversion processes and from extraction processes applied to certain straight-run and cracked gasolines, the general problem of dealkylation of polyalkylbenzenes to monoalkylbenzenes is of practical interest when applied to higher members of the series such as diethylbenzene and polyisopropylbenzenes. Moreover, a clearer understanding of some theoretical aspects of the mechanism of catalytic cracking and reforming may be obtained from a study of the reactions of the simpler alkylaromatics in the presence of usual petroleum cracking catalysts.

Earlier work (9) showed that a high-boiling polyalkylbenzene fraction could be converted in good yields in the presence of benzene to a lower-boiling fraction consisting entirely of simple alkylbenzenes such as toluene, ethylbenzene, and others boiling below 150° C. For example, a 150–250° C. fraction of alkylbenzenes, consisting for the most part of mono and poly isopropyl-, butyl-, and amylbenzenes, was converted at 482° C. in the presence of benzene and an activated clay catalyst to some 62% by weight of a 95–150° C. fraction of alkylbenzenes. Consumption of about 16% of benzene based on alkylbenzene charge was observed, showing a substantial transfer of alkyl groups to benzene. Under the same conditions in the absence of benzene the yield of the 95–150° C. fraction was only 25%.

These results suggested that alkyl group transfer to benzene might be effected in the presence of a typical cracking catalyst even in the case of xylene, where previous attempts with aluminum chloride catalyst had failed. A study of the transfer of ethyl groups was also made for comparison.

CATALYTIC RUNS

MATERIALS. The usual c.p. grades of benzene and *m*-xylene were used. Diethylbenzene was obtained by distillation of the polyalkylated fraction from the alkylation of benzene with ethylene. A 175–185° C. cut of this material, corresponding to the boiling points of the isomeric diethylbenzenes, was obtained by fractionation through a fifteen-plate Fenske column. The pseudocumene and α -methylnaphthalene were Eastman's Technical grade. While the purity of the Eastman materials was not determined with respect to individual isomers, physical properties (density and boiling range) indicated that they were substantially pure trimethylbenzenes and methylnaphthalenes, respectively.

A commercial synthetic silica-alumina catalyst was prepared by coprecipitation of the hydrous oxides in a ratio of about 9 to 1 by weight of silica to alumina. Its properties were similar to

TABLE I. CONVERSION OF *m*-XYLENE

Experiment No.	1	2	3	4	5	6
Temperature, ° C.	538 ^d	538	538	538	538	538 ^e
Ratio, benzene:xylene	2:1	0:1	1:1	2:1	2:1	2:1
Molar Weight	59.5:40.5	0:100	42.4:57.6	59.5:40.5	59.5:40.5	59.5:40.5
Space rate, vol. charged/vol. catalyst/hr.	1.09	1.05	1.04	0.36	1.05	1.13
Time on stream, min.	76	76	76	22.5	76
Reaction products, wt. % of charge						
Coke	0.0	1.7	0.6	2.0	0.5	1.6
Gas	0.0	1.4	1.0	1.8	0.3	0.9
Liquid products ^a	100.0	96.9	98.4	96.2	99.2	97.5
78–95° C., C ₆ H ₆	57.4	1.2	39.2	55.4	56.1	54.9
95–115° C., C ₆ H ₅ CH ₃	0.4	11.7	10.0	15.2	7.6	9.9
115–135° C.	0.8	2.7	2.3	2.4	3.8	2.4
135–150° C., C ₆ H ₄ (CH ₃) ₂	40.4	66.9	38.4	19.2	31.7	25.9
150–180° C., C ₆ H ₃ (CH ₃) ₃	0.0	11.8	8.5 ^e	4.0 ^e	3.2
>180° C., residue	1.0	2.6	1.2
Compn. of gas produced, vol. %						
Olefins	10.3	8.5	15.7	12.0
Paraffins + H ₂	89.7	89.3	91.5	84.3	88.0
Mol. wt. of gas produced	18	19	17	17	21
Benzene recovered, wt. %	97	93	93	94	92
Toluene yield, wt. % on xylene charged ^b						
Per pass	0	13	19	40	23	27
Ultimate ^c	0	41	62	82	83
Mole toluene produced per mole xylene						
Charged	0	0.15	0.22	0.46	0.27	0.31
Consumed	0	0.47	0.71	0.94	0.95
Mole benzene consumed per mole xylene						
Charged	0	0.075	0.14	0.11	0.15
Consumed	0	0.24	0.28	0.47
Molar ratio of toluene produced to benzene consumed	0	3.0	3.4	2.5	2.1

^a Difference between 100% and gas + coke.

^b Based on 95–115° C. cut + half of 115–135° C. cut.

^c Xylene only considered as recycle stock.

^d Noncatalytic run.

^e Total residue above 150° C.

Total residue above 135° C.

^f Cyclic run: 15 min. on stream and 15-min. air regeneration.

those of the silica-alumina catalyst described by Thomas, Hoekstra, and Pinkston (10).

APPARATUS AND PROCEDURE. The apparatus for processing the materials consisted of a 110-cc. stainless-steel catalyst chamber immersed in a thermostated molten lead bath; a charging system, comprising a Manzel chemical-feeder-type pump and a graduated charge cylinder; and a conventional collecting system, comprising a coil condenser, liquid-gas separator, calibrated gas receiving bottles, and wet test meter. The charge was pumped to the reaction chamber indirectly by displacement with ethylene glycol from a 500-cc. glass buret. The glycol was pumped into the bottom of the buret, and the amount of charge displaced through the top was measured by the difference in the position of the interface at the beginning and end of the run. The pressure on the reactor was maintained at 15 ± 0.5 pounds per square inch (gauge) by means of a manually controlled Hoke needle valve at the exit.

Special precautions were taken to ensure accurate material balances by thermostating the buret, and by purging the system with a small amount of charge stock prior to the main run to wet the condenser walls and thus minimize drainage errors.

The initial free space in the condenser was filled with carbon dioxide in order to allow an accurate analysis of the gas produced from the reaction, when the amount of this gas was only one to two times the volume of the dead space in the condenser system. Gas analysis was made on the collected gas by Orsat absorption for carbon dioxide, oxygen, and olefins, the hydrocarbon content and weight being corrected to a carbon-dioxide-free basis. Gas densities were determined by a modified precision Schilling effusimeter.

Coke was determined by burning the catalyst, after purging hydrocarbon vapors with nitrogen, in a stream of air flowing at 500–1000 cc. per minute. The regeneration gases were passed through a hot copper oxide catalyst to convert carbon monoxide to carbon dioxide. The carbon dioxide was measured by absorption in a tared Ascarite bulb, and the equivalent carbon was calculated.

The determination of weight of gas and coke is to be considered quite accurate as compared to the experimental errors involved in measuring the recovery of liquid product. The material balance is based on the accurate determination of gas and coke and the calculation of weight of liquid product by difference. The deviation of the calculated recovery of liquid product from its experimental value was seldom greater than about 1%, which is within the experimental error.

Several experiments were made in cyclic operation; i.e., the charge was pumped to the reactor for a given time, usually 15

minutes, after which the system was purged with nitrogen and the coke deposit on the catalyst burned off in a stream of air for a time equal to the on-stream period. The charge was then pumped to the reactor for the same period, followed by regeneration, and so on for a number of such cycles. The catalyst was thereby maintained in a state of high activity, resulting in reaction conditions effectively more severe than those where the catalyst was not reactivated during a 1-2 hour run.

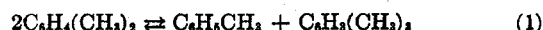
The synthetic crude was analyzed by careful fractionation through a fifteen-plate Fenske distillation column with total reflux-variable takeoff type head. The small residues from this distillation were further distilled through a semimicrocolumn packed with a nichrome wire spiral. Cuts were analyzed for specific gravity and iodine numbers. In all cases the latter value was zero, and the specific gravity corresponded to that of the pure compound included in the cut.

EXPERIMENTAL DATA

Table I shows the results of the investigation of methyl group transfer between *m*-xylene and benzene, and between one molecule of xylene and another at 538° C. It was found that at lower temperatures (510° C.) the rate of reaction with benzene was too slow for practicable space rates, but at 538° C. satisfactory reaction rates were obtained.

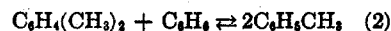
The noncatalytic run with benzene (experiment 1) shows no reaction of xylene, although according to the distillation some benzene has disappeared. It is believed that the small amounts of product boiling between 95° and 135° C. are not due to toluene formation, but rather to poor fractionation in this case. Hence, conversion of xylene to toluene under these conditions has been assigned a value of zero in the calculations.

The data listed for the next five experiments show conclusively that xylene is converted to toluene and trimethylbenzenes. It is interesting that in the absence of benzene (experiment 2) the catalytic conversion of xylene produces nearly equal molar amounts of toluene and trimethylbenzenes according to the equation:



This is essentially the reaction reported by Anschütz (1) with aluminum chloride, showing disproportionation involving methyl group transfer between xylene molecules.

The addition of benzene to the reaction system gives rise to the competing reaction:



Experiments 3 to 6 show that transfer of methyl groups from xylene to benzene actually occurs to about as great an extent as it occurs between xylene molecules. As a matter of fact, experiment 3 shows that the molar ratio of products to reactants corresponds approximately to the sum of Equations 1 and 2. Experiment 6, on the other hand, shows a somewhat higher consumption of benzene, due possibly to a greater proportion of reaction 2.

According to Pitzer and Scott (8), the equilibrium constant for reaction 2 at 527° C. is calculated to be 3.3. This corresponds to the formation of 1.3 moles of toluene per mole of xylene charged in experiments 4 to 6. Even at the low space rate of experiment 4 the extent of reaction apparently has not reached more than 35% of its equilibrium value. Lower space rates than that used in experiment 4 probably would give higher yields

TABLE II. CONVERSION OF PSEUDOCUMENE

Experiment No.	7	8
Temperature, ° C.	510	538
Ratio, benzene:pseudocumene		
Molar	2:1	2:1
Weight	56.5:43.5	56.5:43.5
Space rate, vol. charged/vol. catalyst/hr.	2.18	1.08
Time on stream, min.	75	75
Reaction products, wt. % of charge		
Coke	0.8	2.4
Gas	1.3	3.4
Liquid products ^a	97.9	94.2
78-95° C., C ₆ H ₆	54.6	52.0
95-115° C., C ₆ H ₅ CH ₃	1.7	3.5
115-130° C.	0.8	1.6
130-150° C., C ₆ H ₄ (CH ₃) ₂	3.9	6.6
150-160° C.	1.7	2.0
160-185° C., C ₉ H ₇ (CH ₃) ₃	32.1	25.0
>185° C., residue	3.1	3.5
Compn. of gas produced, vol. %		
Olefins	28.7	21.2
Paraffins + H ₂	71.3	78.8
Mol. wt. of gas produced	24	21
Benzene recovered, wt. %	97	92
Toluene yield, wt. % on C ₆ H ₄ (CH ₃) ₂ charged ^b		
Per pass	5	10
Ultimate ^c	20	25
Xylene yield, wt. % on C ₆ H ₄ (CH ₃) ₂ charged ^d		
Per pass	12	19
Ultimate ^c	49	48
Mole toluene + xylene produced per mole pseudocumene		
Charged	0.20	0.35
Consumed	0.81	0.87
Mole benzene consumed per mole pseudocumene		
Charged	0.067	0.16
Consumed	0.28	0.40
Molar ratio of toluene + xylene produced to benzene consumed	3.0	2.2

^a Difference between 100% and gas + coke.

^b Based on 95-115° C. cut + half of 115-130° C. cut.

^c Trimethylbenzenes only considered as recycle stock.

^d Based on 130-150° C. cut + half of 115-130° C. cut + half of 150-160° C.

of toluene, but side reactions leading to coke and gas formation have already become bothersome. For this reason more severe conditions of reaction time were not investigated, since any conclusions regarding the reaction equilibrium would be subject to considerable doubt.

Table II shows the results of the investigation of methyl group transfer from pseudocumene to benzene at 510° and 538° C. The same general conclusions can be drawn for the pseudocu-

TABLE III. CONVERSION OF α -METHYLNAPHTHALENE

Experiment No.	9	10	11	12	13
Temperature, ° C.	538/	538	510	538	538
Ratio, benzene: α -methylnaphthalene					
Molar	0:1	0:1	2:1	2:1	5.5:1
Weight	0:100	0:100	54.5:45.5	54.5:45.5	75.5:24.5
Space rate, vol. charged/vol. catalyst/hr.	1.10	1.11	2.18	1.11	1.09
Time on stream, min.	75	75	70	147	260
Reaction products, wt. % of charge					
Coke	0.0	3.8	1.2	1.9	1.2
Gas	0.0	1.6	0.8	1.7	0.7
Liquid products ^a	100.0	94.6	98.0	96.4	98.1
78-95° C., C ₆ H ₆	0.0	0.5	53.8	53.6	74.0
95-115° C., C ₆ H ₅ CH ₃	0.0	0.0	0.0	0.2	0.0
115-200° C. ^b	0.3 _g	1.2	0.8	0.6	0.4
200-225° C., C ₆ H ₄	0.1 _g	8.2	1.6	4.2	2.7
225-230° C., C ₉ H ₇	0.5 _g	2.6	0.5	0.9	0.4
C ₁₀ H ₇ CH ₃	99.1 _h	74	37	33	19
Residue ^c	8.1	4.3	3.9	1.6
Compn. of gas produced, vol. %					
Olefins	7.3	18.6	10.6	9.8
Paraffins + H ₂	92.7	81.4	89.4	90.2
Mol. wt. of gas produced	15	18	16	15
Benzene recovered, wt. %	99	98	98
Naphthalene yields, wt. % on methylnaphthalene charged ^d					
Per pass	0	10	4	10	12
Approx. ultimate	0	40	25	40	55
Molar ratio of naphthalene produced to methylnaphthalene charged	0	0.11	0.05	0.11	0.13

^a Difference between 100% and gas + coke.

^b Mostly alkylbenzenes.

^c About half naphthalene.

^d Estimated by Engler distillation of >230° C. residuum, showing about 10% heavier products in all catalytic runs.

^e Based on 200-225° C. cut + half of 225-230° C. cut.

^f Noncatalytic run.

^g Liquid.

^h Total residue above 230° C.

TABLE IV. CONVERSION OF DIETHYLBENZENE

Experiment No.	14	15	16	17	18	19	20	21	22	23
Temperature, ° C.	510°	510°	510	454 ^d	454 ^d	454	482	482	510	524
Ratio, benzene: diethylbenzene										
Molar	0:1	3:1	0:1	2:1	2:1	3:1	3:1	3:1	3:1	3:1
Weight	0:100	63.6:36.4	0:100	53.8:46.2	53.8:46.2	63.6:36.4	63.6:36.4	63.6:36.4	63.6:36.4	63.6:36.4
Space rate, vol. charged/vol. catalyst/hr.	1.09	1.08	1.09	1.08	1.10	1.10	1.08	2.20	1.08	1.04
Time on stream, min.	50	82	50	99	102	49	101	85
Reaction products, wt. % of charge										
Coke	0.0	0.0	2.0	3.0	2.3	0.5	0.5	0.4	1.0	1.6
Gas	0.1	0.2	8.4	1.3	1.5	1.0	2.2	1.4	2.7	2.7
Liquid products ^a	99.9	99.8	89.6	95.7	96.2	98.5	97.3	98.2	96.3	96.0
78-100° C., C ₆ H ₆	0.0	61.6	3.5	49.1	49.0	58.2	59.0	59.5	60.2	60.4
100-132° C.	0.0	0.0	2.3	1.5	1.4	1.2	1.8	1.2	0.5	1.4
132-140° C., C ₆ H ₅ C ₂ H ₅	0.0	0.0	23.3	13.5	14.0	10.1	14.3	11.0	15.6	11.6
140-175° C.	3.0	0.6	7.0	1.8	2.2	2.7	1.8	2.3	1.6	2.3
175-185° C., C ₆ H ₄ (C ₂ H ₅) ₂	91.9	35.5	39.6	25.1	22.9	23.0	17.5	21.0	15.6	15.8
>185° C., residue	5.0	2.1	13.9	4.7	6.7	3.3	2.9	3.2	2.8	4.5
Compn. of gas produced, vol. %										
C ₂ H ₄	41.5	43.2	41.9	46.2	54.9	61.7	53.2	34.5
Other olefins	7.1	8.8	8.5	10.5	10.5	12.6	6.5	5.0
Paraffins + H ₂	51.4	50.0	49.6	43.3	34.6	25.7	40.3	60.5
Mol. wt. of gas produced	28	26	30	29	32	30	20	19
Benzene recovered, wt. %	97	93	92	92	94	94	95	96
Ethylbenzene yield, wt. % on diethylbenzene ^b										
Per pass	0	0	28	33	34	33	44	35	46	37
Ultimate	0	0	49	75	71	100	90	90	84	69
Moles ethylbenzene produced per mole diethylbenzene										
Charged	0	0	0.35	0.42	0.43	0.42	0.56	0.44	0.58	0.47
Consumed	0	0	0.62	0.95	0.90	1.26	1.14	1.14	1.06	0.87
Mole benzene consumed per mole diethylbenzene										
Charged	0.15	0.15	0.23	0.17	0.17	0.15	0.12
Consumed	0.34	0.32	0.68	0.35	0.42	0.27	0.22
Molar ratio of ethylbenzene produced to benzene consumed	2.8	2.9	1.9	3.3	2.7	3.9	4.0

^a Difference between 100% and gas + coke.

^b Based on 132-140° C. cut + half of 100-132° C. cut + half of 140-175° C. cut.

^c Noncatalytic run.

^d Cyclic run: 15 min. on stream and 15-min. air regeneration.

rene reaction as have been reached for xylene conversions. Methyl groups are readily transferred to benzene, with the formation of toluene and xylene. At the same time methyl group transfer between trimethylbenzene molecules probably occurs with the formation of tetramethylbenzenes and xylenes.

As Table III shows, methyl groups do not transfer from methylnaphthalene to benzene under the conditions investigated. However, there is apparently a transfer of methyl groups between methylnaphthalene molecules, with the formation of naphthalene and dimethylnaphthalenes. The reason for the failure of methyl groups to transfer from methylnaphthalene to benzene is not readily apparent. It is difficult to imagine that the methyl group in methylnaphthalene is more tightly bound to the bicyclic aromatic nucleus than it is to the monocyclic nucleus.

Qualitatively it appears that "activation" of a hydrogen atom of the acceptor molecule is necessary before alkyl group transfer can occur. It seems reasonable to suppose that hydrogen atoms of the naphthalene nucleus are much more readily activated than those of the benzene nucleus. The relative ease of such classical reactions as sulfonation, chlorination, and nitration of naphthalene and its homologs as compared to benzene supports such an assumption. Therefore, one might expect that the rate of methyl group transfer from methylnaphthalene to methylnaphthalene is much greater than that from methylnaphthalene to benzene. On the other hand, the apparent complete failure of methyl group transfer to benzene might be explained by steric factors involved in the adsorption of the reactants on the catalyst. Possibly the catalyst surface is preferentially covered with methylnaphthalene, effectively denying access of benzene to the surface for activation or reaction.

Table IV shows results of the investigation of ethyl group migration between diethylbenzene and benzene in the range 454° to 524° C. Similar yields of the monoalkyl derivative are obtained from diethylbenzene as from xylene, but the mechanism of the reaction appears to be somewhat different from that shown for xylene.

In the catalytic conversion of diethylbenzene in the absence of benzene, the 14% of residuum boiling above 185° C. was not prin-

cipally triethylbenzenes. The specific gravity was 0.93, indicating a polycyclic structure. In the presence of benzene also, the amount of this residuum is from 3 to 7% per pass, and careful fractionation failed to show a plateau in the boiling range of triethylbenzenes. The specific gravity of the residua produced in all catalytic runs in the presence of benzene was about 0.95.

The mechanism of the diethylbenzene conversion appears to be a simple splitting out of an ethyl group to form ethylene and ethylbenzene. In the presence of benzene part of this ethylene alkylates benzene to form more ethylbenzene. A side reaction of unknown nature occurs, forming appreciable amounts of polycyclic hydrocarbons.

The dealkylation of diethylbenzene apparently does not involve any appreciable cracking of ethyl groups to methyl groups. The 3-5% intermediate fraction between benzene and ethylbenzene showed no plateau at the boiling point of toluene. The 132-140° C. fraction was examined carefully for the presence of xylenes. Oxidation gave only benzoic acid. Further confirmation of the absence of xylenes was obtained by the method of selective hydrolysis of the sulfonic acids described by White and Rose (11). No hydrocarbon was liberated by steam hydrolysis of the sulfonic acids between 125° and 145° C. The hydrocarbon liberated between 145° and 175° C. represented about 85% of the original oil. Its refractive index, n_D^{20} , was 1.4960, the same value as that of the original fraction.

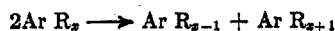
Since the absence of dimethylbenzenes in the reaction products has been proved, it seems reasonable to suppose that ethyltoluene also is not a product of the conversion of diethylbenzene. Hence, in the calculations shown in Table IV, half of the fraction boiling between 140° and 175° C. has been assigned to the ethylbenzene yield and half to diethylbenzene. Likewise, the 100-132° C. fraction has been divided between benzene and ethylbenzene.

The absence of cracking of the side chain to one of shorter length in the case of diethylbenzene is in confirmation of the general conclusions reached by Thomas, Hoekstra, and Pinkston (10) that side chains of alkylbenzenes are removed intact. We are inclined to agree with this conclusion up to a certain point.

However, if the alkyl side chain is large enough, we believe that cracking to shorter chains does occur to a considerable extent. Apparently the maximum length of the side chain which is relatively unsusceptible to cracking is about C₄. In our earlier work (9) we found considerable amounts of toluene in the catalytically cracked products from a mixture of alkylbenzenes containing large amounts of amyl- and diamylbenzenes. Part of this toluene undoubtedly was produced by nonselective thermal cracking, since the reaction was carried out in batch operation under more severe conditions than those used by Thomas *et al.* However, in the presence of the catalyst much higher yields of toluene were produced under the same conditions.

CONCLUSIONS

The conversion of alkylaromatic hydrocarbons in the presence of a typical silica-alumina cracking catalyst, under conditions similar to those encountered in commercial catalytic cracking, consists of essentially two types of reactions, depending on the nature of the alkyl group. If the side chains are methyl groups, transfer of alkyl group occurs through bimolecular disproportionation according to the equation:



where Ar is an aromatic nucleus, R is a methyl group, and x is the number of methyl groups. If the side chains are longer than methyl, simple dealkylation of one or more alkyl groups to form the corresponding olefin and lower aromatic derivatives is the primary reaction. For example, xylene is converted selectively

to toluene and trimethylbenzenes in equimolar amounts, while diethylbenzene is converted to ethylbenzene and ethylene, apparently without formation of triethylbenzenes under the conditions investigated.

The addition of benzene to the reaction system serves to double the yield of lower alkylbenzenes due to the competition of benzene for alkyl groups in both reactions. Activation of a hydrogen atom of the acceptor molecule, as well as the activation of alkyl group of the donor molecule, appears to be a necessary prerequisite for alkyl group transfer, since methyl group transfer from methylnaphthalene to benzene does not occur under the conditions of this investigation. In this case the much greater ease of hydrogen activation in the naphthalene series as compared to that in benzene, or the exclusion of benzene from the catalyst surface by methylnaphthalene, accounts for the absence of methyl group transfer to benzene.

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POLYISOBUTYLENE TANK LINING

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MANY manufacturing processes require noncorrosive ducts, containers, storage tanks, and vessels in which a wide variety of chemical reactions are conducted. Much work has been devoted to the development of corrosion-resistant linings for use in such containers. The oldest containers were enamel or tin, lead, and gold platings. Then rubber was used, and later acid-resistant stones embedded in water-glass cements were successful. Recent developments in the field of resistant coatings use high-molecular-weight synthetic thermoplastic protective agents.

A review of literature indicates that the resistance of polyisobutylene to inorganic-process liquors is being recognized. A recent paper by Krannich (4) states: "Polybutene represents a material with a range of corrosion resistance that is wider than that of hitherto known materials. Polybutene is one of the first materials which is simultaneously resistant to dilute and concentrated alkalies and acids, even to oxidizing acids. These excellent chemical properties, as well as the good workability, will assure a special position for polybutene in the field of corrosion prevention." Krannich reported that polyisobutylene was stable to 102 corrosive agents over a wide temperature range.

The 1939 progress report on rubber technology (1) states that products of Vistanex (polyisobutylene) are more resistant to extremes of heat and cold than natural rubber, but that they are attacked by oils and some chlorinated solvents. It is pointed out that they can be compounded with high proportions of fillers.

Thus, the olefinic type of polymer, such as polyisobutylene, has been recognized as a highly resistant material for several years. Its commercial utilization as a corrosion-resistant liner, however, has been dependent upon the development of a feasible

method for bonding the polymer to metal. A successful bonding method has been devised, and tests on polyisobutylene-coated metal specimens indicate that this method can now be used in commercial applications for a wide variety of corrosive liquids and gases.

The objects of this investigation were to develop a process whereby polyisobutylene compounds could be bound to metal, and to determine the strength and resistance of the resulting tank lining to attack by acids and alkalies.

PREPARATION OF TANK LINING

POLYMER. The polyisobutylene was prepared by polymerizing isobutylene at -87°C . with a Friedel-Crafts type catalyst, such as boron trifluoride gas. Thomas *et al.* (5) reported information on the preparation and structure of the polymer. Under these conditions a polyisobutylene is produced having an intrinsic viscosity in diisobutylene at 20°C . of approximately 3.0, where

$$\text{intrinsic viscosity} = \frac{\log_e \left(\frac{\text{viscosity of soln.}}{\text{viscosity of solvent}} \right)}{\text{concn. of polymer (g./100 cc.)}}$$

This intrinsic viscosity value is equivalent to a molecular weight of about 95,000, or a viscosity-average molecular weight of 1,500,000 (9).

Such a polymer is plastic and elastic, much like slightly broken down natural rubber, and is an aliphatic hydrocarbon with a chemical inertness essentially that of other saturated hydrocarbons. Inorganic salts and their solutions are non-reactive with polyisobutylene. Similarly, alkalies and acids,