CATALYTIC ALKYLATION of BENZENE with ETHYLENE

▶ ▶ The reaction between ethylene and benzene vapors at pressures up to 200 pounds per square inch gage, temperatures of 230-270°C. and space velocities of about 11-50 cc. (gas, 0°C. and 760 mm.) per hour per cc. of catalyst have been investigated in a flowing system under the influence of eleven different catalysts.

Sodium chloride-aluminum chloride-pumice and phosphoric acid-kieselguhr were the only catalysts giving detectable reactions. Mono- and diethylbenzenes were identified in the liquid products. The former catalysts under some conditions converted as much as 95 per cent of the ethylene to ethylbenzenes.

A series of runs was made to determine the effect of time, pressure, and space velocity on the reaction when the sodium chloride-aluminum chloride-pumice was used. The catalyst was found to have a very short life, the ethylene conversion decreased from 93 to 75 per cent over a period necessary for the conversion of 0 to 1.16 gram mole of ethylene to ethylbenzenes.

Pressure had a surprising influence on the reaction. At atmospheric pressure there was no detectable conversion, while at 200 pounds gage pressure as much as 95 per cent of the ethylene was converted to ethylbenzenes.

The effect of space velocity on the conversion was negligible over the range of about 11 to 50 cc. per hour per cc. of catalyst.

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ITH the development of the uses of styrene over the past few years in the manufacture of resins and synthetic rubber, processes by which it might be synthesized have been of interest. When dehydrogenated, monoethylbenzene produces styrene by the reaction:

$$C_{e}H_{b}C_{2}H_{5} \xrightarrow{heat}_{catalyst} C_{e}H_{b}CH = CH_{2} + H_{2}$$
(1)

It is believed that the most important processes in operation at this time for the manufacture of styrene involve monoethylbenzene as the starting material. The large producers of ethylbenzene use an agitated liquid phase for contacting benzene with ethylene in the presence of a metal halide catalyst, such as aluminum chloride. Recently a process for the production of ethylbenzene from ethyl alcohol and benzene has been publicized. Apparently, however, this process is not yet producing commercial quantities of ethylbenzene.

The present investigation is concerned with the reaction of ethylene with benzene in the vapor phase, utilizing an apparatus in which the mixed vapors of ethylene and benzene pass through a catalyst bed where the reaction takes place. Since only one investigator, Komarewsky (13), has reported results on this vapor-phase flowing system, the data on the effect of different operating variables, such as pressure, temperature, and catalyst, are meager. The object of this investigation was to find a suitable catalyst to promote the reaction of ethylene with benzene in the vapor phase to form predominantly monoethylbenzene,

$$C_{\mathfrak{s}}H_{\mathfrak{s}}(g) + C_{\mathfrak{s}}H_{\mathfrak{s}}(g) \longrightarrow C_{\mathfrak{s}}H_{\mathfrak{s}}C_{\mathfrak{s}}H_{\mathfrak{s}}(g) \tag{2}$$

which might be dehydrogenated to form styrene as indicated in reaction (1). After a suitable catalyst for the reaction was found, the next object was to study the action of this

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catalyst under various conditions of pressure, temperature, and space velocity.

Previous Work

The alkylation of benzene with olefins has been widely investigated, but most of the work has been confined to liquidphase batch experiments. The only work of note reported in the literature in which a vapor-phase flow system was employed is that of Komarewsky (13). A dehydrogenation catalyst, nickel-alumina, was used in this experiment, and vapors of ethylene and benzene at 350° C. and atmospheric pressure were passed over this catalyst. Analysis of the liquid product led to the conclusion that 5 per cent of the ben-zene charged was converted to toluene. The remainder was unconverted benzene and some high-boiling residue, representing about 2 per cent of the benzene charge and identified as a mixture of naphthalene and diphenyl. The gas produced by the reaction consisted of hydrogen, methane, and ethane. When benzene alone was passed over the catalyst under the same conditions only a small fraction of it reacted, the products being diphenyl and hydrogen. Under the same conditions ethylene alone was completely decomposed to form carbon, hydrogen, methane, and ethane. According to previous results of Ipatieff and Komarewsky (10), ethylbenzene in the presence of the nickel-alumina catalyst at 350° C. decomposed to toluene and methane.

Much work has been done on the benzene-ethylene reaction in which a liquid phase was present. Results of these investigations show that such materials as metal halides, inorganic acids, and acid anhydrides (for example, P_2O_5) catalyze the reaction with the resulting formation of ethylbenzenes, from





Figure 1. Flow Diagram for Synthesis Apparatus Used in Vapor-Phase Reaction between Ethylene and Benzene

the mono- to the hexaethylbenzene. Low temperatures favor the formation of these ethylbenzenes, but good conversions have been obtained up to $300-400^{\circ}$ C. As would be expected, greater conversions occur at high pressures than at low. (Pressures up to 50-60 atmospheres have been reported for the benzene-ethylene reaction.) Since all of the published data resulted from investigations carried out in a batch process where a constant pressure of ethylene was maintained on the reaction mixture for periods of 12 to 60 hours, it is meaningless to give definite conversion figures without complete details of the experiments; these details are beyond the scope of this paper. However, it may be said that benzene conversions to mono-, di-, and higher alkylbenzenes were as high as 100 per cent under certain conditions.

It has been generally concluded that the metal halides are the best catalysts for the aromatic-olefin condensations. Many investigators, dating back to Balsohn in 1879 (2), have studied the catalytic effect of these metal halides under various conditions of pressure, temperature, and ratio of reactants. Some of these recent investigators include Ipatieff and Grosse (6, 9), Huber and Reid (7), Milligan and Reid (16, 17), and Amos, Dreisbach, and Williams (1).

Among the inorganic acids which have been tested as catalysts for the benzene-olefin condensations are sulfuric, ophosphoric, and hydrofluoric. Ipatieff, Corson, and Pines

(8) and Wunderly, Sowa, and Nieuwland (24) reached the conclusion that sulfuric acid does not catalyze the benzene-ethylene reaction but does catalyze the reaction between benzene and olefins of three or more carbon atoms. Ipatieff, Pines, and Komarewsky (11) found that o-phosphoric acid catalyzed the benzeneethylene reaction. Hydrofluoric acid was tested by Simons and Archer, (20, 21) and by Calcott, Tinker, and Weinmayr (5), and was found to promote the reaction of benzene with olefins of three or more carbons, but these investigators do not mention the use of hydrofluoric acid with benzene and ethylene. The acid anhydride, phosphorus pentoxide, was used by Malishev (14, 15) and by Truffault (23) to effect condensation.

The products resulting from the reaction of benzene with ethylene in the presence of a liquid phase consist essentially of mono- to hexaethylbenzenes. The catalysts mentioned in the above discussion seem to exhibit very little difference in selectivity in the range of conditions where they are appreciably active.

Thermodynamics of the Reaction

The best available thermal data have been used to calculate an equilibrium constant for the reaction between ethylene and benzene in the vapor phase to form monoethylbenzene (vapor),

$$C_{6}H_{6}(g) + C_{2}H_{4}(g) \rightleftharpoons C_{6}H_{5}C_{2}H_{5}(g)$$
⁽²⁾

The only data which are lacking for this calculation are the specific heat data for ethylbenzene vapor. By subtracting the specific heat equation of methanol vapor (19) from the equation of ethanol vapor (19), the effect of adding a $-CH_2$ -group to a carbon chain was evaluated. Then by adding the equation for this $-CH_2$ -group to the specific heat equation of toluene (19) the following equation was obtained:

$$C_p = 10.3 + 0.072 T$$

		Table	I. Thermal	Dataa	
Compound	State	Heat of Vaporiza- tion	Heat of Formation	Standard Free Energy of Formation	Specific Heat (19)
Ethylene	Gas	0100 (10)	11,975 (18)	15,840 (<i>18</i>)	$C_p = 6 + 0.015T$
Benzene	Gas	8100 (19)	11,630 (19)	30,640 (19)	$C_p = 6.5 + 0.052T$
Ethylbenzene	Gas	9900 (1%)	- 5,070 (19)	28,460 (19)	·····
Ethyl alcohol	Gas	· • · •	• • • •	• • • •	$C_p = 2 + 0.030T$ $C_p = 4.5 + 0.038T$
^a Units are gra are 298.1° K. and	Gas m calories 1 760 mm	 s, ° K., and . Hg. respec	gram moles; t tively.	he reference te	$C_p = 7.8 \pm 0.064T$ mperature and pressure

This equation should represent the specific heat of ethylbenzene. The units for this equation are gram calories, degrees Kelvin, and gram moles.

Table I lists the data from which the following equation for the calculation of the equilibrium constant, K_p , as a function of temperature may be derived:

$$\log_{10} K_p = \frac{5800}{T} + 5.475 \times 10^{-4} T - 1.11 \log_{10} T - 3.691$$
 (3)

Table II contains equilibrium constants, K_p , calculated from Equation 3 for Equation 2. Calculations based on a 1:1 molal ratio of ethylene to benzene, atmospheric pressure, and 327° C. indicate that at equilibrium more than 99 per cent of the ethylene should be converted to ethylbenzene.

Table	II. Equilib	rium Constants for	Reaction 2
	$[C_6H_6(g) + C_2]$	$H_4(g) = C_6 H_5 C_2$	$H_5(g)$]
Temper	ature	· · · · · ·	
° K.	° C.	$Log_{10} K_p$	K_p
$298.1 \\ 350.1$	$\frac{25}{77}$	$13.22 \\ 10.28$	1.66×10^{13} 1.91×10^{10}
400.1	127 227	$8.14 \\ 5.18$	1.38×10^{8} 1.51×10^{5}
600.1	327	3.22	1.66×10^{3}

Catalysts

Eleven different catalysts were prepared and tested. In these preparations, outlined briefly in the following paragraphs, the following materials were used unless otherwise specified:

Charcoal, activated, animal, 6-20 mesh, J. T. Baker Chemical Company.

Alfrax, 10-16 mesh, Carborundum Company.

Phosphoric acid, 85 per cent (specific gravity 1.71), J. T. Baker Chemical Company

Boric acid (H₈BO₂), Howe and French, Inc. Sulfuric acid, 96 per cent reagent. Zinc_sulfate (ZnSO₄·6H₂O), technical grade, Merck & Com-

pany, Inc. Sodium phosphate (Na₂HPO₄·12H₂O), Baker & Adamson.

Strontium chloride (SrCl₂·6H₂O), c. p. granular, J. T. Baker Chemical Company

Zinc chloride (ZnCl2), c. p. granular, J. T. Baker Chemical Company.

Ferric chloride (FeCl₂·6H₂O), c. p. granular, Eimer & Amend. Aluminum chloride (AlCls), anhydrous, Mallinckrodt Chemical Works.

Silver sulfate (Ag₂SO₄), c. p. powder, J. T. Baker Chemical Company. Water, distilled.

The percentage catalytic material referred to in each case is based on the difference between the total weight of catalyst and the weight of support (charcoal, Alfrax, etc.) used. Solutions are aqueous unless otherwise specified.

Z-1, PHOSPHORIC ACID-KIESELGUHR. This was the regular Universal Oil Products Company polymerization catalyst. Minute details for its preparation are not available, but from information obtained, it was concluded that a 3:1 weight mixture of phosphoric acid and kieselguhr was extruded from a 1/s-inch orifice into pellets which were baked at 200-260° C. A catalyst prepared in this manner was tested in the synthesis unit and was found to give results almost identical with those obtained when the U. O. P. catalyst was used.

Z-2, PHOSPHORIC ACID-CHARCOAL. Phosphoric acid was poured over charcoal, and the mixture (1.5:1 weight ratio of acid:charcoal) was heated at 250-280° C. for 17 hours and at about 370° C. for 1 hour; after this treatment the material was dry at room temperature and contained about 42 per cent acid.

Z-3, BORON PHOSPHATE-PHOSPHORIC ACID-CHARCOAL. A 14.9 per cent boric acid solution was poured over a phosphoric acid-charcoal mixture and heated with stirring to 240° C. (5.5 hours of heating time). The weight ratio of boric acid solution to 85 per cent phosphoric acid to charcoal was 3:1:1.6. The resulting catalyst contained approximately 18 per cent catalytic material.

Z-4, PHOSPHORIC ACID-SULFURIC ACID-CHARCOAL. A solution of phosphoric acid and concentrated sulfuric acid was poured over charcoal (11.1:1:9.3 weight ratio). This mixture was heated with stirring at 200° C. for about 30 minutes. The excess liquid was separated from the solid by filtration through glass wool; then the solid material was heated at 213° C. for 1.5 hours. The resulting mixture contained about 21 per cent catalyst.

Z-5, ZINC PHOSPHATE PELLETS. Zinc phosphate was precipitated from a hot 56.5 per cent Zn₂SO₄·6H₂O solution by addition of a hot 52.5 per cent solution of Na₂HPO₄·12H₂O. The weight ratio of sulfate to phosphate solution was 1.1:1. The precipitate was filtered from the mixture and washed several times with a total of about 0.5 weight ratio of water (based on phosphate solution) followed by drying at 110° C. for 11 hours. About 3 per cent by weight of graphite was incorporated in the powder to act as a binder; then the mixture was made into pellets 7/82 inch in diameter and 1/8 inch long.

Z-6, STRONTIUM CHLORIDE-CHARCOAL. A hot 16.7 per cent solution of $SrCl_2 \cdot 6H_2O$ was poured over charcoal (weight ratio, 2.8:1). This mixture was heated, with frequent mixing, over a hot plate until practically dry and was then dried for 30 minutes at 110°C. Catalytic material contained in the mass was about 30 per cent.

Z-7, ZINC CHLORIDE-ALFRAX. Alfrax was stirred into a 50 per cent $ZnCl_2$ solution (1.75:1 weight ratio). The mixture was stirred, allowed to stand for several minutes, filtered over glass wool, and dried at 110° C. for about 40 hours. The resulting material contained about 14.1 per cent catalyst.

Z-8, FERRIC CHLORIDE-ALFRAX. The method employed in the preparation of this catalyst was similar to that used in Z-7. Hydrogen chloride was evolved during the drying operation, and the result was the formation of iron oxide. For this reason the material was dried for only 1.75 hours at 103° C. The resulting mass contained about 10 per cent catalyst.

Z-9, Sodium Chloride-Aluminum Chloride-Pumice. The method employed in the preparation of this catalyst was similar to that used by Blunck and Carmody (4). The sodium chloride-aluminum chloride salt consisted of approximately a 1:1 molal complex of aluminum chloride and sodium chloride. The complex was made by fusing the salts (with a slight excess of aluminum chloride to take care of sublimation loss in the early stage of the heating process) in a pressure bomb at temperatures up to 265° C. After cooling to room temperature, the bomb was opened and heated again to drive off the excess aluminum chloride. The fused salt was then poured over an equal weight of dry pumice (8-10 mesh) with thorough mixing. The final catalyst contained about 50 per cent catalytic material. This material was very hygroscopic and necessitated storage in a gastight container until it was placed in the catalyst chamber.

The Z-9 catalysts listed in Table III were all prepared ac-

cording to the above procedure. The different letters (e. g., Z-9a, Z-9c, etc.) signify different batches of catalyst.

Z-10, SULFURIC ACID-ALFRAX. Alfrax was stirred into a 77 per cent solution of sulfuric acid; the mixture was heated for one hour at 100° C. and was then filtered over glass wool. The solid was heated for 4 hours until the temperature



276

INDUSTRIAL AND ENGINEERING CHEMISTRY

Vol. 35, No. 3

						Table	II. Su	mmary	of Data												
Run No.	4	12	19a	19b	19e	19d	20b	20c	20d	23	24	25	26	27	29	30	31a	31b	31c	31d	32
Catalyst, <i>T</i> - Pressure, Ib./sq. in. gage Premperature, ° C. Saae velocity a Cata CAH molal ratio Cata Gratt molal ratio Cata feed rate, grans/hr. Gata feed rate, grans/hr. Jaquid product analysis, volume % Barzene Michylbenzene Michylbenzene Biethylbenzene Biethylbenzene Ethane To an ethal Denzene Ethane To an ethal Denzene Ethane To an ethane To an ethane To tan	$\begin{array}{c} 1 \\ 100 \\ 233 \\ 233 \\ 233 \\ 233 \\ 233 \\ 233 \\ 233 \\ 233 \\ 233 \\ 233 \\ 10 \\ 1.3 \\ 1.3 \\ 1.3 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.4 \\ 1.6 \\ 1.$	98 100 100 1.83 1.83 1.83 1.95 6.0 6.0 6.0 6.0 6.3 8.1 1.8 8.1 1.8 8.5 1.8 8.6 1.8 8.7 7.0 1.8 8.6 1.8 8.7 7.0 7.0 8.6 8.7 8.7 8.7 8.7 8.7 8.7 8.6 1.8 8.6 1.8 8.7 8.7 8.7 8.7 8.7 8.7 8.7 8.7 8.7 8	9d 11111 11111 11111 11111 111111	9d 11.95 11.	9d 100 100 11.3 11.4 11.3 11.3 11.3 11.3 11.3 11.3	$\begin{smallmatrix} & 9d \\ 100 \\ 228 \\ 1.73 \\ 1.73 \\ 1.80 \\ 16.3 \\ 16.3 \\ 16.3 \\ 10.0 \\ 10.0 \\ 10.0 \\ 10.0 \\ 21.4 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ $	$\begin{array}{c} \begin{array}{c} 9c\\ 200\\ 200\\ 200\\ 119.4\\ 180\\ 11.2\\ 9.2\\ 9.2\\ 9.2\\ 1.7\\ 1.7\\ 1.7\\ 88.1\\ 88.1\\ 88.1\end{array}$	$\begin{array}{c} \begin{array}{c} & 9c \\ 200 \\ 200 \\ 21.55 \\ 22.26 \\ 11.20 \\ 14.4 \\ 9.3 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1.20 \\ 0 \\ 0 \\ 1.20 \\ 0 \\ 0 \\ 1.20 \\ 0 \\ 0 \\ 1.20 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	$\begin{smallmatrix} 96\\50\\37.67\\1120\\17.9\\7.1\\22.28\\7.1\\17.9\\7.1\\120\\16.3\\16.3\\16.3\\16.3$	$\begin{array}{c} & 2\\ & 2\\ & 2\\ & 2\\ & 2\\ & 2\\ & 2\\ & 2$	$\begin{array}{c} & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 1 \\ & 1 \\ & 1 \\ & 2 \\ & 2 \\ & 2 \\ & 2 \\ & 1 \\ & 1 \\ & 2 \\$	$\begin{smallmatrix} & & & & & & & & & & & & & & & & & & &$	$\begin{smallmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $	$\begin{smallmatrix} & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & $	$\begin{array}{c} & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & &$	22201 22201 22201 22201 22201 22201 22201 22201 22201 201	22200 22220 22200 22200 22200 22200 22200 22200 22200 22200 22200 22200 22200 22200 22200 22200 22200 22200 2000 2000000	22 200 22 200 22 200 22 200 22 200 22 200 22 200 22 200 22 200 26 2 27 4 26 2 27 4 26 2 27 4 26 2 27 4 26 2 27 4 26 2 20 2 20 2 20 2 20 2 20 2 20 2 20 2	$\begin{smallmatrix} & & & & & & & & & & & & & & & & & & &$	22222222222222222222222222222222222222	$\begin{array}{c} & & & & & & & & & & & & & & & & & & &$
^a Expressed as ce. vapor (at 0° C., 760 mm.) p	er hour pe	r ee. cat	alyst																		



Figure 2. Decrease in Catalyst Activity with Amount of Ethylene Converted

reached 300° C. After this treatment the catalytic content was about 26 per cent.

Z-11, SILVER SULFATE-SULFURIC ACID-ALFRAX. The method for the preparation of this catalyst was similar to that employed by Stanley, Youell, and Dymock (22) and by Bliss and Dodge (3). By saturating Alfrax with a solution of silver sulfate and sulfuric acid, filtering, and drying the residue, a material was produced which contained about 4 per cent silver sulfate and about 21 per cent sulfuric acid.

Apparatus and Procedure

The ethylene used in this work came from U.S. Industrial Chemical, Inc., and was at least 99 per cent pure (prepared March, 1943

by dehydration of ethanol over phosphoric acid). The benzene used was Merck's nitration grade which had been further fractionally distilled.

Figure 1 is a flow diagram for the synthesis unit. Ethylene passed from cylinder A through pressure regulating valve W_1 , purifier N, trap M, flowmeter T_1 , expansion valve W_2 , and into benzene dropper H. The ethylene-benzene mixture passed from vaporizer V, leaving as vapors, and entering reactor R, from which the reaction product was expanded through valve W_4 , to practically atmospheric pressure. The reaction mixture then passed into a condenser system from which emerged the gaseous product. This flow of gaseous product was noted on flowmeter T_2 , sampled continuously by gas sampler O, and finally measured by displacement of brine solution from gas receiver P. The benzene liquid was fed from tank G by gravity into dropper H, where it mixed with the ethylene and then passed through the apparatus as noted above. The flow rates were controlled by 1/4-inch, V-point, needle

The flow rates were controlled by 1/4-inch, V-point, needle valves. The ethylene was throttled through valve W_2 , from a pressure usually 50-100 pounds per square inch higher than the reactor pressure. The flow rate was noted by reading a pressure differential on manometer T_1 , developed by passage of the gas through a short capillary tube. The benzene flow rate was regulated by valve W_3 , and noted by counting drops falling through sight glass and dropper H. The reactor pressure was maintained by throttling the reaction vapors through valve W_4 . The liquid product was fractionated at atmospheric pressure

The liquid product was fractionated at atmospheric pressure through a 1/2-inch glass, vacuum, silver-jacketed column packed with 24 inches of 3/16-inch stainless steel rings. The various cuts were identified by refractive index measurements as well as by their boiling points.

The effluent gases were analyzed by means of a standard U. S. Steel gas analysis set.



Figure 3. Effect of Pressure on Conversion

Each catalyst was tested by passing through the catalyst bed a mixture of benzene and ethylene vapors in molal ratio of about 2:1, at temperatures of 228° to 245° C., gage pressure of 100 pounds per square inch, and vapor space velocities of 25 to 40 cc. (0° C. and atmospheric pressure) per hour per cc. of catalyst. Sixteen runs were made in this preliminary catalyst study, and



Figure 4. Effect of Space Velocity on Conversion

only two of the catalysts were found to promote a detectable reaction between the ethylene and benzene (the phosphoric acidkieselguhr and the sodium chloride-aluminum chloride-pumice catalysts).

Following the preliminary catalyst study, the sodium chloride-aluminum chloride-pumice catalyst was investigated in further detail. The activity of this catalyst was studied over a period of time, and the pressure and space velocities were varied in a series of runs. In the investigation of the effect of pressure on the reaction, gage pressures of 0, 50, 100, and 200 pounds per square inch were employed. The effect of space velocity was studied over the range 11.6 to 47.2 cc. per hour per cc. of catalyst (contact times of about 20 to 5 minutes).

A summary of the runs in which reaction was noted is given in Table III. No data are listed for the catalyst test runs where no reaction occurred, but it may be assumed that the operating data and analytical procedures were similar to those listed under runs 4 and 12.

Since the yields of triethylbenzene were only estimated from the distillation residue, they are not plotted as separate curves in Figures 2, 3, and 4. However, they are contained in the "total" conversion curves in these figures. This explains why the sum of the mono- and di- ordinates are not always equal to the total ordinates.

Preliminary Catalyst Study

Phosphoric acid supported on kieselguhr was the first catalyst to be tested. The results indicate that 13-15 per cent

of the ethylene was converted to ethylbenzene, predominantly monoethylbenzene with small amounts of diethylbenzene (about 10:1 weight ratio). Since pressure has been found to have such a pronounced effect on the reaction when the sodium chloridealuminum chloride-pumice catalyst was used, this phosphoric acid-kieselguhr catalyst would



probably give satisfactory conversions at pressures of 300-400 pounds per square inch.

Phosphoric acid in forms other than that mentioned above (with kieselguhr) failed to promote any noticeable reaction. Thus, phosphoric acid-charcoal, boron phosphate-phosphoric acid-charcoal, and phosphoric acid-sulfuric acid-charcoal failed to cause ethylene and benzene to react at 100 pounds per square inch and about 240° C.

Sulfuric acid supported on Alfrax was inactive as was also the mixed catalyst, silver sulfate-sulfuric acid-Alfrax. Thus, it stands that sulfuric acid, even though it is a good catalyst for benzene alkylation by olefins of three or more carbon atoms in the liquid phase, does not promote the reaction of ethylene and benzene either in the vapor phase or liquid phase.

Strontium, zinc, and ferric chlorides supported on activated charcoal, Alfrax, and Alfrax, respectively, were found to be inactive in the form employed. Aluminum chloride, in the form of a fused equimolar mixture with sodium chloride supported on pumice, was quite active; ethylene conversion was about 69 per cent under the same conditions of test on the other catalysts (100 pounds per square inch, 246° C., 26.6 cc. per hour per cc. catalyst).

Sodium Chloride-Aluminum Chloride-Pumice Catalyst

Under the conditions of these tests, the sodium chloridealuminum chloride was in the liquid state; therefore, it was necessary to support the material on a carrier. Pumice (8-10 mesh) was used as the carrier but was not satisfactory because of its varying properties from one lot to another. For example, two different lots of pumice were used; one gave an active and the other an inactive catalyst. It was concluded that the variation in activity was due to the difference in density of the two lots. The more active catalyst was prepared from the less porous lot (density of about 0.46 gram per cc.), and its greater activity may be attributed to a greater and thicker catalytic surface on this pumice than on the more porous material (density of about 0.26 gram per cc.). Some "prepared" carrier would probably be much better than the pumice, but due to lack of time, other carriers were not tested except for one test with activated alumina. In this test the ratios of materials were the same as with pumice, but this catalyst gave only about 20 per cent conversion. It is believed, however, that the only function of these different carriers is to support the catalyst, and that with the same area and thickness of catalytic surface the carrier material would have no effect on the reaction. Tests were made to show that the pumice and the alumina alone had negligible catalytic effect on the benzene-ethylene mixture under the conditions used.

In order to determine the effect of the catalyst on the individual reactants, the benzene and ethylene vapors were passed separately through the catalyst bed. The benzene vapors were unaffected, and the ethylene was decomposed slightly, with about 2 per cent ethane and 0.5 per cent hydrogen in the effluent gas.

CATALYST ACTIVITY. Runs 19 and 31 were made to determine the activity of the catalyst over a period of time at 100 and 200 pounds per square inch, respectively. The data used to plot Figure 2 are listed in Table IV, and illustrate the decrease in activity of the catalyst as a function of moles of ethylene converted.

There was a decrease in total conversion from 93 to 75 per cent resulting from the conversion of about 0.19 to 1.16 gram moles of ethylene to ethylbenzene. Indications are that the formation of higher ethylated benzenes is favored with use of the catalyst over a period of time.

PRESSURE AS A VARIABLE. Runs were made at pressures of 0, 50, 100, and 200 pounds per square inch gage. A 300pound run was attempted, but the capacity of the benzene vaporizer was not sufficient for operation at this pressure.

The great effect of pressure on the reaction is shown in Figure 3. Conversion ranged from 0 at atmospheric pressure to about 90 per cent at 200 pounds per square inch gage. Since the points in this plot are scattered, the reliability of the different analyses has been evaluated, and the points were weighed accordingly in drawing the curve to best represent the true conditions.

	Table IV. Catalyst Activity									
Run No.	Total Gram Moles Ethyl- ene Converted	Pressure, Lb./Sq. In. Gage	<u>% Eth</u> Mono-	ylene (Di-	Convert Tri-	ed to: Total				
9a 9b 9d 31a 31b 31c 31d	$\begin{array}{c} 0.131 \\ 0.383 \\ 0.683 \\ 0.991 \\ 0.180 \\ 0.521 \\ 0.851 \\ 1.164 \end{array}$	100 100 100 100 200	54.4 44.3 19.7 29.9 64.7 44.6 39.3 36.1	$15.5 \\ 19.6 \\ 21.5 \\ 22.2 \\ 26.9 \\ 25.1 \\ 23.4 \\ 23.4 \\ 23.4 \\$	$\begin{smallmatrix} 0 \\ 0 \\ 23.2 \\ 0 \\ 1.6 \\ 14.1 \\ 16.2 \\ 15.6 \end{smallmatrix}$	$\begin{array}{c} 69.9\\ 63.9\\ 64.4\\ 52.1\\ 93.2\\ 84.0\\ 78.9\\ 75.1 \end{array}$				

SPACE VELOCITY AS A VARIABLE. The vapor space velocity was varied from 47.2 to 11.6 cc. (vapor, calculated at 0° C. and atmospheric pressure) per hour per cc. of catalyst. The data for these runs are plotted in Figure 4. It is concluded that the total conversion of ethylene to ethylbenzenes was independent of the space velocity in the range studied. However, there are indications that more of the mono- and less of the diethylbenzenes are produced at the higher than at the lower velocities.

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