ETHYLBENZENE

High Yield and Rate of Production by Liquid-Phase Ethylation

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The ethylation of benzene with ethylene by the Friedel-Crafts reaction has been controlled so as to give yields of monoethylbenzene about 15% higher than those reported in most other investigations at corresponding mole ratios of reagents. The conditions are 100° C. and ethylene pressure of 100 to 300 pounds applied above the catalyst. These conditions also increase the reaction rate nearly a hundred fold over some industrial processes, so that they are better adapted for a continuous operation. Yields of ethylbenzene reported in sixty investigations are correlated, and relations to mole ratios of reagents and to reaction conditions are shown. They are compared with theoretical curves for multiple-stage reactions with a common reagent. Evidence is presented that, contrary to a common opinion, the ethylation of benzene takes place at the same rate as that of ethylbenzene and other partly ethylated benzenes. Some observations are best explained by supposing that under suitable conditions the ethylation reactions are practically instantaneous. Conditions are given for making pure ethylbenzene from ethylene mixed with paraffin gases, or from a low concentration of benzene in a mixture with nonaromatic hydrocarbons.

LARGE quantities of ethylbenzene are made by the liquid-phase alkylation of benzene with ethylene in the presence of aluminum chloride (*24*). This reaction was discovered by Balsohn (*7*) in 1879. He used several days of reaction time, and only 29% of the ethylene which reacted and 31% of the total benzene appeared in the form of ethylbenzene. Interest has recently been intensified, as indicated by twenty-six citations in 1945. Altogether, over ninety investigations have produced ethylbenzene by ethylation of benzene, and sixty of these have reported yields in some numerical form.

The practicability of the use of ethylene for the production of ethylbenzene was demonstrated in studies at Johns Hopkins University (*11, 17, 45, 66*). These were purely academic but pointed the way for commercial development. The reaction was accelerated greatly by the use of intensive stirring to promote contact of the ethylene with the hydrocarbon liquid and catalyst. There was usually an "incubation period" of 20 minutes to an hour, after which the absorption was rapid. Recently Marks, Almand, and Reid (*61*) reported a rate of 0.07 mole ethylene absorption per minute per mole of benzene, but this was attained only after there had been considerable ethylation. The amount of aluminum chloride required was small—0.07 mole to 1 of benzene, and could be used repeatedly (*66*) unless contaminated or lost.

Natelson (*69*) investigated the reaction but did not reduce the time below 6 hours. Davidson (*18*), who seems to have the first United States patent covering ethylbenzene, emphasized the removal of sulfur during the ethylation. Several improvements have been made by the Dow Chemical Company (*2, 23, 24*); in one (*2*) the addition of isopropylbenzene was recommended. The reaction time was 4.75 hours. A recent study of the reaction was made by Sisido (*90*). Gaylor (*39*) found that pretreatment of the benzene with aluminum chloride improved the catalyst life and reaction rate. Blanding (*12*) used aluminum halides for ethylation of benzene in the vapor phase.

Most of the ethylations just described were made at substantially atmospheric pressure and at moderate temperatures, starting below 80° C. None of them was so rapid as was desired for continuous operation. Liquid-phase ethylation with other reagents is not more rapid, no process being reported with less than 2-hour reaction time. Only one disclosure has been found for the use of ethylene under substantial pressure for making ethylbenzene with aluminum chloride. Schmerling (*84*) used 40 atmospheres pressure with the catalyst dissolved in nitromethane. Mills (*67*) ethylated benzene for 4 hours at 125° C. and 60 pounds per square inch pressure, from which should be subtracted 34 pounds for the vapor pressure of benzene. D'Ouville and Evering (*22*) ethylated toluene with ethylene under pressure, using a complex formed by the action of aluminum chloride upon iso-octane.

As catalyst for the reaction of ethylene with benzene, Wunderly and co-workers (*103*) used sulfuric acid with boron trifluoride as promoter. Ipatieff and Grosse employed boron trifluoride alone (*47*), and chlorides of beryllium, titanium, zirconium, columbium, and tantalum (*41*); the reaction times were 8 hours and 12–60 hours, respectively (for analyzed products). Bruner and co-workers (*15*) used a large volume of aqueous boron trifluoride. Other catalysts used with ethylene were hydrogen fluoride (*15A, 35, 78*), phosphorus pentoxide (*59, 96*), phosphoric acid (*25, 48, 50, 51, 62, 77, 96*), calcium and magnesium acid phosphate (*83*), gallium chloride (*98, 99*), silica-alumina (*3, 68, 76, 85, 87, 87A, 95*), and sodium aluminum chloride (*77*). Catalysts employed with other ethylating agents were aluminum chloride (*4, 4A, 5, 9, 10, 13, 14, 16, 19, 37, 38, 52, 53, 57, 69–74, 80, 81, 88, 97, 101, 104*), aluminum bromide (*56, 101*), hydrogen fluoride (*35, 89*), boron trifluoride (*58, 75*), zinc chloride (*8, 40, 86*), zinc oxide and alumina (*63, 63A, 64, 85*), silica-alumina (*44, 63, 63A, 82, 85, 95*), phosphoric acid (*6, 50, 60, 93*), amalgamated aluminum and hydrogen chloride (*20, 80A*), and ferric chloride (*102*). Noncatalytic ethylation of benzene has been reported (*26, 36, 46*). Good yields of ethylbenzene were claimed (*100*) by copper-catalyzed pyrolysis of olefins without benzene.

DISCUSSION OF REACTION

If the ratio of ethylene to benzene is kept very low, it is evident that most of the ethylene will go to form monoethylbenzene and will give a good yield based on ethylene; but the conversion of benzene will be poor and require recycling. On the other hand, if ethylation is continued until most of the benzene is consumed, much of the ethylene will go to form higher ethylated products of little value in themselves. They can be de-ethylated (*5, 13, 17, 31, 44, 63, 63A, 64, 66, 80, 80A, 86*), but this also requires recycling (*17, 54, 63, 63A, 80, 80A, 87A, 92*). These considerations apply to any ethylation of benzene, including those with ethyl halides (*9, 20, 35, 37, 69, 70, 73, 80, 80A, 85, 88, 89, 94, 101, 102, 104*), ethanol (*6, 40, 50, 60, 74, 89, 93, 95, 97*), ethyl ethers (*8, 38, 74, 75, 89*), esters (*10, 14, 16, 26, 37, 46, 52, 53, 56, 57, 58, 72, 81, 89*), ethane (*36*), higher paraffins (*42*), vinyl bromide (*4A, 19*), and ethylidine halides (*4*), and with other catalysts, and in the vapor phase (*3, 6, 12, 25, 36, 44, 48, 50, 51, 60, 62, 63, 63A, 64, 68, 76, 77, 83, 85, 86, 87, 87A, 93, 95, 100*). For any set of conditions the yield is some function of mole ratio; this is indicated in Figure 1, which shows yields based on ethylene or other ethylating agent and also yields based on benzene. The function depends upon the conditions, which may change the effective ratio of velocity constants of ethylation. It will be shown that this factor is at least as important for yield as is the mole ratio of reagents. The mole ratio used in this paper is that of ethylene to benzene (as in citations *11, 54, 61, 66, 73*) rather than the reverse (as in citations *15, 39, 62, 63, 63A, 68, 77, 83, 95*), so as to simplify the mathematics and plotting. Both forms were used by O'Kelly and co-workers (*76*).

The expected yield of ethylbenzene with various mole ratios has been computed on the basis of assumed relations among the velocity constants. The differential equations employed are the same as those used in a study of the bromination of phenols and aromatic amines (*28*), except that six successive steps are involved instead of two or three. If the velocity constants for the six reactions were all different, the solution of these equations would be exceedingly complex. The situation would be still further complicated by consideration of de-ethylation velocity constants. However the de-ethylation reactions are probably substantially slower than the ethylations; otherwise the distribution of ethyl groups among the products would be always the same for the same mole ratio. An unconsidered redistribution of ethyl groups could result only in a distribution nearer to equilibrium. A further simplifying assumption that all six velocity constants are equal permits a solution of the short form[1]:

$$Y = 100e^{-m}$$

where Y = percentage of ethylene converted to ethylbenzene
m = mole ratio of ethylene (reacted) to benzene
e = base of natural logarithms

This equation is plotted as the middle curve in the upper graph of Figure 1.

The above assumption is apparently contrary to the common experience that ethylbenzene (*69*) and cumene and toluene (*11*) are ethylated more rapidly than benzene, and that the rate at which ethylene is consumed increases as the reaction proceeds (*11, 66*). Moreover, hexaethylbenzene is often formed in surprisingly large amounts in the early stages of ethylation (*11, 59, 61, 66, 69, 101*). The preferential formation of triethylbenzene (*61, 72, 73*) also seems inconsistent. If ethylbenzene were really ethylated more rapidly than benzene, however, it would be impossible to get yields as high as the middle curves of the figure without recycling or physical selection of the reagents.

TABLE I. DISTRIBUTION OF ETHYLBENZENES, IN MOLE PER CENT

Layer	Benzene	Ethylbenzene					
		Mono	Di	Tri	Tetra	Penta	Hexa
Upper	50	27	12	3	1	2	3
Lower	16	41[a]	8	15	10	3	7

[a] In the paper as printed this was 14, a typographical error.

The low temperature ethylations at atmospheric pressure and with conventional stirring have given yields close to the lowest curve in each graph, which is computed on the assumption that the first substitution in benzene is only one third as rapid as those that follow. It must be considered, however, that under the usual conditions mentioned, substantially all the ethylation takes place in the heavy lower layer, since it contains practically all of the catalyst. It seems probable that at low temperature the solubility of aluminum chloride in the benzene layer is too low to cause appreciable ethylation in that layer. This is the situation in Figure 2*a*, where the cross hatching represents an effective concentration of catalyst. This reasoning implies that the catalytic activity of aluminum chloride is not parallel with its thermodynamic activity, which is identical for each of two liquid phases in physical equilibrium. Each aromatic hydrocarbon present is partitioned between the two layers. The speed of ethylation of any one of them depends on its ethylation velocity constant multiplied by its concentration in the catalyst layer. In a recorded experiment (*61*) in which about one mole of ethylene per mole of benzene had reacted, the compositions of the two layers are shown in Table I.

The concentration of monoethylbenzene in the catalytic layer was over two and a half times that of the benzene. This probably accounts for the relatively slower ethylation of the benzene. On the other hand, the higher alkylated benzenes have fewer points of attack for further alkylation and are more subject to dealkyla-

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[1] Since the ethylation is typical of multistage reactions with a common reagent, the derivation is given, as follows: Considering the total concentration of aromatic hydrocarbons as unity, let u, v, w, x, y, and z be the mole fractions of substitution in the first, second, third, fourth, fifth, and sixth positions, so that $1 - u$ is the mole fraction of benzene, $u - v$ that of ethylbenzene, $v - w$ that of diethylbenzene, etc., and $m = u + v + w + x + y + z$ is the mole ratio of ethylene reacted.

Then $$du/dt = K_1(1 - u)E$$

where E = concentration of ethylene

$$dv/dt = K_2(u - v)E, \text{ etc.}$$

$$\frac{dv}{du} = \frac{K_2(u - v)}{K_1(1 - u)} = \frac{n(u - v)}{1 - u}$$

where n is the first ratio of velocity constants. Integrating and adjusting the integration constant so that $v = 0$ when $u = 0$:

$$v = \frac{(1 - u)^n + nu - 1}{n - 1}$$

(If $n = 0$, $v = 0$ and the yield of ethylbenzene would be 100% on upper graph, dotted line on lower graph of Figure 1.) For values of n = 0.5, 1.0, and 3.0 (as in the three curves plotted),

$v = 2 - u - 2\sqrt{1 - u}$; $v = u + (1 - u)\ln(1 - u)$; $v = {}^1/_2(3u^2 - u^3)$ (The second case requires a special integration.) If $K_1 = K_2 = K_3 = K_4 = K_5 = K_6$ (middle curve), and $r = -\ln(1 - u)$, the complete solution is:

Benzene $= 1 - u = e^{-r}$
Ethylbenzene $= u - v = r(1 - u)$
Diethylbenzene $= v - w = r^2/2(1 - u) = r/2(u - v)$
Triethylbenzene $= w - x = r^3/6(1 - u) = r/3(v - w)$
Tetraethylbenzene $= x - y = r^4/24(1 - u) = r/4(w - x)$
Pentaethylbenzene $= y - z = r^5/120\ (1 - u) = r/5\ (x - y)$
Hexaethylbenzene $= z = 1 - [(1 - u) + (u - v) + (v - w) + (w - x) + (x - y) + (y - z)]$

For low values of m, $z = r/6(y - z)$, but at higher values z is greater because hexaethylbenzene is not further ethylated, and so accumulates. However, it is convenient for the mathematics to consider tentatively that the ethylation proceeds through an unlimited number of steps:

$$\begin{aligned} m &= (u - v) + 2(v - w) + 3(w - x) + 4(x - y) + 5(y - z) + 6(z - \ldots) + \ldots \\ &= (1 - u)(r + r^2 + r^3/2 + r^4/6 + r^5/24 + r^6/120 + \ldots) \\ &= e^{-r}\cdot r\cdot e^{r} = r \text{ (from Taylor's theorem)} \end{aligned}$$

The yield of ethylbenzene based on benzene is $100(u - v)$, and that based on ethylene is

$$100(u - v)/m = 100(1 - u) = 100e^{-r} = 100e^{-m}$$

This equation is rigorous only if the number of steps is infinite; but with six steps the yield calculated by it is not in error by more than 0.1% (absolute value).

The maximum yields of the ethylbenzenes (based on benzene) calculated for equal-velocity constants are as follows:

Mono	36.8%	Tri	22.4%	Penta	17.5%
Di	27.1%	Tetra	19.6%	Hexa	100.0%

Higher yields of some of these products actually obtained (*11, 61, 66, 72, 73, 101*, and the present investigation) may be due to some physical selection of the reagents or removal of the products. The complete solutions for the velocity ratios represented by the highest and lowest curves can be supplied on request.

Another plausible assumption is that each unsubstituted position in the benzene ring reacts with equal velocity, so that $K_2 = {}^5/_6K_1$, $K_3 = {}^2/_3K_1$, etc., and $K_5 = {}^1/_5K_1$. This relation is improbable in view of the substantial amounts of hexaethylbenzene often found. The mathematics would be complex, but the effect on yield of ethylbenzene would be not very different from the above.

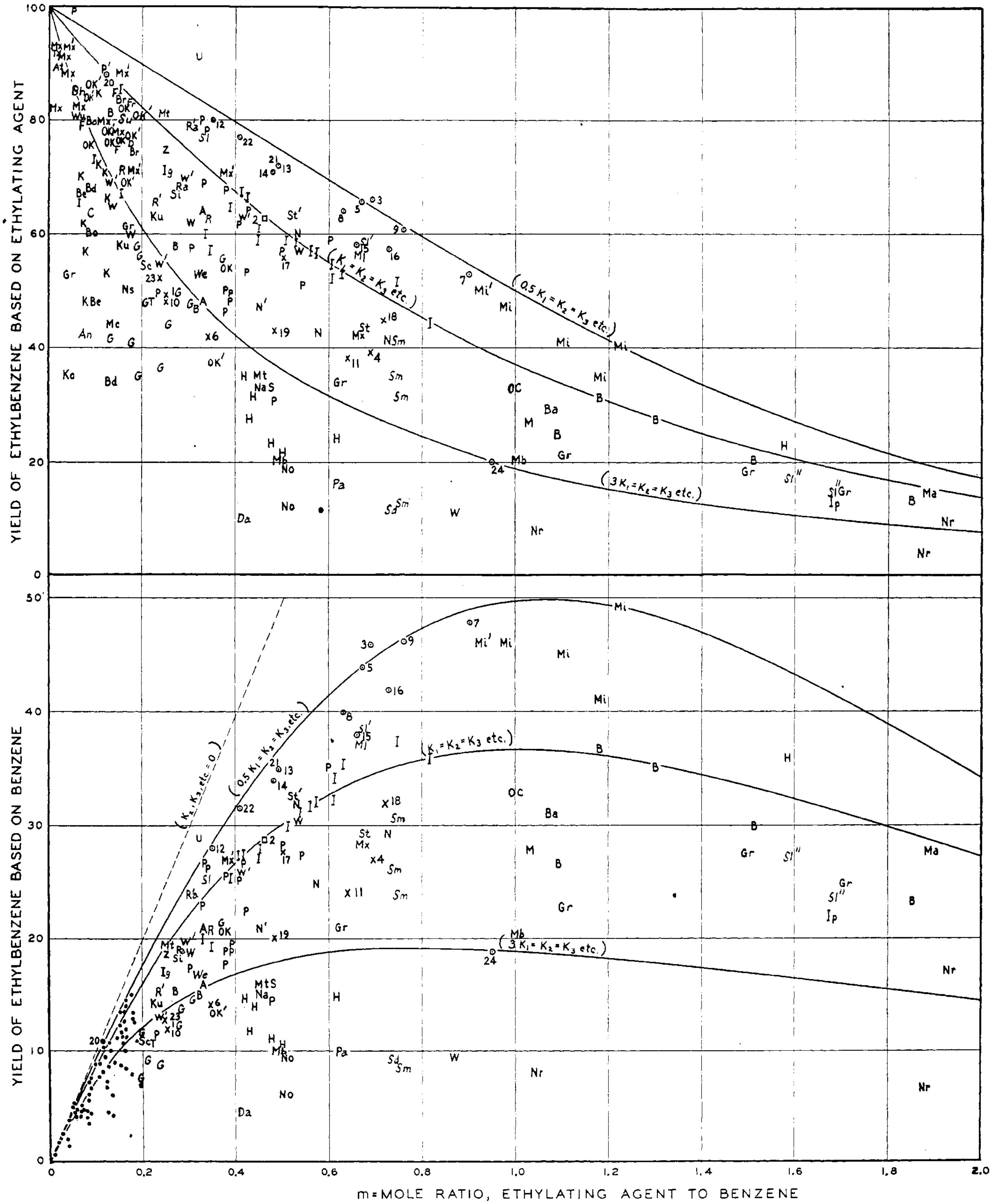

Figure 1. Yields of Ethylbenzene from Benzene as Functions of Mole Ratio of Ethylating Agent

tion, which is known to take place. Bowden (*14*) considered that slower reaction is favorable to high yields of monoethylbenzene. A fair comparison of the rates of ethylation of the various hydrocarbons present can be made only when all are in homogeneous mixture as in experiment 2 of this paper. This gave yields of the monoethylbenzene which fall on the middle curve of each graph. Several results from vapor-phase ethylation also come close to these curves. That is another method of providing a homogeneous mixture of reagents. Such observations support the view that the several velocity constants are fundamentally equal. The middle curves may also represent an equilibrium distribution of ethyl groups among the ethylbenzenes. This view is favored by observations of Anschutz (*4*) and by extrapolation of thermodynamic data (*1*).

The fact that cumene is so readily ethylated was the basis for Amos' proposal (*2*) to add it to the reaction mixture. This would certainly diminish the incubation period (*11*). Amos claimed an increase in yield from 48% (on lowest curve, upper graph of Figure 1) to about 64% (both at $m = 0.34$), still considerably below the middle curve.

Marks, Almand, and Reid (*61*) showed that the distribution of ethylene (reacted) among the products depends largely on the conditions of its introduction. Temperature has a marked effect as shown in Table II.

Thus, when about two moles of ethylene were put in at 55° C., 27% went to form penta- and hexaethylbenzene as contrasted with 3.3% at 95° C. For about three moles of ethylene these amounts were 38 and 7%. At the higher reaction temperature there was a marked concentration of ethyl groups in the products, corresponding to the number of moles of ethylene introduced. Increasing the rate of stirring had a similar effect on the distribution of the ethylene reacted as raising the temperature. Both caused the system of two layers to simulate a single phase, possibly by facilitating redistribution of ethyl groups.

The suggested equality of velocity constants implies a lack of directive influence by ethyl groups upon further ethylation, in marked contrast to other substitution reactions such as nitration or halogenation. This view is supported by a lack of uniformity in the composition of the isomeric polyalkylbenzenes formed by alkylation. Methylation with aluminum halides favors *o*- and *p*-xylene at low temperatures, and *m*-xylene at 55° C. or higher (*73*). Predominance of the meta isomer has been observed for dialkylation using phosphoric acid (*48*) and with aluminum chloride in most cases (*72*). Exceptions reported are the cymenes (*11*) and diethylbenzenes (*4*, *90*). Assuming correct analyses, it is not always clear what changes in conditions result in different isomers. Sisido considered (*90*) that the *meta* isomer is formed first and isomerizes to *p*-diethylbenzene, in direct contrast to the observations of Norris and Rubinstein (*73*) on xylenes. Price (*79*) suggested that the formation of *m*-dialkylbenzenes results from further alkylation of *p*-dialkylbenzenes, followed by dealkylation. However, since the thermodynamic stabilities of *m*- and *p*-dialkylbenzenes are nearly equal (*1*), the isomer first formed must remain in the product in substantial amount. The literature on such orientations is extensive, as reviewed by Nightingale (*71*) and Thomas (*94*). Other catalysts, boron trifluoride and sulfuric acid (*103*), give mostly the *p*-dialkylbenzenes, at least in the case of propylation. Some of these observations suggest steric effects. These are usually weak and would have a negligible effect upon the curves of Figure 1.

TABLE II. DISTRIBUTION OF ETHYLENE

Temp. ° C.	Ethylene, Mole Ratio	% to Form Various Products					
		Mono	Di	Tri	Tetra	Penta	Hexa
55	2.09	9	28	27	9	11	16
95[a]	2.17	8	45	41	3	0.3	3
55	3.03	2	17	31	12	14	24
95[a]	3.22	0.1	6	59	28	3	4

[a] The temperature was at reflux until 95° C. could be attained.

PRESENT INVESTIGATION

The object was twofold: to direct a larger proportion of the ethylene to the formation of monoethylbenzene so as to minimize

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Caption to Figure 1

Catalyst was aluminum chloride and reagent was ethylene unless indicated otherwise. Numbered points indicate this research. Plots of yields reported in U. S. Patents 2,403,124 and 2,403,785 (July, 1946) are slightly above the middle curve in each graph. The vapor phase de-ethylations of Kutz and Corson (*57A*) give plots below the lowest curves.

○	Recommended conditions.
□	Homogeneous reaction.
X	Other experiments.
●	Literature yields on benzene when mole ratio is less than 0.2.
A	Amos (*2*).
An	Anschutz (*4A*). Reagent, vinyl bromide.
At	Atlantic Refining Company (*6*). Vapor phase; catalyst, supported phosphoric acid; reagent, ethanol.
B	Berry and Reid (*11*).
Ba	Balsohn (*7*).
Bd	Boedtker and Halse (*13*). De-ethylation; reagent, polyethylbenzenes.
Be	Berman and Lowy (*10*). Reagent, triethyl phosphate.
Bh	Béhal and Choay (*9*). Reagent, ethyl bromide.
Bo	Bowden (*14*). Reagents, ethyl acetate and sulfate.
Br	Bruner, Clarke, and Sawyer (*15*). Catalyst, aqueous boron trifluoride.
C	Clemo and Walton (*16*). Reagent, ethyl *p*-toluenesulfonate.
D	Diuguid (*20*). Catalyst, amalgamated aluminum and hydrogen chloride; reagent, ethyl chloride.
Da	Davidson and Lowy (*19*). Catalyst, aluminum chloride with mercury; reagent, vinyl bromide.
F	Frey (*35*). Catalyst, hydrogen fluoride.
Fr	Francis and Reid (*31*). Continuous removal of product as vapor.
G	Grosse, Mavity, and Ipatieff (*42*). Reagents, paraffins C_5 to C_{16}.
Gr	Grosse and Ipatieff (*41*). Catalysts, chlorides of Ti, Be, Cb, Zr, Ta, Be (in order of increasing mole ratio).
H	Hansford, Myers, and Sachanen (*44*). Vapor-phase de-ethylation; catalyst, silica-alumina; reagent, diethylbenzene.
I	Ipatieff and Schmerling (*51*). Vapor phase; catalyst, phosphoric acid.
Ig	Ipatieff and Grosse (*47*). Catalyst, boron trifluoride.
Ip	Ipatieff, Pines, and Komarewsky (*48*). Catalyst, phosphoric acid.
K	Kane and Lowy (*52*). Reagents, ethyl sulfate, silicate, and carbonate.
Ko	Korshak and Kolesnikov (*56*). Catalyst, aluminum bromide; reagent, ethyl chloroformate.
Ku	Kursanov and Zel'vin (*57*). Reagents, ethyl formate and acetate.
M	Marks, Almand, and Reid (*61*).
Ma	Malishev (*59*). Catalyst, phosphorus pentoxide, lampblack, and cresol.
Mb	Mattox and Benedict (*64*). Vapor phase; catalyst, zinc oxide and silica; reagent, diethylbenzene.
Mc	McKenna and Sowa (*58*). Catalyst, boron trifluoride; reagent, ethyl formate.
Mi	Milligan and Reid (*66*). Point Mi', de-ethylation of polyethylbenzenes.
Ml	Mills (*67*). Temperature, 125° C.
Mt	Mattox (*63A*). Vapor-phase de-ethylation; catalyst, alumina or clay with hydrogen chloride; reagent, diethylbenzene.
Mx	Mattox (*62*). Vapor phase; catalyst, supported phosphoric acid. Points Mx', multiple-pass runs.
N	Natelson (*69*). Point N', reagent, ethyl chloride.
Na	Natanson and Kagan (*68*). Vapor phase; catalyst, silica-alumina.
No	Norris and Arthur (*72*). Reagents, ethyl formate and acetate.
Nr	Norris and Rubinstein (*73*). Reagent, ethyl bromide.
Ns	Norris and Sturgis (*74*). Reagents, ethanol and ethyl ether.
OC	O'Connor and Sowa (*75*). Catalyst, boron trifluoride; reagent, ethyl ether.
OK	O'Kelly, Kellett, and Plucker (*76*). Vapor phase; catalyst, silica-alumina. Points OK', continuous runs.
P	Pardee and Dodge (*77*). Vapor phase; catalyst, supported sodium aluminum chloride. Point P', catalyst, supported phosphoric acid.
Pa	Passino (*78*). Catalyst, hydrogen fluoride.
R	Radziewanowski (*80A*). Catalyst, aluminum chips with hydrogen chloride or mercuric chloride; reagent, ethyl bromide. Point R', de-ethylation with latter catalyst.
Ra	Radziewanowski (*80*). Reagent, ethyl bromide. Point Ra', de-ethylation of polyethylbenzenes.
S	Sempotowski (*88*). Reagent, ethyl bromide.
Sc	Schmerling (*84*). Catalyst, aluminum chloride dissolved in nitromethane.
Sd	Schaad (*83*). Vapor phase; catalyst, calcium acid phosphate.
Si	Sisido (*90*).
Sl	Schulze and Lyon (*87A*). Catalyst, boron trifluoride and phosphoric acid. Point Sl': vapor phase; catalyst, silica-alumina. Points Sl": vapor-phase de-ethylation; same catalyst.
Sm	Schmerling and Ipatieff (*86*). Vapor-phase de-ethylation; catalyst, zinc chloride on alumina; reagent, triethyl benzenes.
St	Stahly (*92*). Point St', de-ethylation of polyethylbenzenes.
Su	Schulze (*87*). Vapor phase; catalyst, silica-alumina.
T	Tsukervanik and Vikbrova (*97*). Reagent, ethanol.
Tx	Texas Co. (*93*). Vapor phase; catalyst, supported phosphoric acid; reagent, ethanol.
U	Ulich (*98*). Catalyst, gallium chloride.
W	Wertyporoch and Firla (*101*). Reagent, ethyl chloride. Points W': catalyst, aluminum bromide; reagent, ethyl bromide.
We	Wertyporoch, Kowalski, and Roeske (*102*). Catalyst, ferric chloride; reagent, ethyl bromide.
Wu	Wunderly, Sowa, and Nieuwland (*103*). Catalyst, sulfuric acid and boron trifluoride.
Z	Zal'kind, Berkovich, and Amusin (*104*). Reagent, ethyl chloride.

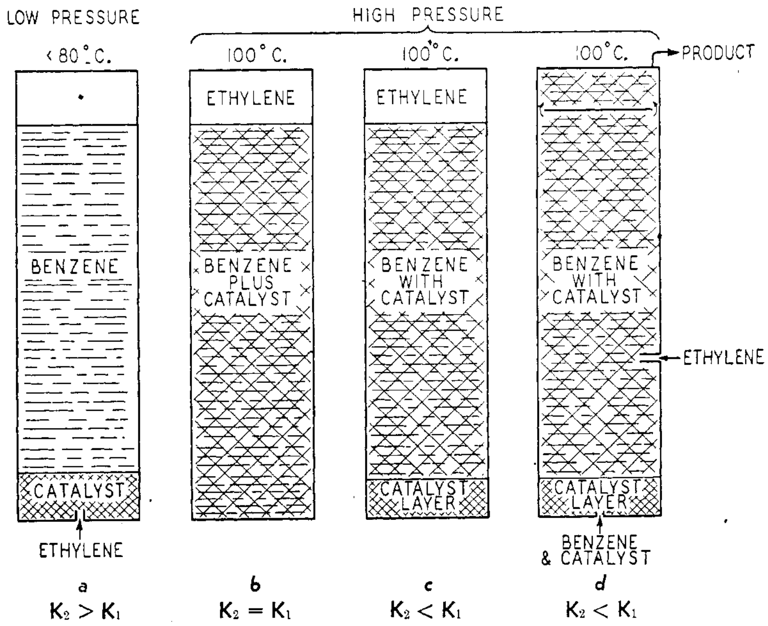

Figure 2. Diagrammatic Conditions for Ethylation of Benzene

a. Laboratory low-temperature operation.
b. Homogeneous (solventized) liquid-phase ethylation.
c. Ethylation with pressure and higher temperature (no homogenizing solvent).
d. Semicontinuous operation.

Cross hatching indicates catalyst dissolved in sufficient quantity for catalytic action.

the amount of hydrocarbons to be recycled, and to accelerate the reaction so that it would be more suitable for continuous operation.

The above considerations led to a simple means of increasing the yields up to the middle curve in each graph of Figure 1—namely, the use of a solvent so as to mix the layers and avoid the unfavorable extraction mentioned. These conditions are illustrated in Figure 2*b*. However, at low temperature the amount of solvent required for complete mixing was excessive, and smaller amounts (experiments 1 and 10) were ineffective. Experiment 2 at 100° C. gave the desired result, as mentioned previously. The layers remained mixed after cooling to room temperature. The solvent was ethyl ether (*27, 29*), but many others such as acetone, esters, alcohols, or other ethers probably would have given the same result. Schmerling (*84*) found small amounts of nitromethane adequate for homogenizing the reaction mixture; but the time was excessive and the plot of his yield falls below the lowest curve, possibly because of his low reaction temperature, 65° C. (cf. experiments 6, 10, and 11 in this investigation).

As a control for experiment 2, number 3 was made without a solvent (Figure 2*c*), at the same temperature and pressure, although it was continued until much more ethylene had been added. It gave a still better yield of 66% on the ethylene or 46% based on the benzene. A low temperature ethylation to the same mole ratio (Figure 2*a*) would have given only 28% on ethylene; and even a "homogeneous run" (Figure 2*b*) would have given only 50%. Five other experiments, 5, 7, 8, 9, and 12, all carried out at 100° C. or higher and without a homogenizing solvent or high speed stirring, gave yields (*32*) much higher than the middle curve in each graph and close to the highest one, calculated on the basis that benzene is ethylated twice as rapidly as its ethyl derivatives. Since this ratio is probably not a true relation between the velocity constants, some other explanation for the high yields was sought.

Consideration of the effects of extraction by the catalyst layer suggested that, under the new conditions, there might be a favorable extraction instead of the unfavorable one of the low temperature ethylations. It was postulated that at 100° C. or higher the solubility of aluminum chloride in benzene is sufficient to make the upper layer catalytic. By adding the ethylene under pressure above the liquid surface, it reacts with the benzene before it reaches the catalyst layer (unless stirred too vigorously). Since the ethylbenzene as formed is partly extracted by the lower layer, it is partly protected from further alkylation, so that the ethylene now reacts by preference with the benzene.

At 80° C. the solubility of aluminum chloride in benzene is only 0.72% (*65*), and by extrapolation it would be not much over 1% at 100° C. Attempts to estimate the solubility by sealed-tube experiments resulted in rapid reaction between the aluminum chloride and benzene to form a very dark red liquid. The upper layer was nearly as dark as the lower one and contained about 13%[2] aluminum chloride, nearly half of which (6.1%[3]) remained in solution on cooling to room temperature. This contrasts with the products of alkylation, in which the upper layer is often colorless, and contains only a trace of aluminum chloride (*11, 66*). A similar dark solution was obtained in a sealed tube at 80° C., although more slowly. The difference between this experiment and the solution of aluminum chloride in benzene under reflux at the same temperature, which is much slower, may be due to the retention of hydrogen chloride. This gas is evolved freely from the reflux experiment, and was found to build up a partial pressure of nearly half an atmosphere[4] in the sealed tube at 80° C. The literature reports frequently that hydrogen chloride is a promoter for aluminum chloride reactions; and the present observations indicate that its effect is increased greatly when its partial pressure is substantial instead of the few millimeters available by mere bubbling (*84*).

In the six experiments mentioned as giving high yields of ethylbenzene, the upper layers in the products were only slightly colored and contained only 0.3 to 0.7%[3] of aluminum chloride, as in the low temperature ethylations. If the solubility were higher, the resulting loss of aluminum chloride might render the process uneconomical. The apparent discrepancy with the high "chemical" solubility noted in the case of benzene may be due partly to the presence of ethylated benzenes. This view is supported by another experiment in a sealed tube containing aluminum chloride and one volume of diethylbenzene to two of benzene. On heating, the aluminum chloride liquefied quickly to a red lower layer much lighter in color than in the case of benzene alone; the upper layer remained light colored even at 100° C. for 2 hours. The tube was cooled and opened, and the upper layer was found to contain only 3.4% of aluminum chloride. Menschutkin (*65*) observed an even greater contrast between benzene and toluene for solubility of aluminum bromide in the upper layer in the presence of hydrogen bromide.

For mole ratios below 1.0, the equation of the highest curve in Figure 1 is approximately the linear one,

$$Y = 100 - 50m$$

although this is empirical, and the fair agreement with several of the experimental yields can be considered coincidental. The advantage of operation under the new conditions over ethylation at lower temperature and pressure is even more striking in the lower graph. Its highest curve suggests that, in order to increase

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[2] Analyzed by synthetic method.

[3] Analyzed by adding water and ammonia, evaporating to dryness, igniting, and weighing as Al_2O_3.

[4] Observed with a glass pressure gage of the type used by Francis and Robbins (*33*).

capacity, it would be preferable to ethylate more completely—for example, to $m = 0.7$ (experiment 3)—provided the temperature can be controlled. No hexaethylbenzene was found in the products of any of the six experiments described, in contrast to the lower temperature ethylations, which usually give some hexaethylbenzene, even when the mole ratio is low (*11, 61, 66, 68, 100,* and experiments 1, 6, 10, and 11 of this investigation).

Under these modified conditions the volume of the catalytic liquid (the whole volume) is increased several fold as compared with ethylation at lower temperature (where only the lower layer is active), so that the rate of reaction is increased greatly. By using increased pressure of ethylene and retention of hydrogen chloride, the speed of reaction is further increased, and is limited only by other considerations such as rate of introduction of reagents, rate of removal of products in a continuous operation, and rate of removal of heat of reaction. This is 27.19 kg.-cal. per mole of ethylene consumed, calculated from the heats of formation at 25° C. of ethylene and liquid benzene and ethylbenzene (*1*), since it probably makes little difference which ethylated benzene is formed, and the heat of reaction is nearly independent of temperature. The heat is sufficient to raise the temperature of the product from equimolar reactants by 358° C. under adiabatic conditions (using $C_p = 32.50 + 0.000134\ T^2$ for liquid ethylbenzene, by correlation of the data of citations *1* and *43*). Evidently, substantial cooling must be supplied if the reaction is rapid.

Experiment 12, the only one tried for speed, was complete in 3 minutes, as compared with hours for previously reported liquid-phase ethylations of benzene with various catalysts and reagents. The extreme speed of the ethylation reaction under these conditions suggests that the low speed of ethylation by ethyl halides (*20, 70, 73, 80, 80A, 88, 101, 104*) in spite of homogeneous mixtures of reagents, might be due to a prerequisite dehydrohalogenation of the alkyl halide to olefin. This is analogous to the mechanism proposed by McKenna and Sowa (*58*) for alkylation with alcohols using boron trifluoride. However, this mechanism is rendered improbable for aluminum chloride catalysis by observations (*49*) that alkylation with higher normal alkyl halides and alcohols may give substantial amounts of *n*-alkylbenzenes. Grosse and Ipatieff (*41*) and Ulich and co-workers (*98, 99*) drew the reverse conclusions, namely, that olefins form the alkyl halides before they alkylate. The mechanism is discussed extensively by Thomas (*94*).

In alkylating benzene with olefins higher than ethylene, the yield of the monoalkylbenzene under previously described conditions (*11, 83, 84, 85, 103, and elsewhere) may be about the same* as that of ethylbenzene under the proposed conditions (near the highest curves); the yield is increased only slightly by higher temperature or pressure. These observations may be due to a lower requirement of catalyst concentration for propylation than *for ethylation, so that propylation proceeds in the upper layer* even at room temperature. The rate of propylation is increased greatly by pressure, however, as example VII of the patent (*32*) shows.

EXPERIMENTAL DETAILS

Chemically pure reagents were used in experiments 1 to 19. Experiment 1 was run in the conventional manner in a balloon flask. Experiments 2 to 12 were carried out in a Monel autoclave of 290-ml. capacity, with a stirrer running at 400 revolutions per minute. The benzene and catalyst were charged, and the autoclave was heated in a bath of water or glycerol. Ethylene was charged from a lecture bottle cyclinder which could be disconnected and weighed to estimate the charge. The valve was opened intermittently to reach the desired pressure. The pressure dropped rapidly for a few seconds, probably because of solution of the ethylene in the benzene, followed by a slower drop in the region of 100 pounds.

On completion of the reaction, the autoclave was cooled, vented, opened, and discharged. The upper and lower layers were separated, weighed, and decomposed by water washing and by pouring into water, respectively. The combined hydrocarbon product was distilled in a packed column equivalent to about eight plates. The distillate came over almost entirely at 80°, 136°, 182–184°, and 215–220° C.; and the small intermediate cuts could be resolved by redistillation into the cuts indicated, corresponding to benzene, ethylbenzene, diethylbenzene, and triethylbenzene, respectively. No attempt was made to separate isomers. The residue at 225° C. was negligible except in experiments 1, 6, 10, and 11, where it solidified; on recrystallization from acetone, it gave crystals melting at 127° C., an indication that it contained hexaethylbenzene, the only solid ethylated benzene. Since a distillation analysis of the accumulated residues above 225° C. showed about equal molar amounts of tetra- and pentaethylbenzenes and twice as much hexaethylbenzene, each small residue was calculated on that basis. These products boiled at 248°, 277°, and 303.4° C. (corrected), respectively, using short-range standardized thermometers graduated to 0.2° C. The last is 7.4° higher than the boiling point given by Doss (*21*) for hexaethylbenzene but is more consistent with an extrapolation from the other boiling points. All liquid fractions were saturated to bromine water and had densities of 0.866 to 0.893, corresponding to aromatic hydrocarbons.

The results are summarized in Table III and Figure 1, which include for comparison some experiments under conditions not recommended. Experiments 1, 2, and 10 have ether present as a solvent (*27, 29*). Experiments 6, 10, and 11 employed ethylene under pressure, but the temperature was too low for adequate solution of the catalyst or for generation of sufficient hydrogen chloride promoter. Experiments 7 and 8 were run at still higher temperatures, but showed no advantage over those at 100° C., the recommended temperature. An excessively small amount of catalyst was present in experiment 4, 0.013 mole per mole of benzene, probably too little for the favorable selective solvent action. A selective solvent effect may explain the observations (*14, 61, 72, 97, 101*) that the mole ratio of catalyst affects the distribution of products. However, the present results are independent of the catalyst ratio over a higher range, 0.035 to 0.06 (experiments 3 and 5), and even down to 0.02 mole aluminum chloride per mole of benzene (experiments 14 and 16 compared with 13 and 15). These ratios are much lower than that recommended in former investigations, 0.07, at lower temperature and pressure (*11, 61*), but are comparable to that used by Amos (*2*)—namely, 0.022.

The decrease in weight of the lecture bottle cylinder estimated the ethylene charge only approximately. Since there was no loss except for the final venting, which was negligible (50 ml. of gas in a typical case), and since the product was wholly aromatic, the moles of ethylene listed in Table III were calculated from the number of ethyl groups found in the product.

PLOTTING OF LITERATURE DATA

The same method of calculation was applied in plotting the results of other investigators in Figure 1, since in some cases more ethyl groups were reported found than "ethylene absorbed". (The explanation may be that "ethylene absorbed" was really "increase in weight", which may have been too low because of loss of benzene.) Moreover, when the reverse was true, the deficiency was presumed to be due to unreacted ethylene or side reactions, such as polymerization, which is not significant from the theoretical standpoint of ethylation of the benzene ring. Polymerization is almost negligible with aluminum chloride catalyst but apparently not so with boron trifluoride, since the alkylated aromatic product may account for less than half of the ethylene reacted (*15*). This method of calculation sometimes results in a higher yield of ethylbenzene based on the ethylating agent than that claimed by the authors (*10, 52, 58, 68, 77, 80, 80A*). On the other hand, the percentage of ethylbenzene in the alkylate boiling

TABLE III. ETHYLATION OF BENZENE WITH ETHYLENE

		Ethylene Added to Vapor Phase											Ethylene Added to Benzene Layer							Dilute Ethylene^a			Dilute Benzene^b	
Expt. No.	1^c	2^c	3	4^c	5	6^c	7	8^c	9	10^c	11^c	12	13	14	15	16	17^c	18^c	19^c	20^c	21	22	23^c	24
Reagents, Moles																								
C_6H_6	7.27	1.50	2.14	2.38	2.18	2.29	2.04	1.83	2.23	2.31	2.33	2.31^d	11.11	11.39^e	11.74	11.37	11.37	11.38	11.39	7.8	8.12^f	6.26^g	0.58	0.58
C_2H_4^{h}	1.84	0.69	1.48	1.65	1.46	0.78	1.83	1.15	1.69	0.58	1.48	0. 1	5.43	5.42^e	7.72	8.34	5.71	8.21	5.47	0.94	3.99	2.59	0.14	0.55
$AlCl_3$	0.43	0.42	0.075	0.03^c	0.12	0.12	0.12	0.09	0.075	0.08	0.075	0.075	0.375	0.225	0.375	0.225	0.15^c	0.15^c	0.375	0.19	0.225	0.19	0.02	0.04
Et_2O	0.23^c	0.25^c	...	...	..	..	..	..	...	0.05^c	...	...	...	....	...	...	...	...	...	..	...	...	..	..
Temp., ° C.	40^c	100	100	100	100	50^c	107	150^c	100	50^c	80^c	100	100	100	100	100	100	100	100	100	100	100	60^c	110
Max. pressure^i, lb. gage	0^c	200	200	200	150	150	200	200	250	300	250	300	300	300	300	300	300	300	300	108^c	250	250	0^c	250
Time, min.	75	30	60	120	45	60	•60	60	10	10	10	3	32	16.5	23	29	23	41	9^c	30	38	100	30	3
Product, grams																								
Upper layer	528	210	205	224	183	174	192	150	206	185	201	190	945	968	1053	1076	1016	1083	966	626	676	565	197	199
Lower layer	165	(One phase)	14	4	44	38	34	36	24	26	28	26	125	78	130	76	52	55	126	50	78	60	6	10
Total moles																								
C_6H_6	6.00	0.95	0.92	1.19	0.98	1.73	0.67	0.90	0.88	1.92	1.42	1.53	6.49	6.70	5.83	4.96	7.20	6.00	7.95	6.88	4.27	3.99	0.44	0.33
EtPh	0.90	0.43	0.98	0.65	0.97	0.33	0.97	0.74	1.03	0.28	0.56	0.65	3.90	3.73	4.46	4.77	3.18	3.67	2.33	0.84	2.86	1.99	0.07	0.11
$Et_2C_6H_4$	0.15	0.08	0.22	0.32	0.20	0.10	0.34	0.13	0.29	0.07	0.16	0.08	0.65	0.58	1.22	1.46	0.69	1.17	0.65	0.05	0.49	0.24	0.06	0.07
$Et_3C_6H_3$	0.09	0.03	0.02	0.12	0.03	0.03	0.06	0.05	0.025	0.02	0.06	...	0.06	0.06	0.17	0.11	0.19	0.28	0.25	..	0.05	0.04	..	..
Residue^j	0.07	.....	...	...	..	0.03	..	..	...	0.02	0.08	...	0.01	0.04	0.06	0.06	0.11	0.26	0.21	..	...	...	0.11	0.07
Mole ratio, $m = C_2H_4/C_6H_6$	0.25	0.46	0.69	0.69	0.67	0.34	0.90	0.63	0.76	0.25	0.64	0.35^d	0.49	0.48	0.66	0.73	0.50	0.72	0.48	0.12	0.49	0.41	0.24	0.95
Yield, %																								
On C_6H_6^{k}	12	29	46	27	44	14	48	40	46	12	24	28^d	35	34	38	42	28	32	20	11	35	31	13	19
On C_2H_4^{l}	49	63	66	39	66	42	53	64	61	48	38	80	72	71	58	57	56	45	43	88	72	77	52	20

[a] Compositions of gas reagent: expt. 20, 35% C_2H_4, 65% C_2H_6; expt. 21, 36.5% C_2H_4, 63.5% C_2H_6; expt. 22, 11.6% C_2H_4, 20.2% C_2H_6, 68.2% CH_4. Pressures given are total pressures in autoclave.

[b] Liquid charge in expt. 23 and 24 was 190 g. of straight-run gasoline cut boiling 71–85° C. and containing 24% by weight of benzene.

[c] Yields inferior because items marked are too high or too low.

[d] In example I (present expt. 12) of the patent (*32*), the benzene charge was given incorrectly as 2.26 moles. Slight corrections in mole ratio and yield on benzene are made.

[e] In expt. 14 there was a loss of 2.5% before treatment of product.

[f] After deducting 61 g. of benzene condensed from exhaust gas.

[g] After deducting 210 g. benzene removed with exhaust gas.

[h] Calculated from moles of ethylated benzenes in product.

[i] In most runs this was also the average pressure.

[j] Calculated as a mixture of tetra-, penta-, and hexaethylbenzene in the mole ratio 1:1:2.

[k] Percentage of benzene converted to ethylbenzene.

[l] Percentage of ethylene converted to ethylbenzene.

above benzene, reported in some investigations (*15, 62*), is not identical with yield, as inferred by abstractors.

When "polyethylbenzenes" were reported together, their distribution between di-, tri-, tetra-, penta-, and hexaethylbenzene was assumed to correspond to the calculations appropriate to the curve of Figure 1 passing nearest the plotted yield, or an interpolation between the curves. For example, a process using two moles of benzene for one of ethylene is reported to produce twice as much ethylbenzene as polyethylbenzenes. Assuming all the ethylene is consumed, the mole ratio, m, is 0.5. A trial plot of the yield on Figure 1 is near point 17, an indication that n, the ratio of K_2 to K_1, is about 1.5. The actual mole fractions in the product may be computed by interpolations between the calculations for $n = 1$ and $n = 2$, with the further restrictions that the total ethyl groups equal 0.5, and the total weight of polyethylbenzenes equals half that of ethylbenzene, as follows: Benzene 0.628, ethylbenzene 0.271, di- 0.080, tri- 0.0175, tetra- 0.0034, penta- 0.00046, hexaethylbenzene 0.0001. The yield of ethylbenzene would be, therefore, 54.2% based on ethylene or 27.1% based on benzene. It would be decreased if appreciable quantities of hexaethylbenzene were formed as a result of concentration of products in the catalyst layer, but this was not assumed unless so reported.

The analyses reported by Milligan and Reid (*66*) were for the upper layers only. In plotting their yields on the basis of complete reaction products, it was assumed that one gram of aromatic hydrocarbons was held in the lower layer per gram of catalyst, and that these hydrocarbons contained an average of one more ethyl group than those in the upper layer. These assumptions are based on the observations of Berry and Reid (*11*) and of Marks, Almand, and Reid (*61*), and are supported by the present investigation. This procedure diminished the apparent yields but increased the mole ratios. The points are still uniformly high, and it is not clear why later investigations (*11, 61*), made apparently under similar conditions, did not give such good yields. Four of the twenty-one vapor-phase experiments of Pardee and Dodge (*77*) showed exceptionally good yields on ethylene but comparatively low conversions of benzene. Ulich (*98*) reported an experiment which seems to indicate a high yield using gallium chloride as a catalyst, but again the conversion and catalyst life were low.

Some inaccuracy in plotting in several cases in the literature results from missing data or imperfect material balances, which had to be reconciled by estimates. The precision of each point of Figure 1 is therefore not better than the area of the letter used to designate it. For clarity the letter chosen is the initial of an author. The high congestion of points in the lower left-hand corner results from the obvious attempt to minimize excessive ethylation by a large excess of benzene. This applies more especially to vapor-phase processes in which the cost of recycling is relatively less. To avoid confusion the literature yields on benzene are indicated by solid dots when the mole ratio is less than 0.2. In these experiments the only yield of interest is that based on ethylene. The observations plotted should not be considered measures of the authors' success, since in some case for example, (*61, 72, 73*) a high yield of ethylbenzene was not their aim, and in several others special conditions or reagents were being tried. However, for completeness all published yields of ethylbenzene by ethylation which could be found are plotted, so as to facilitate evaluation of the effects of conditions used.

The numbered points in both graphs of Figure 1 correspond to the numbers of the experiments in Table III. The three curves in the two graphs correspond to each other, respectively, and are calculated according to certain assumptions as explained above. They are not plots of the points, except for some experiments under special conditions, but they are drawn to facilitate comparison of different experiments, since those with plots on the same curve have equivalent yields. All the yields plotted in Figure 1 are on a once-through basis, except four multiple-pass runs of Mattox (*62*), which were not recycling in the sense of intermediate removal of product. Results of recycling (*17*, *63*, *63A*, *80*, *80A*, *92*), which are higher, are not comparable. The yields both for the points and the curves are interrelated, those based on benzene being *m* times those based on ethylene (or other ethylating agent), respectively. Points showing yields on benzene are directly under those showing yields on the ethylating agent.

OPERATION WITHOUT VAPOR SPACE

The ethylene may also be added to the benzene layer above the catalyst layer. This method is satisfactory if the stirring is efficient and if the rate of introduction of ethylene is not excessive. Too rapid addition of ethylene in this manner causes local excesses which react almost instantly, with formation of some hexaethylbenzene and other highly ethylated products and with lower yields of ethylbenzene resulting. Multiple injection would help and would increase the permissible speed of addition of ethylene. The ideal multiple injection is by means of a vapor phase, as in the six experiments described earlier; this method is preferred if substantially pure ethylene is available as a reagent. If a mixture of ethylene and paraffins must be employed, however, passage through the benzene layer is recommended so as to scrub out the reactive ethylene from the inert gases.

This method of operation was investigated in experiments 13 to 19 in a 1100-ml. autoclave equipped with a stirrer running at 400 r.p.m., an inlet tube extending halfway down, an exhaust from the top, and a horizontal disk partition near the top with a narrow clearance around it, to minimize agitation above it, so that the effluent would consist only of the upper layer. The arrangement is illustrated schematically in Figure 2*d*.

The autoclave was charged with catalyst, filled completely with liquid benzene, and heated to 100° C. in a bath of boiling water while enough benzene was released to hold the pressure at 200 pounds per square inch, the excess being deducted from the charge. Ethylene pressure at 300 pounds was then applied and maintained throughout the run. A slow, steady withdrawal of liquid from the exhaust controlled the rate of reaction, since ethylene entered and reacted as fast as there was room for it, as proved by the nonappearance of appreciable amounts of gas in the effluent.

Experiments 13 to 16 gave satisfactory results, although not quite such high yields as those obtained with ethylene added to the vapor phase. Experiments 17 and 18, made with only 0.013 mole aluminum chloride per mole of benzene, gave a decreased yield, as in experiment 4 with the same catalyst ratio. Experiment 19, which was almost the equivalent of 13, gave a poor result, presumably because of too rapid withdrawal of liquid, causing local excesses of ethylene, which the stirrer was unable to dissipate before reaction. The high speed of the ethylation reaction is evidenced by the presence of hexaethylbenzene in the products of runs 13 to 19, as contrasted with those from experiments made without bubbling of the ethylene. This is one reason for the slightly lower yields in experiments 13 to 16 than in 3, 5, and 9. Another reason is the fact that in the early part of a run almost pure benzene was being withdrawn and included in the product.

In continuous operation ethylene, fresh and recycle benzene, and recycle polyethylbenzenes should be charged in suitable proportions; and the upper layer should overflow into a cooled settling chamber so arranged that the catalyst precipitating out is returned to the reaction chamber. To avoid corrosion of the still and regeneration of benzene[5] during distillation, the remaining dissolved catalyst must be removed by washing the alkylate with water or sodium carbonate solution before distillation. One mole of aluminum chloride for forty or fifty of benzene in the reaction zone is sufficient. The consumption of aluminum chloride (due mostly to solubility in the cold product, which is less than 1%) is estimated at about 1 pound for 60 pounds of ethylbenzene produced.

OPERATION WITH DILUTED ETHYLENE

With some exceptions (included in citations *22*, *24*, *55*, *62*), the ethylations reported as using ethylene seem to have used it in substantially pure form. The only numerical result with diluted ethylene is from an experiment (*62*) with an extremely low mole ratio of ethylene, 0.0074, which gave necessarily a low conversion of benzene.

The use of diluted ethylene was studied in experiments 20 to 22 in the same autoclave but operated as batch runs. Smaller charges of benzene were used. At 100° C. before introducing ethylene, the observed pressure was 20 pounds gage, of which 11 pounds is due to the vapor pressure of benzene (26 pounds absolute) and the balance is presumably due to hydrogen chloride.

Mixtures of ethylene with paraffin gases were made up in a charge cylinder which was connected to the autoclave. The gas bubbled through the benzene layer and raised the pressure to that indicated in Table III; the pressure was maintained at that point until that in the charge cylinder was reduced to the same value. Meanwhile unreacted gas was exhausted from the top of the autoclave through a worm condenser intended to condense the benzene vapor into a trap. This arrangement was satisfactory for experiments 20 and 21, but in 22 the volume of the inert gas was so great that the benzene loss was substantial. The amount of loss could be estimated readily from the total molar content of the product. On a larger scale most of this benzene could have been returned to the autoclave by reflux through a different line from the gases. The use of pressure is advantageous in this respect, since without pressure Kimberlin (*55*) encountered severe losses of benzene, which he prevented by scrubbing the exhaust gases with recycle polyethylbenzenes.

The exhaust gas was analyzed for ethylene by absorption in mercuric sulfate solution (*30*) near the end of run 20, and near the beginning, middle, and end of the other two runs; the seven results were: run 20, 5%; run 21, 3.5, 1.5, and 0%; run 22, 0, 3.7, and 4.5%. The first figure indicates about 90% utilization of ethylene in run 20. At the higher pressure of run 21 this was improved to an average of 97% utilization. The decrease in efficiency in the latter part of run 22 was due probably to the lower level of benzene in the autoclave resulting from the loss, so that the gas bubbled through a shallower depth of liquid. The yields from these three experiments, corrected for the benzene vaporized, were comparable to those using pure ethylene; in no case was hexaethylbenzene found in the products.

The times given for experiments 13 to 22 are not quite comparable to that of 12 because the rate of exhaust, which controlled the reaction, was limited by mixing factors not involved in experiment 12.

The proposed conditions (higher temperature and pressure) could be applied to ethylation with ethyl halides only with additional complications. The reagent would require liquid-phase injection at a controlled rate. Furthermore, the reaction would evolve equivalent amounts of hydrogen halide, which would have to be released to relieve excess pressure, with provision for refluxing benzene. This arrangement would be similar to that applicable to operation with diluted ethylene.

OPERATION WITH DILUTED BENZENE

Pure ethylbenzene or other monoalkylbenzenes and wholly aromatic mixtures of isomers can be made from hydrocarbon mixtures containing low concentrations of benzene and toluene (*34*). The method consists in distilling the mixture to an end point slightly above the boiling point of benzene or toluene, alkylating the mixture with appropriate amounts of ethylene, propylene, or butenes, and redistilling the product to the same end

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[5] Even at room temperature ethylbenzene stirred with aluminum chloride forms benzene and polyethylbenzenes in a few minutes (*4*); but the ethylation should not be considered reversible, since no ethylene is evolved even at the boiling point.

point or a little higher. The residue is wholly aromatic, and from it the several alkylbenzenes can be separated by distillation. This process has the effect of preparing benzene or toluene from mixtures with nonaromatic hydrocarbons as reagents for alkylation, an otherwise expensive process. Experiment 23 illustrates the operation. Sowa (*91*) used a similar method to make toluene from hydrocarbon mixtures containing benzene, the alkylating agent being a polymethylbenzene. Alternatively, the method can be used to eliminate aromatics from hydrocarbon mixtures such as kerosene or Diesel fuel by a somewhat heavier alkylation followed by distillation.

The use of higher temperature and ethylene pressure for ethylating dilute aromatics gave only a slight improvement in yield (experiment 24), probably because the solubility of aluminum chloride is low in a largely nonaromatic hydrocarbon mixture; but pressure accelerated the reaction greatly. The fractions shown in Table III had the following densities, d_4^{20}, compared to literature values:

	Observed	Literature (*21*)
Ethylbenzene	0.8661	0.8669[a]
Diethylbenzenes	0.8670	0.8617[b] to 0.8811[b] (mean 0.8684)
Polyethylbenzenes	0.8925	0.8608[b] to 0.916[b] (mean 0.892)

[a] The National Bureau of Standards made the following selection (*1*) of properties of ethylbenzene: boiling point, 136.189° C.; d_4^{20}, 0.86696; n_D, 1.49584.

[b] Corrected to 20° C.

Since the nonaromatic portion of the charge had a density of only 0.720, the ethylbenzene product seems to be over 99% pure; and the other products appear to be completely aromatic.

ACKNOWLEDGMENT

The authors are indebted to W. P. Hawthorne and A. N. Sachanen of this laboratory for helpful suggestions during this research.

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PRESENTED before the Division of Petroleum Chemistry at the 109th Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

CORRESPONDENCE

Moisture Adsorption of Textile Yarns at Low Temperatures

SIR: In regard to the article by R. C. Darling and H. S. Belding in the May issue of INDUSTRIAL AND ENGINEERING CHEMISTRY, we wish to point out that moisture regained by textile fibers can hardly follow the course indicated by the interpolated data in Table II, page 527, of the article cited. Two obvious faults appear when one inspects the usual plot, regain *vs.* relative humidity, for wool, purified cotton, and viscose rayon (Figure 1). First, the form of these interpolated isotherms, shown dotted, in no way approximates that of Wiegerink's, with which the data are compared. In fact, Darling and Belding's isotherms intersect the Wiegerink isotherms which are of the recognized form. Second, continuation of their interpolated curves to zero regain would result in intersection on the abscissa at a positive value of relative humidity, a situation which seems completely unjustifiable.

Darling and Belding note the preparation of their samples in the same manner used by Wiegerink. This fact is not sufficient evidence to justify the incorporation of his data into their correlation, since it is well known that history of growth and treatment affect fiber properties including moisture regain. Therefore, it is nearly impossible for the samples to be identical, and an exact correlation would be fortuitous. If the materials were the same, the spacing between Wiegerink's 158° and 96° F. lines should be of the same order of magnitude as between his 96° F. line and the Darling-Belding 40° F. line. As Figure 1 shows, the points at 50% humidity are almost on the 96° F. Wiegerink line for wool and purified cotton and directly on the line for viscose. The 90% relative humidity points are above the range of Wiegerink's data but generally show the same lack of evidence of sample similarity. As further evidence, lines are included on the wool and cotton figures showing the position which is predicted from the Wiegerink data for the 40° F. isotherm by a device of the writers[1]. It will be seen that the isotherms are much more reasonably placed than the experimental points of Darling and Belding, also noted on Figure 1. It should be noted that the two experimental points obtained and reported for the 40° F. isotherm are entirely reasonable in comparison with the Wiegerink data if the normal assumption of different history of samples is made and if the suggested method for interpolation is not proposed.

It is startling to find that below the freezing point of water the curves give evidence of a complete reversal of the previously established temperature trend. While quantitative proof to the contrary is not available, the following deductions indicate the improbability of such an occurrence. Below freezing, a portion of the water on the fiber may be expected to freeze while another portion, probably that held by adsorption or in the capillaries, may not. On an Othmer plot of fiber data[1] a change of slope on any constant regain line may be expected when change of phase occurs. The situation is illustrated in Figure 2*B*. If none of the water on the fiber froze, there would be no break in the Othmer line. If all froze, the break would be as shown with the difference in the slopes of two parts of the lines directly calculable in terms of the latent heat of fusion. If, as postulated, only a portion of the water were to freeze, a slope intermediate between these two extremes should exist and be in the same direction. In contrast to these conclusions, Figure 2*A* shows the trend which the data of Darling and Belding would indicate on a similar Othmer plot. The slope will be noted to be in the wrong direction, indicating the wrong sign on ΔH for the phase change.

With data so contrary to previously established and expected trends, the study of the positive sorption process only is insufficient. It would be necessary to duplicate the results in desorption in order to prove the existence of the trends indicated. It seems probable that desorption results would follow normal isothermal form, since in sorption there is the strong probability that ice crystals form, block otherwise sorptive surfaces, and thus reduce the moisture regain so measured below its true equilibrium value. If this is the case, the Darling and Belding results at 0° and −20° F. would be understandable although incorrect.

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[1] Whitwell and Toner, *Textile Research J.*, **16**, 255 (1946).