freshly prepared alkali blue ink may be placed upon the glass surface and viewed as illustrated in Figure 8; the spectrophotometric measurement of the observed yellow color is also shown. On the other hand, if the viewing conditions are changed to those of Figure 9, the observed color will be green. The spectrophotometric curve of this color is also given. The reason the color changes from yellow to green in the two cases is that the angle at which the light strikes the sample is changed. This experiment may not be of practical importance to the paint or ink man, but the various colors exhibited by alkali blue, which include blue, yellow, violet, and green, are all to be expected from a consideration of the Fresnel equation. This is evidence of the soundness of the optical explanation of the phemonenon of interface bronze.

CONTROL OF BRONZE

The appearance of bronze can be controlled to some extent by formulation. For instance, if alkali blue is made up with one part of varnish and compared with a second sample made up with three parts of varnish, the pulldown with lesser varnish will appear more bronzy. However, since the purpose of this paper is to define bronze, give the optical explanations, and present some illustrative measurements, consideration of the factors of formulation, manufacture, or application by which bronze may be altered is outside the scope of this discussion.

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Monoalkylbenzenes by Vapor-Phase Alkylation with Silica-Alumina Catalyst

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The monoalkylation of benzene with olefins of low molecular weight, over silica-alumina catalysts of the type used in commercial catalytic cracking and at elevated temperatures, is accomplished with substantial yields of monoalkylbenzenes at relatively low pressures. The utilization of ethylene was found to be favored by increased reaction time, increased temperature, and increased molar ratio of benzene to ethylene. Small amounts of polyethylbenzenes produced may be recycled in the charge stream to give increased yields of monoethylbenzene based on ethylene and benzene consumed. The catalyst indicates long life and sustained activity under the conditions used. A cyclic operation such as is used in catalytic cracking is adaptable to the production of monoethylbenzene in which air regeneration of the catalyst is carried out at temperatures in the same range as the reaction temperatures.

THE low temperature alkylation of aromatic hydrocarbons with olefins in the presence of various catalysts has been liberally described. Ipatieff, Corson, and Pines (*5*) showed that sulfuric acid catalyzes the reaction between benzene and amylene to give good yields of mono-, di-, and triamylbenzenes. Propylene and butenes are also readily reacted with benzene in the presence of sulfuric acid (*5, 17*). Substantially the same results were obtained by the use of hydrogen fluoride (*15*). Ethylene, however, did not give appreciable yields of ethylbenzene in either case.

The standard method for effecting the reaction of ethylene with benzene at relatively low temperatures to give ethylbenzenes was described by Balsohn (*1*) and was the subject of numerous investigations (*2, 3, 4, 9, 11*). The catalyst for the reaction consists mainly of metal halides of the Friedel-Crafts type.

Ipatieff, Pines, and Komarewsky (*7*) used *o*-phosphoric acid at 300° C. to effect the reaction. Pardee and Dodge (*12*) described the use of sodium-aluminum chloride complexes supported on pumice, and extruded phosphoric acid-kieselguhr catalysts, in the formation of ethylbenzene from ethylene and benzene in the vapor phase at 230–270° C., with pressures in the order of 200 pounds per square inch. More recently extensive investigations of the use of an extruded phosphoric acid-kieselguhr catalyst in pellet form containing 62–63% by weight of P_2O_5 for the reaction were reported by Mattox (*10*) and Ipatieff (*8*). The temperature used was 270–300° C.; this indicated vapor phase operation. The maximum pressure used was 900 pounds per square inch. Results obtained indicated a high conversion of ethylene and benzene to ethylbenzene per pound of catalyst consumed over the catalyst life range. The ultimate life indicated under the conditions of the run was 48 days.

Schollkopf (*14*) disclosed the use of an activated hydrosilicate catalyst at elevated temperatures for effecting the addition of unsaturated hydrocarbons to compounds containing the benzene or naphthalene ring.

The removal and transfer of side chains from aromatics at elevated temperatures by the use of silica-alumina catalysts of the type used in commercial catalytic cracking operations was described by Thomas, Hockstra, and Pinkston (*16*) and Hansford, Myers, and Sachanen (*4*). Sachanen and O'Kelly (*13*) described

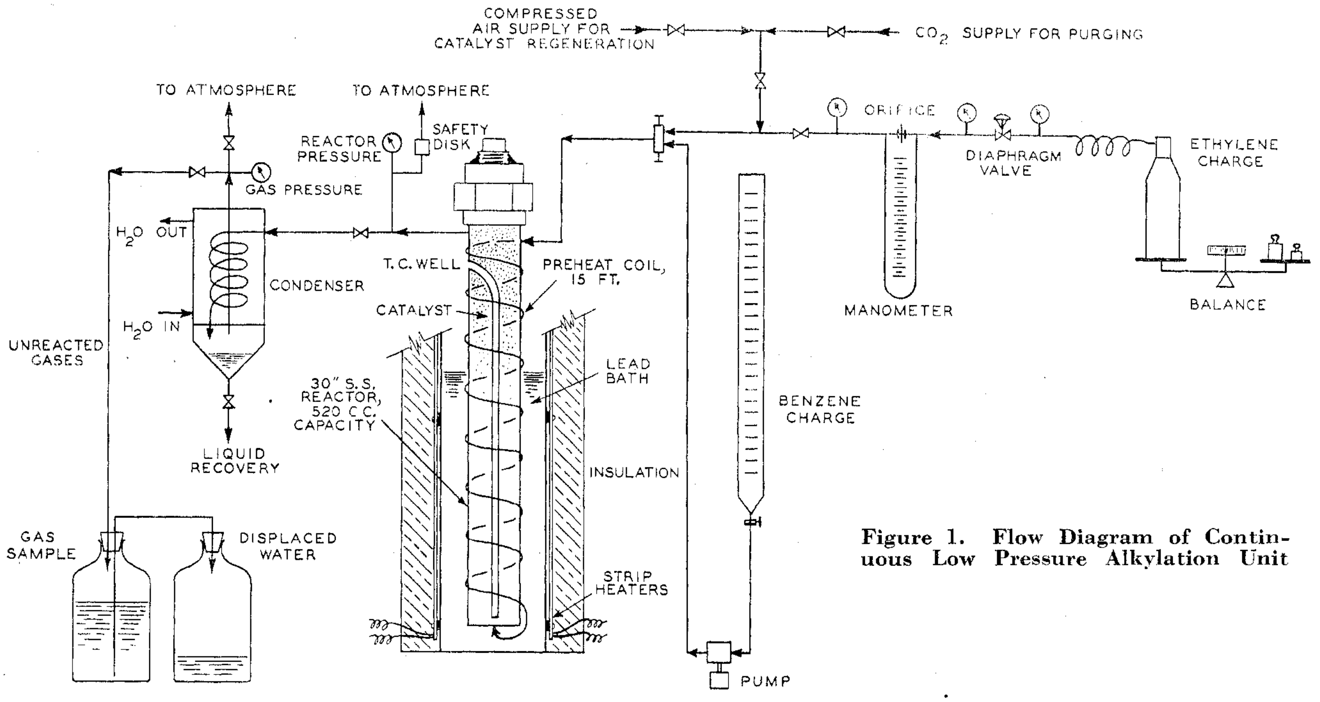

Figure 1. Flow Diagram of Continuous Low Pressure Alkylation Unit

the vapor-phase destructive alkylation of aromatics, benzene, and toluene with various olefins at elevated temperatures (400–480° C.) and at pressures as high as 3200 pounds per square inch. A clay catalyst in pellet form was employed. Under such drastic temperature conditions a series of alkyl aromatics was produced.

This article describes the direct alkylation of benzene with ethylene in the vapor phase over a silica-alumina catalyst for the production of monoethylbenzene. Both batch and continuous operations were conducted and are described. Several continuous runs with propylene and benzene for the formation of cumene were made with the same catalyst and are included in this paper.

MATERIALS FOR CATALYTIC RUNS

The benzene was the standard C.P. thiophene-free grade containing at least 99% benzene. The polyethylbenzene used in the dealkylation run was obtained from the Dow Chemical Company. Although it was not analyzed for the relative amounts of polyethylbenzenes, all the material boiled above monoethylbenzene. The ethylene used was Matheson's 98% grade, which indicated 94 volume % total olefin by bromine absorption and less than 1% olefin above ethylene by absorption in 92% sulfuric acid. The propylene used was supplied by Matheson and indicated 95 volume % olefin higher than ethylene by absorption in 92% sulfuric acid, and less than 1% isobutene by absorption in 70% sulfuric acid. The propylene-propane mixture used in the experiments was obtained from refinery gases by distillation under pressure and was analyzed by absorption in sulfuric acid.

The catalyst employed was a synthetic silica-alumina catalyst that is used in the commercial catalytic cracking process. It was prepared by the coprecipitation of the hydrous oxides in a weight ratio of about 9 to 1 of silica to alumina. This catalyst was similar to that described by Hansford, Myers, and Sachanen (*4*).

APPARATUS AND PROCEDURE

BATCH RUNS. The reactor for processing the materials consisted of a 2-liter stainless steel bomb made by the American Instrument Company. A small ethylene lecture bottle with attached valve was used to charge the ethylene under pressure. The bottle could be weighed to the nearest gram.

The cold bomb was charged with catalyst and benzene and sealed in the customary manner. The proper amount of ethylene was previously transferred from a large cylinder into the lecture bottle and weighed. The lecture bottle was then connected to a high pressure needle valve in the bomb by means of a short piece of high pressure tubing of small inside diameter. The bomb was tilted down so as to bubble the ethylene through the liquid benzene sealed in the bomb; this assured partial solution of the ethylene. The lecture bottle containing a small residual amount of ethylene was then weighed to determine the actual amount of ethylene introduced. The bomb was then placed in its electrically heated shaker jacket, connected to a pressure gage, and heated as rapidly as possible with constant rocking (heating usually required 1 hour) to the desired reaction temperature. The temperature was read by means of a thermocouple extending into the bomb. Temperature and pressure readings were recorded at definite time intervals during the entire run.

When the desired temperature was attained it was held at ±3° C. during the reaction period. After the reaction period was completed, the bomb and its contents were cooled as rapidly as was felt safe by passing an air stream between the bomb and enclosing jacket; this required approximately 2 hours. When the bomb was substantially at room temperature, it was vented and opened, and its contents were poured into a cooled flask. The catalyst was separated from the liquid product by filtration. Weights were recorded in each operation. The liquid product was then distilled through a Fenske distillation column having twenty-five plates and a total reflux-variable take-off head. The reflux ratio used during the plateau period of a compound was approximately 20 to 1. The specific gravities of the definite fractions agreed well with the values of the particular compounds in the literature, and the iodine number of all fractions was zero. The composite residues of several runs were distilled through the same column.

CONTINUOUS RUNS. The continuous alkylation reaction was studied in a small laboratory unit illustrated in Figure 1. The reactor consisted of a length of 1-inch seamless steel tubing of 520-cc. capacity, with a high pressure union at one end for closure. The reactor and preheat line were immersed in an electrically heated molten lead bath to give accurate heat control. A thermowell was welded into the reactor so that temperatures could be read at any longitudinal position in the catalyst bed. It was found that the temperature did not vary more than 5° C. in the catalyst bed with the rates used. The charge was preheated by means of a 15-foot length of small diameter, high pressure tubing wrapped around the reactor and entering the bottom. The benzene was charged directly from a calibrated buret into the preheat line by means of a Manzel chemical feeder. The ethylene was charged from a lecture bottle placed on a balance and connected to a reducing valve by means of coiled copper tubing of small diameter. After passing through the reducing valve, the ethylene was metered by means of a calibrated flow meter and charged into the preheat line. The flow meter was used only to give instantaneous rates of flow; the weights on the balance were taken at definite time intervals and used in calculating the over-all charge. The reaction was maintained at the desired pressure ±1 pound by means of a manually operated needle valve placed at the exit of the gas stream coming from the reactor. The hot gases passed to a water condenser and gas separator, from which the liquid product was drained. The noncondensed gases from the gas separator were collected by water displacement in a 5-gallon glass bottle, the volume of the gas being measured by the weight of the water displaced and the temperature. The gas was collected at substantially atmospheric pressure by means of a leveling device on the water outlet.

At the beginning of a run the reactor and condensing system were purged with carbon dioxide. The benzene pump was started first and run for approximately 2 minutes before the ethylene supply was started. This was done to minimize the drainage losses in the condensing system and to purge the reaction zone of any fixed gases. The pressure of the reactor rapidly built up to the desired pressure and was maintained by the manually controlled valve. After the benzene had been drained from the preliminary purge, the ethylene supply was turned on and the run conducted under the desired conditions. Some runs were operated on a cyclic basis. The system was purged with carbon dioxide to remove vapors of the previous run. Coke deposit on the catalyst was burned off by passing preheated air at 40 pounds pressure through the catalyst bed at a rate of approximately 2 liters per minute, until the carbon dioxide concentration in the exit gas was reduced to 1.5–2.0 volume %, as determined by absorption in 40% potassium hydroxide solution. The system was purged again with carbon dioxide before the next run. A typical cycle comprised 30 minutes on-stream, 1 minute for purge, 15 minutes for air regeneration at reaction temperature, and 1 minute for purge, or a total of 47 minutes.

The noncondensed gas was stripped of carbon dioxide by absorption in 40% potassium hydroxide solution and analyzed for total olefin by bromine absorption. The accuracy of this determination might be open to question, since the bromine absorption would indicate all olefin present plus any benzene that was carried along in the gas stream. However, several low temperature Podbielniak distillation analyses showed that, within the limit of error of the distillation, all the unsaturated hydrocarbon present was ethylene. Hydrogen also was detected in the exit gas, but the weight percentage was so small that it was not included in the material balance calculations.

Coke deposition on the catalyst was determined after several runs by purging the system with nitrogen and by prolonged passage of controlled amounts of preheated air through the catalyst bed. The regeneration gases were passed through hot copper oxide to convert any carbon monoxide present to carbon dioxide. The gas was then passed through a weighed Ascarite bulb and the increase in weight calculated to percentage carbon based on the total charge of the previous run. The maximum amount of carbon based on the total charge was 0.5 weight % in the case of run at higher temperatures (496° C.). Since this is below the experimental error involved in charge and product determinations, it was used as a constant value throughout the material balance calculations.

The liquid products from the continuous runs were analyzed in the same manner as indicated in the batch runs.

EXPERIMENTAL DATA

BATCH RUNS. The batch runs were made to qualify the reaction for further study and positive results were obtained (Table I). The pressure drop due to reaction at constant temperature was approximately 50 pounds in all runs. In addition to conventional methods of estimation, the yields were also calculated by the method proposed by Francis and Reid (*2*), in which the selectivity of monoethylbenzene formation based on liquid product distribution is calculated with regard to competing secondary reactions—that is, polyethylbenzene formation—and the molar excess of benzene necessary to attain this distribution. Table I shows that the highest temperature (399° C.) and highest molar ratio of benzene to ethylene were most favorable to the yield of monoethylbenzene based on the total ethyl groups present.

Batch operations of this type are unsatisfactory because the reaction time, temperature, and pressure are indefinite as a result of the relatively long heating and cooling periods in the operation. For this reason attendant secondary reactions, such as cracking, polymerization, and polyethylation, could conceivably alter the reaction picture.

CONTINUOUS RUNS. The continuous operation of the reaction on a small laboratory unit (Figure 1) eliminated the objections to the batch procedure. Increased yields are probably favored by the use of high pressures. However, to make the process adaptable to existing facilities at the time of the investigation, only relatively low pressures (50–75 pounds gage) were used. The effects of low pressure and short residence time were compensated by a much higher reaction temperature. Since monoethylbenzene was the desired product, a molar excess of benzene was used in all experimental runs.

TABLE I. BATCH VAPOR PHASE ETHYLATION OF BENZENE WITH ETHYLENE WITH SYNTHETIC SILICA-ALUMINA CATALYST

Run number	1	2	3	4
Wt. benzene charged, grams	780	936	780	702
Wt. ethylene charged, grams	105	44	28	45
Benzene, moles	10	12	10	9
Ethylene, moles	3.74	1.56	1	1.6
Wt. catalyst, grams	100	100	100	100
Reaction temp., ° C.	344	366	322	399
Time held at reaction temp., min.	30	30	30	30
Max. reaction pressure, lb./sq. in. gage	1740	1770	1350	1470
Wt. product recovered, grams	808	901	731	662
Wt. absorbed on catalyst, grams	65	70	70	70
Product analysis, wt. % of charge				
Benzene (78–100° C.)	61.9	83.7	88.1	77.4
Intermediate (100–132° C.)[a]	0.4	0.8	0.9	1.3
Ethylbenzene (132–140°)	24.8	12.8	8.6	18.6
Residue (above 140° C.)[b]	12.7	2.6	1.6	2.6
Distillation losses	0.2	0.1	0.8	0.1
Total	100.0	100.0	100.0	100.0
% theoretical based on ethylbenzene	54.8	77.4	68.1	82.9
Product distribution				
Mole ratio[c]	0.378	0.133	0.087	0.183
Yield on benzene[d]	20.9	10.2	6.9	15.0
Yield on ethylene[e]	55.5	76.6	79.5	82.5

[a] Regarded as half benzene and half ethylbenzene in product distribution calculations.

[b] Regarded as diethylbenzene in product distribution calculations.

[c] Ratio of total ethyl groups to total benzene rings in product.

[d] Percentage of total benzene rings as ethylbenzene.

[e] Percentage of total ethyl groups as ethylbenzene.

Table II lists data from the low pressure experimental runs. The effect of temperature variation with constant molar ratio of benzene to ethylene and constant space rate can be seen from comparison of runs 1, 2, and 3. The highest temperature investigated (496° C.) produced the highest yield of ethylbenzene in the liquid product. Reduction in temperature resulted in lower percentages of ethylbenzene and larger amounts of unreacted ethylene. The effect of variation of molar ratio of benzene to ethylene at approximately constant temperature and space velocity can be seen by comparison of runs 3, 8, and 9. As would be expected from the law of mass action, the higher molar ratio favored more complete reaction of the ethylene charged. The effect of liquid space velocity or reaction time can be seen by comparison of runs 1 and 6. Although the reaction temperature of run 6 was 68° C. below that of run 1, approximately the same product distribution was obtained by using twice the reaction time in run 6 with the same molar ratio of benzene to ethylene.

The data based on product distribution calculations do not seem to give a definite trend with respect to the variables involved. This may be explained by the fact that these values are very sensitive to the per cent residue, assumed to be diethylbenzene, found in the product distillation. Since this value is small (1–3%) with respect to the total product, small errors in distillation analysis are amplified. Although this method of calculation is desirable theoretically, precise analysis is necessary to obtain concordant results.

Most of the runs performed failed to react all the ethylene charged. However, by using a molar ratio of benzene to ethylene of 10 to 1, substantially all the ethylene was reacted, as indicated in runs 5 and 9. The use of higher pressures would probably aid in reacting a higher percentage of ethylene.

The coke deposition on the catalyst was extremely small under the reaction conditions. This would be expected because of the high thermal stability of the reactants. Regeneration at a temperature approximately equal to that of the preceding run was easily accomplished. Successive runs were readily duplicated after catalyst regeneration. The decrease in catalyst activity in successive runs was not noticeable in the number of reaction

TABLE II. CONTINUOUS VAPOR PHASE ETHYLATION OF BENZENE WITH ETHYLENE (SINGLE-PASS) WITH SYNTHETIC SILICA-ALUMINA CATALYST

Run No.	1	2	3	4	5	6	7	8	9	10	11
Charge, wt. %											
Benzene	92.8	93.2	93.2	95.8	96.5	92.8	70	94.4	96.5	93.4	93.2
94% ethylene	7.2	6.8	6.8	4.2	3.5	7.2	...	5.6	3.5	6.6	6.8
Polyethylbenzenes	...	...	...	...	...	...	30	...	...	...	...
Mole ratio, benzene to ethylene	4.64	4.91	4.91	7.85	10.55	4.64	...	6.06	10.5	5.09	4.9
Space velocity of liquid, cc. at 25° C./cc. catalyst/hr.	1.97	1.97	1.97	1.68	2.01	1.07	2.0	2.08	2.2	2.06	0.94
Temp., ° C.	496	468	448	468	468	428	463	468	471	469	468
Pressure, lb./sq. in. gage	50	50	50	75	75	50	50	50	50	50	50
On-stream time, min.	30	30	30	30	90	30	30	30	30	35	30
Catalyst treatment	Fresh catalyst	Regenerated from run 1	Regenerated from run 2	Regenerated from run 3	Regenerated from run 4	Regenerated from run 5	Fresh catalyst	Fresh catalyst	Regenerated from run 8	Aged catalyst	Aged catalyst
Products, wt. % of charge (no loss basis)											
Benzene (78–100° C.)	78.2	81.0	83.7	84.7	87.96	78.8	66.1	79.8	88.2	86.9	82.8
Intermediate 100–132° C.)[a]	0.7	0.5	0.2	0.5	0.3	0.4	0.4	1.3	0.2	0.2	0.5
Ethylbenzene (132–140° C.)	17.2	13.9	11.3	12.0	10.1	17.0	16.1	15.0	9.6	8.3	12.1
Residue (above 140° C.)[b]	2.7	2.2	2.3	2.2	1.1	2.3	16.7	2.9	1.5	1.1	2.2
Unreacted ethylene	0.7	1.9	2.0	0.1	0.04	1.0	0.2	0.5	Nil	3.0	1.9
Coke deposit	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ethylene reacted, %	89.7	70.2	68.7	97.5	98.8	85.2	...	90.5	100	51.6	70.3
Theoretical yield based on ethylene to monoethylbenzene, %	67.2	57.3	46.6	80.2	81.1	66.4	...	75.3	77.0	35.3	50.0
Product distribution											
Mole ratio[c]	0.173	0.141	0.117	0.122	0.091	0.165	...	0.161	0.094	0.079	0.115
Yield on benzene[d]	13.9	11.1	8.98	9.55	7.82	13.6	...	12.5	7.45	6.56	9.7
Yield on ethylene[e]	80.5	79.0	76.4	78.5	85.7	82.8	...	78.0	79.4	83.5	78.8

[a] Regarded as half benzene and half ethylbenzene in product distribution calculations.
[b] Regarded as diethylbenzene in product distribution calculations (except in run 8 where polyethylbenzenes were charged).
[c] Ratio of total ethyl groups to total benzene rings in product.
[d] Percentage of total benzene rings as ethylbenzene.
[e] Percentage of total ethyl groups as ethylbenzene.

and regeneration cycles performed. However, a representative sample of the same catalyst which had been through 3700 cycles (equivalent to 100 days of continuous operation) in a semicommercial catalytic cracking unit under somewhat more drastic thermal conditions was tested for the ethylation reaction. This catalyst is designated as aged in runs 10 and 11 (Table II). Although the percentage of unreacted ethylene at the same temperature and space rate increased (comparison of runs 2 and 10) with the aged catalyst, substantially the same yields were obtained by reducing the space rate (runs 2 and 11). This is a conservative indication of catalyst life, since coke deposition is much greater under cracking conditions; therefore the regeneration conditions are more severe. The residue of the reaction product in the single pass operation contained mainly diethylbenzene with small amounts of higher ethylbenzenes, as distillation analysis of combined residues indicated. This residue would not be lost to monoethylbenzene production, since it is possible to recycle these polyethylbenzenes with a molar excess of benzene and obtain increased yields of monoethylbenzene based on ethylene consumed. This procedure of alkyl group transfer has been reported (*4, 16*). Run 7 was made to verify these conclusions; polyethylbenzene was charged with benzene under the conditions used in the straight ethylation runs. There was a net loss of polyethylbenzenes in favor of monoethylbenzene formation under the conditions of the experiment.

The intermediate fraction between benzene and monoethylbenzene in the liquid product distillation (100–132° C.) suggested

TABLE III. CONTINUOUS VAPOR PHASE PROPYLATION OF BENZENE (SINGLE-PASS) WITH SYNTHETIC SILICA-ALUMINA CATALYST

Run No.	1	2	3[a]	4[a]	5[a]
Charge, wt. %					
Benzene	88.3	91.5	81.0	81.5	81.0
Propylene	11.7	8.5	7.6	7.4	7.6
Propane	...	...	11.4	11.1	11.4
Mole ratio, benzene to propylene	4.05	5.78	5.9	6.0	5.9
Space velocity liquid, cc. at 25° C./cc. catalyst/hr.	2	2	3	3	3
Temp., ° C.	382	382	422	462	377
Pressure, lb./sq. in. gage	75	75	500	500	500
On-stream time, min.	20	20	30	30	30
Catalyst treatment	Fresh catalyst	Regenerated from run 1	Fresh catalyst	Regenerated from run 3	Regenerated from run 4
Products, wt. % of charge (no loss basis)					
Benzene (80–100° C.)	76.8	81.8	75.0	76.2	71.1
Intermediate (100–145° C.)	0.9	1.0	1.3	2.1	0.9
Isopropylbenzene (145–155° C.)	18.0	13.2	11.9	7.9	14.5
Residue (above 155° C.)	3.1	3.5	3.2	3.4	2.5
Unreacted gas	0.7	Nil	8.2	9.6	10.4
Coke	0.5	0.5	0.5	0.8	0.6
Total	100.0	100.0	100.0	100.0	100.0
Yield monopropylbenzene, % of theoretical based on propylene	55.0	56.6	57.8	47.5	68.8

[a] Runs 3, 4, and 5 were conducted with apparatus similar to that described, adapted for use of higher pressures.

the presence of toluene. However, in reported results (*4, 16*) under similar conditions of catalyst and temperature, there was no indication of toluene formation from ethyl group decomposition in the ethyl group transfer between polyethylbenzene and benzene. In the product distribution calculation this small intermediate fraction was considered to be half benzene and half monoethylbenzene.

Several continuous experimental runs were made with propylene, propylene-propane mixtures, and benzene for the formation of cumene. Data for these runs appear in Table III. Temperature conditions for this reaction are less severe than those for the ethylation reaction, and the reaction proceeds with greater ease. Runs 3, 4, and 5 indicate that substantial selective reaction occurred in the presence of paraffin gases which were inert under the conditions of the experiment.

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Phase Study of Commercial Soap-Alkaline Electrolyte Water-Systems

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A phase study of commercial mixed soap-water-electrolyte systems was made using sodium chloride and nine salts industrially important as soap builders. The data cover soap concentrations to 50%, electrolyte concentrations to 27%, and temperatures to 180° C. The salts used were sodium chloride, carbonate, and tetraborate, trisodium phosphate, tetrasodium pyrophosphate, Calgon (sodium hexametaphosphate), sodium metasilicate, sodium silicates of SiO_2/Na_2O ratios by weight of 2.46 and 3.93, and a potassium silicate of SiO_2/K_2O ratio by weight of 2.04. The solubility of the soap in solutions of these salts and their effect on the transition from crystalline to liquid crystalline soap varies widely both on weight and molecular bases. The order of increasing effect differs with concentration and temperature; however, sufficient regularities exist to enable predictions to be made of the phase diagrams for other soaps and at other concentrations.

THE value of adding alkaline electrolytes or builders, such as the soluble silicates, to soaps is attested by many years of experience and numerous publications (*1, 3, 5, 6, 25, 26*). In 1937, the last year for which accurate data on consumption are apparently available, 160,000 tons of 40° Baumé sodium silicates and 39,500 tons of sodium phosphates were consumed by the United States soap industry according to the Bureau of the Census (*23*). Since then the amounts of such builders used have substantially increased. Wartime shortages of fats, oils, and rosins for soapmaking re-emphasized the value of builders in soap. Attention has been focused on the amounts of various builders which can be added to different soaps under varying conditions and on the nature of such systems.

During the past twenty-five years the manufacture of soap, previously an industrial art, has been studied scientifically from the phase-rule point of view by McBain and collaborators (*13, 16, 18*), Ferguson and Richardson (*7*), and others. Phase diagrams of approximately a dozen ternary aqueous soap systems with sodium or potassium chloride have been published (*7, 13, 18*). Only incomplete data on the behavior of soaps with other salts are available. Probably the earliest work was done in 1888 by Hofmeister, who studied the salting out of sodium oleate from solution by several salts (*10*). Later workers (*2, 12, 21, 22, 24*) measured the amounts of sodium and potassium chloride, carbonate, and hydroxide required to salt out various single and mixed soaps. These data were summarized and interpreted by McBain and Walls (*20*). Qualitative observations on gelation of soaps in the presence of sodium carbonate, borate, and silicate were reported by Fischer (*9*). McBain and Pitter (*17*) measured the concentrations of eleven electrolytes required to salt out 0.25 weight normal (approximately 6.5%) sodium palmitate. McBain, Vold, and Gardiner (*18*) found that substituting for sodium chloride a sodium silicate, having a SiO_2/Na_2O weight ratio of 3.18 in concentrations of 3.6 and 5.6%, caused 10% sodium oleate to set to an elastic, transparent jelly instead of a liquid crystal.

If a determination is made of the relative efficiency of various salts in salting out soap at a single concentration and temperature, hypothetical phase diagrams can be outlined for aqueous systems of that soap with all of these salts. The diagram for one of them must be known; the assumption is then made that the relative efficiency is the same for different soap concentrations involving several crystalline and liquid-crystalline phases at different temperatures.

This paper reports a study of the phase behavior of a typical commercial mixed soap with one potassium and nine sodium salts. The salts used were sodium chloride, carbonate, and