173. *Some Catalysed Gas-phase Reactions of Aromatic Hydrocarbons. Part I. The Interaction of Benzene with Methyl Ether.*

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Methyl ether interacts with benzene at 400—500° in the presence of metal oxide catalysts to give toluene and polymethylbenzenes. The most effective catalysts are of the synthetic aluminosilicate type. The reaction has been investigated under various conditions of temperature, contact time, etc.; the gaseous products have been determined. Under the optimum conditions for the reaction, 12—15% (moles) of toluene per pass is formed, or 35—50% calculated on the benzene consumed; the total methylation (on benzene consumed) is about 70%. Wastage of the rectants is low.

The results obtained are compared with those of previous work, and the nature of the reaction is briefly discussed.

THE various known methods for alkylating aromatic hydrocarbons in solution, *e.g.*, the Friedel–Crafts reaction and its modifications, have been thoroughly investigated (see, *e.g.*, Calloway, *Chem. Reviews*, 1935, **17**, 327; Linstead, *Ann. Reports*, 1937, **34**, 254); they have been very widely applied, and their mechanisms have been elucidated. In recent years, several processes for the production of certain alkylbenzenes in the gas phase have been reported, but gas-phase alkylation as a general method has not been investigated nearly so extensively as the corresponding reaction in solution, and available data on the reactions which have been studied are limited in scope.

The catalytic ethylation of benzene by means of ethanol or ethylene in the gas phase is a reaction now widely used in the United States in the manufacture of ethylbenzene (and hence styrene) for the production of plastics and synthetic rubber (Anon., *Oil and Gas J.*, 1942, **41**, No. 13, 14). Kieselguhr, impregnated with phosphoric acid, and aluminium silicates are suitable catalysts (see, *e.g.*, Standard Oil Co., U.S.PP. 2,238,594, 2,390,211, 2,067,764; Ipatieff and Schmerling, *Ind. Eng. Chem.*, 1946, **38**, 400; Pardee and Dodge, *ibid.*, 1943, **36**, 273). Other olefins, such as propene and the butenes, or alcohols or ethers which can give rise to them, have been used in similar processes (see Universal Oil Co., B.P. 464,752, 1935; Ipatieff, Pines, and Schaad, *J. Amer. Chem. Soc.*, 1944, **66**, 816).

The particular case of methylation is of interest, since the reaction cannot proceed by way of an olefin. Methanol, methyl ether, and methyl chloride have been used as methylating agents in gas-phase reactions. For instance, Jenkins (B.Sc. Thesis, Oxford, 1940) observed that when benzene and methanol were passed over bauxite heated to 400°, about 2% of toluene was formed, together with much methyl ether and water. (Other published work is reviewed, and considered in relation to the present work, below, under "Discussion.") It is well known that methanol is rapidly converted into methyl ether and water in the presence of certain metal oxide catalysts: $2CH_3{\cdot}OH = (CH_3)_2O + H_2O$ (see, *e.g.*, Adkins and Perkins, *J. Physical Chem.*, 1928, **32**, 221). Hence, when benzene and methanol vapours are led over a catalyst, it is uncertain whether the alcohol or the ether is the actual reactant.

Our experiments confirm that methyl ether interacts with benzene in the presence of catalysts to give methylbenzenes, and show that water is one of the reaction products. We find that, under the conditions we have employed, the ether is a more effective methylating agent than the alcohol. We obtain yields of toluene comparable with those claimed by previous workers (see p. 933), *viz.*, 15% (moles) per pass, and 35—50% on the benzene consumed, the total methylation (on benzene consumed) being about 70%. (Here and throughout the paper, all yields are given as moles %.) The wastage of methyl ether is 10—15% per pass.

In the present communication we present a study of the interaction of benzene and methyl ether. A number of catalysts have been examined, and the reaction investigated under various conditions of temperature, contact time, etc. The gaseous products of the reaction have been determined. Subsequent communications will describe the isomeric composition of the polymethyl derivatives formed in the methylation of benzene and its homologues, and also the methylation of thiophen and pyridine. Certain catalytic rearrangements and cracking reactions undergone by the aromatic compounds will also be reported later.

EXPERIMENTAL.

The vapours of benzene and methyl ether were led at known and constant rates through an electrically heated horizontal Pyrex tube containing the catalyst. The liquid products were analysed by fractional distillation in a Podbielniak still, and gaseous products were collected and also analysed.

1. *Materials.*—*Benzene.* "AnalaR" Benzene was purified by crystallisation, and distillation from phosphoric oxide; $n_D^{20°}$ 1·5007—1·5010, m. p. 5·4°.

Methyl ether. This was prepared by passing methanol over alumina at 375°, and collected in sulphuric acid. The ether was regenerated by running the sulphuric acid solution into water, and was dried, liquefied by cooling, and poured into a cylinder while cold. A needle valve was then screwed into the cylinder.

Catalysts. Three naturally-occurring materials have been used as catalysts, *viz.*, two specimens of bauxite, and a Scottish bauxitic clay. Two further catalysts were made by extraction of the bauxitic clay with acids to reduce, first, the alumina (Silica "O"), and secondly, the titania content (Silica "T"). The analyses were as shown in Table I.

Alumina A. Activated alumina, supplied by Peter Spence, Ltd.

Alumina B. "Special activated alumina", supplied by Peter Spence, Ltd.

Alumina C. Prepared by running 8% sodium hydroxide solution into 36% aluminium nitrate solution at 50—55°; 8/14 mesh.

Alumina D. Prepared by precipitation of aluminium nitrate solution with ammonia, by the method of Adkins and Krause (*J. Amer. Chem. Soc.*, 1922, **44**, 385).

Alumina E. Supplied by I.C.I. Ltd.; screened 10/18 mesh.

Ferric oxide. Prepared in the same way as Alumina C.

TABLE I.

	Bauxite A.[1]	Bauxite B.[2]	Natural alumino-silicate.[3]	Silica-"O".[3]	Silica "T."[3]
Loss on ignition, %	22·7	21·7	7	0·78	0·92
Al_2O_3, %	35·6	67·9	41—42	7·44	2·11
SiO_2, %	30·9	0·96	48	85·95	92·06
Fe_2O_3, %	6·9	7·17	1	0·27	0·27
TiO_2, %	4·3	2·83	1—2	4·04	2·52

[1] Traces of Cr, Mn, and SO_4''; analysis made by I.C.I. Ltd.

[2] Trace of Mg; analysis by Dr. Hartley, Inorganic Chemistry Laboratory, Oxford.

[3] The materials and their analyses were supplied by Messrs. Peter Spence Ltd.; all three had been heated to 500° before analysis.

Titania gel. Titanium tetrachloride was run slowly into excess of 10% ammonia.

Silica gel, basic aluminium phosphate, boron phosphate, and thoria gel. Supplied by I.C.I. Ltd.

Chromic oxide gel. A dilute solution of chomic nitrate was precipitated at 78—84° with 17% ammonia solution.

Zinc oxide gel. Zinc chloride solution was precipitated with sodium hydroxide solution (see Adkins and Millington, *J. Amer. Chem. Soc.*, 1929, **51**, 2452).

Nickel–alumina. A method of Balandin and Rubinstein (*Z. physikal. Chem.*, 1935, *B*, **31**, 793) was used. Sufficient 10% sodium hydroxide was run into 0·25M-aluminium nitrate solution just to redissolve the precipitate first formed. An equivalent quantity of nickel nitrate in 0·5M-solution was run in with stirring. After being washed, filtered off, and dried, the product was reduced in hydrogen at 320—340°.

Mixed oxide–silica catalysts. The following mixtures of silica with other oxides were prepared by Dr. W. Cule Davies, of Peter Spence Ltd., by precipitation of sodium silicate solution with an appropriate salt: Al_2O_3–SiO_2, 3 : 1, 1 : 1, 1 : 2, 1 : 4; Cr_2O_3–SiO_2, 1 : 2; TiO_2–SiO_2, 1 : 2; BeO–SiO_2, 1 : 1.

Except where otherwise stated, all materials were screened 4/8 mesh.

2. *Apparatus.*—The rate of flow of methyl ether was measured with a flow-meter; this was calibrated for rates of flow of 0—40 g. (0—20 l.) per hour by absorption in concentrated sulphuric acid and weighing the methyl ether passed in a known time for a known deflection of the flow-meter. The gas was freed from water, carbon dioxide, and methanol by passing through a long tube packed with soda–lime and calcium chloride.

The benzene was vaporised in a Dewar vessel by heating electrically with a small element immersed in the liquid (principle suggested by Adkins, *J. Amer. Chem. Soc.*, 1922, **44**, 2175). Since the insulation provided by a Dewar vessel is not perfect, the apparatus had to be calibrated directly. Benzene could be vaporised conveniently at rates of 15—100 g. per hour.

The vapours were mixed, preheated, and injected into the catalyst chamber, a Pyrex tube 2·9 cm. in diameter; the catalyst column in the evenly heated section of the furnace was 84 cm. long. The tube was heated in an electric furnace whose temperature could be kept constant ±2° by suitable adjustment of a rheostat. The temperature was measured with a thermocouple and millivoltmeter. The charge of catalyst was 200—450 g., depending on its bulk density.

The liquid reaction products were collected, separated from water, dried and analysed by fractional distillation.

Podbielniak still used in analysis. Analyses of the liquid products of reaction were made by means of a Podbielniak-type still (column of 0·55 cm. internal diameter); this enabled benzene and its homologues to be separated without difficulty. For instance, 1·5 c.c. of toluene in 20 c.c. of benzene could be determined with a maximum uncertainty of 0·1 c.c., and larger samples were analysed with corresponding or greater accuracy.

Gas analyses. These were performed with the standard Bone and Wheeler apparatus. As absorbents, 86% H_2SO_4, 20% KOH, 20% oleum, and alkaline pyrogallol were used for methyl ether, CO_2, C_2H_4, and O_2 respectively; H_2 and CO were determined by combustion in a copper oxide pipette, and paraffins by explosion.

3. *Method of Working.*—Before use, each catalyst was heated to 500° in a stream of nitrogen; it was then repacked in the tube to ensure that no apppeciable space was left above the solid catalyst. Benzene and methyl ether were passed over the heated catalyst at known rates and for a known length of time. The liquid products (50—100 c.c.) were collected, separated from water, and analysed by fractional distillation. The gaseous products were led through a trap cooled in a freezing mixture of ice and salt (to remove benzene vapour) before collection.

It was found that the activity of the catalysts fell with continued use; hence they were re-activated as necessary by heating in a stream of oxygen for 1—2 hours at 500° (oxides such as Cr_2O_3 which are oxidizable were not so treated).

Results.—1. *Search for active catalysts.* As a primary step, methyl ether was passed with benzene over a heated sample of the specimen of bauxite used by Jenkins (*loc. cit.*) in his experiments with benzene and methanol. The yield of toluene was small (3—5% per pass), although greater than that obtained by Jenkins. Therefore a search for more active catalysts was undertaken.

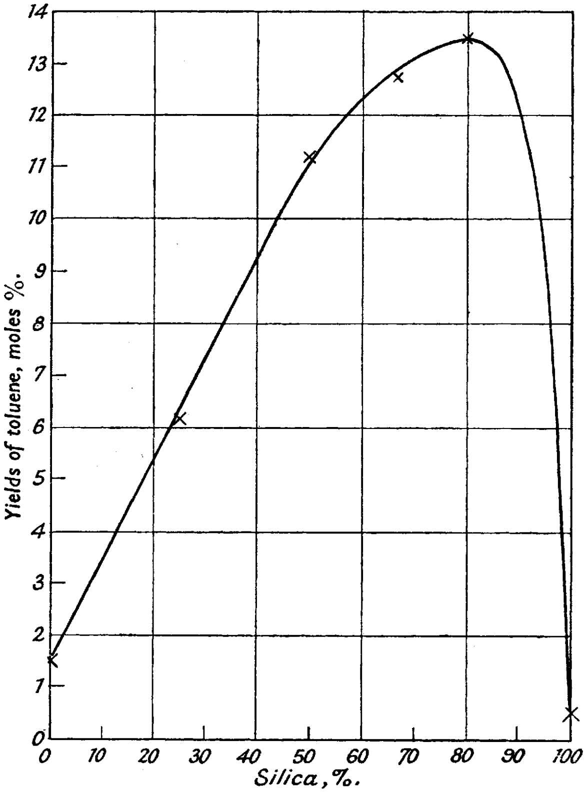
(i) A preliminary survey of the effect of catalysts on the rate of production of methylbenzenes was carried out in an apparatus of the type used for studying the kinetics of gaseous reactions. Methyl ether was found to be strongly adsorbed on the catalysts examined, and to undergo faster and more complex decomposition than the homogeneous reactions in the gas phase (cf. Hinshelwood and Askey, *Proc. Roy. Soc.*, 1927, *A*, **115**, 215; Staveley and Hinshelwood, *J.*, 1937, 1568). By comparing the pressure–time curves, and the analyses of the gaseous products, obtained when pure methyl ether, and ether plus benzene, were admitted to the apparatus, a qualitative series of catalytic activities was obtained. Alumina B, C, D, and E, ferric oxide, titania, silica, thoria, chromic oxide, zinc oxide, and nickel–alumina appeared to be ineffective as catalysts. Alumina A, basic aluminium phosphate, and boron phosphate were deemed worthy of further study.

(ii) The search was continued by the flow method described above. In all cases the criterion of the activity of a catalyst was the yield of toluene (moles of toluene as percentage of moles of benzene passed) under the following standard conditions: Vol. of packed catalyst space, 600 c.c.; temp. 450°; rate of flow of benzene, 42 g. per hour; of methyl ether, 12 g. per hour; molar ratio, benzene to ether, 1·8; contact time of benzene 30 secs.; space rate of flow of benzene about 0·15 c.c. of liquid per hour per volume of catalyst. It may be noted that the yield of polymethylbenzene was in all cases less than that of toluene. The average yields under the above conditions are given below in Table II.

TABLE II.

Catalyst.	Yield of toluene (moles %).	Catalyst.	Yield of toluene (moles %).
Bauxite A	4·0	Alumina–silica 1 : 1	11·3
Bauxite B	0·5	,, ,, 1 : 2	13·0
Alumina A	1·5	,, ,, 1 : 4	13·6
Silica	0·5	Chromic oxide–silica	1·7
Boron phosphate	2·0	Titania–silica	5·2
Basic aluminium phosphate	2·7	Beryllia–silica	6·7
Bauxitic clay	4·5	Silica " O "	6·5
Alumina–silica 3 : 1	6·2	Silica " T "	0·8

The plot of yield of toluene against percentage of silica for the alumina–silica mixtures is reproduced in the figure.



Yields of toluene as a function of composition of alumina–silica mixtures.

The mixtures of silica and other oxides are evidently the most effective catalysts, and the **1 : 4** mixture was adopted for all further work.

3. *More detailed investigation of the reaction on alumina–silica catalyst* (1 : 4). Some experiments were made to determine the effect on the reaction between benzene and methyl ether of varying the reaction conditions. The alumina–silica (1 : 4) catalyst was used throughout.

(i) Rate of flow of reactants. The yield of toluene was surprisingly insensitive to variations in the time of contact with the catalyst (see runs 179, 178, 181 in Table III),

Table III.

Catalyst: Alumina–silica 1 : 4.

Run.	Temp.	Rate of flow (g./hr.). Benzene.	Ether.	Molar ratio, $C_6H_6/C_4H_{10}O$.	Percentage yields of Toluene.	Xylene.	Higher.
179	450°	15·5	7·5	1·1	12·1	4·3	4·1
178	450	42·0	22·9	1·1	12·3	3·8	3·0
181	450	80·0	47·5	1·1	11·0	3·3	3·8
174	450	42·0	7·2	3·4	8·5	—	—
176	450	42·0	15·5	1·6	13·2	4·8	2·7
184	450	42·0	30·0	0·83	13·0	3·3	6·1
186	400	38·5	22·9	1·0	9·1	2·0	3·5
187	400	38·5	12·5	1·9	8·4	1·9	2·9
192*	500	38·5	12·0	1·9	17·3	4·9	2·2
193	500	25·5	22·7	0·65	15·0	5·9	3·2
194	500	27·2	12·0	1·3	15·5	4·0	3·2

* First use of new batch of catalyst.

(ii) Ratio of benzene to ether. It is seen from Table III (runs 174, 176, 184; also 186, 187) that when the rate of flow of benzene is kept constant, an increase in the molar ratio benzene : ether causes only a slight decrease in the yield of methylated products.

(iii) Temperature. The results of experiments at 400° and 500° are given in Table III (runs 186, 187, 192—194). The yields are not markedly temperature-dependent. Experiments over a wider range of temperatures were performed with Bauxite A as catalyst (300—500°). The yield of toluene fell off from 4·0 at 450° to 2·4 at 400°, 1·6 at 350°, and 0·6 at 300°.

(iv) Wastage of reactants, and yields calculated on benzene consumed. In Table IV some representative figures for the recovery of unchanged benzene are given in col. 3; in col. 4, 5, and 6 are given the yields of methylated products calculated on the benzene consumed, *i.e.*, input of benzene less recovered benzene. The total methylation is given in col. 7, the total methylation calculated on the input of benzene in col. 8, and in col. 9 is shown the loss of benzene, *i.e.*, the defect from 100% of the sum of the total methylation (calculated on input) and the benzene recovered.

Table IV.

1. Run.	2. Temp.	3. C_6H_6 recovered, %.	4. Percentage yields of Toluene.	5. Xylene.	6. Higher.	7. Total methyln. on C_6H_6 recovered.	8. Total methyln. on C_6H_6 input.	9. % Loss of C_6H_6.
172	450°	68	46·3	15·4	9·0	70·7	22·5	9·5
176	450	71	45·3	16·6	9·4	71·3	20·7	8·3
186	400	68	28·1	6·4	10·9	45·4	14·6	17·4
189	500	73	51·1	13·7	5·2	70·0	19·2	7·8
192	500	65	49·6	14·0	6·2	69·8	24·4	10·6

The wastage of methyl ether per run is estimated below.

4. *Some general observations on the reaction of benzene with methyl ether.* The products of reaction were in all cases pale yellow or orange liquids with a green fluorescence, and contained water (see below). The polymethylbenzenes collected from a large number of runs were found on distillation to contain a small quantity of material boiling above hexamethylbenzene (the polymethylbenzenes will be dealt with more fully in a subsequent communication); this amounted to about 1% of the yield of methylated products, and was possibly a mixture of diphenyl derivatives. Apart from this (and water), no other products than methylbenzenes were detected, except in the methylation of benzene on the beryllia–silica catalyst when methanol was formed, in amount roughly equivalent to the toluene produced. The methanol was separated as its azeotrope with benzene, and characterised by means of its 3 : 5-dinitrobenzoate (m. p. 107°). A certain amount of carbon deposition was observed on all the catalysts.

As already noted, catalysts were reactivated when necessary by heating to 500° in a stream of oxygen for 1—2 hours. The activity of the most active catalyst, alumina–silica (1 : 4), decreased appreciably with continued use, in spite of reactivation; for instance, comparable figures for total methylation (at 500°) are: on a fresh batch of the material, 24%; on one which had been used in 20 previous runs (*i.e.*, *ca.* 800 g. of benzene had passed over it), 19%.

5. *Use of methanol as a methylating agent.* In view of the fact that other workers have used methanol as a methylating agent, it was thought of interest to compare its reaction with benzene with that of methyl ether with benzene, under the same conditions. It was found that methanol is a much less effective methylating agent than the ether; *e.g.*, when basic aluminium phosphate and the alumina–silica (1 : 4) were used as catalysts at 450°, the yields of toluene were $\frac{1}{2}$% and 1% respectively when methanol was the reactant, and 2·7% and 13·0% with methyl ether, for corresponding rates of flow of the reactants. Water and methyl ether were by-products of the reaction of methanol and benzene.

6. *Decomposition of methyl ether.* It was of obvious interest to determine the fate in a methylation experiment of the methyl ether which does not react with benzene. The gaseous products of reaction consist mainly of hydrogen, carbon monoxide, and paraffin, but whereas in the homogeneous decomposition of the ether these products are formed in nearly equal amounts (Hinshelwood and Askey, *loc. cit.*), in

the heterogeneous reaction (in the presence or absence of benzene) they are formed in widely differing proportions in the presence of different catalysts (see Table V). Water was always found in the products of the reaction of benzene with methyl ether, and of the decomposition of the ether alone. When the alumina–silica mixtures were used as catalysts, the ratio of total weight of ether passed to water produced was more or less constant: 1 mole of ether gave about 0·8—1·0 mole of water. Water is therefore one of the products of decomposition of methyl ether on these catalysts. In no case of the surface reaction studied here has it been possible to write a simple stoicheiometric equation between methyl ether and its products of decomposition. Therefore it has not been possible to calculate accurately the wastage of ether in a methylation run from the amount and composition of the gaseous products of reaction. However, from measurements of the volume of gas produced in a known time, during the course of an experiment, and its analysis, the amount of ether decomposed in passage over the catalyst was calculated, on the assumption that the decomposition is accompanied by a trebling of the initial volume. Thus, in the course of a methylation experiment with the alumina–silica (1 : 4) catalyst at 450°, about 10—15% of the ether is decomposed to permanent gases and water; if ether alone is passed over the catalyst the figure is about 20%.

In Table V are presented some representative analyses of the gaseous products resulting from experiments in which (*a*) methyl ether alone, (*b*) methanol alone, and (*c*) benzene plus methyl ether were passed over various catalysts. In addition to the observations quoted above, the following points may be noted: (1) The average carbon number, *n*, of the paraffins was nearly always greater than unity. (2) In most cases, the gases had nearly the same composition when (*a*) methyl ether alone or (*b*) methyl ether plus benzene were passed over the same catalyst. (3) A comparison of the decompositions of methanol and methyl ether is interesting: when these substances decompose on the surface of boron phosphate, the gaseous products have nearly the same composition in each case, and the same is true of several other materials which are known to catalyse the conversion of methanol into methyl ether (*e.g.*, alumina, titania, thoria, bauxite, chromic oxide; see Sabatier and Mailhe, *Ann. Chim. Phys.*, 1910, **20**, 298).

TABLE V.

Analysis of the gaseous products of reaction.

(All the figures are on a nitrogen-free, ether-free basis, except those for ether itself, which are on a nitrogen-free basis; the analyses are percentage volumes.)

Catalyst.	Temp.	Me_2O.	CO_2.	C_2H_4.	H_2.	CO.	C_nH_{2n+2}.	*n*.
Bauxite A	480°	1·3	5·0	0·4	36·0	24·8	34·7	1·2
,, *	480	2·9	3·4	0·4	32·6	26·6	33·8	1·2
Alumina A	440	8·4	0·7	13·3	33·4	18·9	35·0	1·3
,, *	440	20·7	2·0	5·3	35·3	22·2	30·8	1·4
Basic Al phosphate	440	16·1	3·3	4·4	8·8	16·8	66·7	1·4
,, ,, †	440	2·7	0·2	1·5	64·7	1·4	32·2	1·25
,, ,, *	440	33·5	16·6	1·9	21·8	25·1	34·6	1·6
,, ,, ‡	440	27·9	4·2	8·4	24·2	29·2	33·6	1·25
Boron phosphate	480	13·6	3·4	5·1	0	8·3	83·3	1·1
,, ,, †	480	3·6	2·3	1·6	0	12·0	84·1	1·4
Thoria	440	2·8	0·8	0·7	70·0	25·1	3·5	1·9
,, †	440	0·2	0·7	0·3	76·6	21·2	1·1	—
Bauxitic clay	450	79·7	7·7	3·6	19·9	13·8	55·1	1·5
,, ,, *	450	68·5	16·7	5·9	14·7	11·8	52·0	1·45
Al_2O_3–SiO_2 (1 : 4)	450	0·8	1·0	1·2	4·2	20·4	73·3	1·1
,, ,, *	450	3·2	1·3	2·3	2·7	14·0	7·90	1·1
,, ,,	500	0·6	1·1	0·7	15·4	9·5	73·4	1·1
,, ,, *	500	0·5	0·6	3·0	8·5	7·7	80·0	1·0
BeO–SiO_2	450	67·3	2·6	3·2	10·7	17·2	66·0	1·1

* Products of reaction of benzene and methyl ether.
† Decomposition of methanol.
‡ Products of reaction of benzene and methanol.

Where no sign appears, the figures refer to the decomposition of methyl ether.

DISCUSSION.

The production of toluene by reaction of methanol or methyl ether with benzene at atmospheric pressure is claimed in B.P. 574,738 (Standard Oil Development Co., application dated April 1942; complete specification accepted January 1946 *). The reactants are passed at 300—460° over a catalyst of the "solid" phosphoric acid type, which is prepared by treating a siliceous material (such as clay, kieselguhr, or a synthetic alumina–silica mixture) with a phosphoric acid. Yields of up to 50 moles of toluene per mole of benzene consumed are claimed, though it is not clear how these are calculated from the figures presented. The yields of toluene

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* It appears that the work which led to this and the following patent specification was being carried out simultaneously with the work described here, which, with that to be described in subsequent papers of the series, was performed in 1940—1944 and was submitted in 1944 in a thesis for the degree of D.Phil., Oxford, by one of us (P. H. G.).

obtained by us are of comparable magnitude. Our optimum temperature range, 450—500°, is higher than that quoted for the above process (*i.e.*, 325—425°). Methanol is a more effective methylating agent in the Standard Oil Co. process than methyl ether; comparable figures are (for a reaction temperature of 354—358°): 12·2% (moles) of toluene per pass for methanol, and 7·9% for methyl ether as reactant (we obtained 1% and 11·0% respectively at 450° for approximately the same space rate of flow, using the alumina–silica catalyst).

A similar process has been patented by the Gas Light and Coke Co. (B.P. 541,534, application dated 1942), which involves bringing a (4 : 1 molecular) mixture of benzene and methanol at 250—600° (480°) and 100—300 atm. into contact with a phosphoric acid (H_3PO_4) or a metal (magnesium) phosphate alone or on an inert support, *e.g.*, coke, charcoal, siliceous material. The yield of toluene claimed is 14% by volume (12·2 moles %) on benzene passed. A further patent of the same company (B.P. 577,314, application dated March 1942, complete specification accepted May 1946) covers the use of methyl ether in a similar process, virtually the same reaction conditions being employed; the yield of toluene claimed is 18% per pass (15·5% moles), xylenes 4%, polymethylbenzenes 4%, *i.e.*, methyl ether is a more effective methylating agent than methanol in this process. The process uses roughly the same reaction temperatures as ours and gives similar yields, but requires the application of 100—300 atm. pressure.

Cullinane and Chard (*J.*, 1945, 821) have described the interaction of phenol and methanol on alumina at 200—375° to give anisole, homologues of phenol, and hexamethylbenzene.

Kutz and Corson (*J. Amer. Chem. Soc.*, 1945, **67**, 1312) have described the methylation of benzene, toluene, and naphthalene with methyl chloride at 400° over alumina, alumina–silica mixtures, and other materials. In the reaction of benzene on alumina they claim yields of 8—15% (moles) of toluene, which are similar to ours obtained by the use of methyl ether. For their reaction, they find alumina a more active catalyst than the synthetic aluminosilicates.

It is noteworthy that in all these processes for the methylation of benzene, monomethylation predominates, and our work confirms this. This characteristic of the gas-phase reaction is in marked contrast to the property of the Friedel–Crafts method, *viz.*, that the monomethyl product is always accompanied by large quantities of polymethyl derivatives. In fact, the latter method is of little value for preparing monoalkylbenzenes.

Comparison of Methanol and Methyl Ether.—It is of interest to enquire whether, when toluene is produced by passing methanol and benzene over a catalyst, the methanol reacts directly, or first gives methyl ether, which then reacts with benzene. Previous workers (see above; and Cullinane and Chard, *loc. cit.*) do not appear to have envisaged the latter possibility. Our results show that, at least under the conditions we have used, methanol very probably acts as a methylating agent only by virtue of its ready conversion into methyl ether. Thus, we find that the ether gives a much better yield of toluene in reaction with benzene than does methanol. On many catalysts the decomposition products of methanol, produced under the same conditions as obtain in the course of a methylation, have very nearly the same composition as those of methyl ether on the same catalyst; this must mean that the alcohol is rapidly converted into the ether and water, and the ether then decomposes to the final products. In this connection, it may be mentioned that McKee and Burke (*Ind. Eng. Chem.*, 1923, **15**, 793) have shown that the equilibrium between methanol, methyl ether, and water is rapidly achieved at 350° on alumina, and have determined the equilibrium constant at that temperature.

It may be noted that at the temperatures used in methylation experiments, the equilibrium constant of the methanol–methyl ether conversion is of the order of magnitude unity. Given (*J.*, 1943, 589) has obtained:

$$2CH_3{\cdot}OH\ (v) = (CH_3)_2O + H_2O\ (v) : \log_e K_p = 7300/\boldsymbol{R}T - 4{\cdot}8$$

The values of $\log_{10} K_p$ at various relevant temperatures, calculated from this equation, are given in Table VI. The equilibrium constant is actually unity at 761° K. (488° C.). Of course, if the methyl ether produced decomposes, or reacts with benzene, the equilibrium will be shifted by a mass-action effect.

TABLE VI.

Equililbrium constants of methanol–methyl ether conversion.

Temp., ° K.	300	400	500	600	700	800	900	1000
$\log_{10} K_p$	3·21	19·8	1·09	0·56	0·19	−0·10	−0·32	−0·50

The Metal Oxide–Silica Catalysts.—Our experiments show that the mixed oxide catalysts are all more active than any of the pure oxides examined and that the catalytic activity of the alumina–silica mixtures varies in an apparently rational way with composition (see Fig.). One would expect there to be some characteristic physical property which distinguishes these materials from the pure oxides, and which varies in a rational manner in a series of mixtures with composition; it is not immediately apparent what that property is. It may be noted that synthetic alumina–silica mixtures have found wide application recently in catalysing many reactions of hydrocarbons, such as polymerisation, isomerisation, and cracking (see, *e.g.*, Nikolaeva and Frost, *Bull. Acad. Sci. U.R.S.S.*, Cl. Sci. Tech., 1944, 536; Thomas, *Ind. Eng. Chem.*, 1945, **37**, 543).

Nature of the Reaction between Methyl Ether and Benzene.—The simplest equation which can be written to represent the reaction of benzene and methyl ether to give toluene is

$$C_6H_6 + (CH_3)_2O = C_6H_5{\cdot}CH_3 + CH_3{\cdot}OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

presumably followed by

$$2CH_3{\cdot}OH = (CH_3)_2O + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

These can be combined into

$$2C_6H_6 + (CH_3)_2O = 2C_6H_5{\cdot}CH_3 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As stated above, the only reaction products we have detected are methylbenzenes, water, and permanent gases. The gases have virtually the same composition as the decomposition products of methyl ether determined in separate experiments on the same catalyst. It is logical to assume, therefore, that the gases produced in the reaction of benzene and methyl ether are not primary products, but result only from secondary cracking of the ether.

With one exception (the beryllia–silica mixture), we have never found methanol in the reaction products of benzene and methyl ether; in view of the known readiness of reaction (2) this is not surprising. Thus the available analytical data are in accordance with the suggestion that reaction (1) represents the course of the interaction of benzene and methyl ether, but are not sufficient to establish this unequivocally.

Thermodynamic Considerations.—It was thought of interest to determine how nearly the yields of toluene so far obtained approach the theoretical equilibrium values. We have calculated the thermodynamic equilibria in both reactions (1) and (3) above.

The change in heat capacity in both reactions is small over the relevant range of temperatures, and so the heats of reaction were taken as independent of temperature. Considering all the reactants in the gaseous state, we obtain :

$$\text{Reaction (1)}: \Delta H^\circ_{298\cdot16} = -10{\cdot}23 \text{ kcals.}; \ \Delta G^\circ_{298\cdot16} = -11{\cdot}68 \text{ kcals.}$$
$$\text{and } \Delta G^\circ = -10{,}230 - 4{\cdot}86T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\text{Reaction (3)}: \Delta H^\circ_{298\cdot16} = -27{\cdot}89 \text{ kcals.}; \ \Delta G^\circ_{298\cdot16} = -29{\cdot}525 \text{ kcals.}$$
$$\text{and } \Delta G^\circ = -27{,}890 - 5{\cdot}48T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We see from equations (4) and (5) that the free-energy changes of both reactions are always negative. Values of the equilibrium constants are given in Table VII.

TABLE VII.

T ° K.	298·16.	500.	723.	1000.
Reaction (1) $\log_{10} K_p$	18·2	5·50	4·13	3·28
Reaction (3) $\log_{10} K_p$	21·5	13·31	9·57	6·25

We conclude from the data here presented that, thermodynamically, the conversion of benzene into toluene by reaction with methyl ether approaches 100%, and is far larger than that so far observed experimentally. (The data employed were obtained from Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803; Prosen, Gilmont, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 65; Bichowsky and Rossini, "Thermochemistry of some Chemical Substances"; Crawford, *J. Chem. Physics*, 1943, **8**, 526; Given, *loc. cit.*).

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