

**16.** *Some Catalysed Gas-phase Reactions of Aromatic Hydrocarbons.  
Part II. The Interaction of Benzene and Ethylene.*

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Methods of preparing ethylbenzene, suitable for industrial application, have been investigated during a programme of research on the catalytic alkylation of aromatic compounds. It was found that, over catalysts of the dehydrating type at temperatures of 450–500°, benzene could be made to react with ethylene at ordinary pressures to give predominantly monoethylated products. Under favourable conditions in a flow apparatus, yields of about 8% of ethylbenzene were obtained over bauxite.

THE preparation of toluene in useful yield by the gas-phase interaction at atmospheric pressures of benzene and dimethyl ether over solid dehydrating catalysts has been carried out by Given and Hammick (*J.*, 1947, 928). Attempts to form ethylbenzene by an analogous reaction

do not promise to be very successful, because diethyl ether is known to decompose almost quantitatively over dehydrating catalysts to give ethylene and water (cf. Senderens, *Ann. Chim. Phys.*, 1885, **8**, 505). Nevertheless, detectable amounts of ethylbenzene can be obtained from benzene and diethyl ether, and yields would presumably be higher if the water produced did not seriously deactivate the catalyst. This suggests the possibility that ethylene itself might be a more satisfactory compound for catalytic gas-phase ethylation under ordinary pressures.

As is well known, a vast industrial production of ethylbenzene has grown up during the last decade in Germany and U.S.A., and it is clear that the catalysed ethylation of benzene by continuous flow methods under pressure using ethylene has been widely exploited (Sachanen and O'Kelly, *Ind. Eng. Chem.*, 1941, **33**, 1540; *Oil and Gas J.*, 1942, **41**, No. 13, p. 14; Pardee and Dodge, *Ind. Eng. Chem.*, 1943, **35**, 273; Schaad, U.S.P. 2,290,211, 1943, for Universal Oil Products Co.; Mattox, *Trans. Amer. Inst. Chem. Eng.*, 1945, **41**, 463).

In the work to be described, however, it has been shown that benzene and ethylene can give reasonable yields of ethylbenzene under flow conditions at ordinary pressures. A number of non-volatile and easily recoverable catalysts of the dehydrating type were tried, including bauxite, aluminium silicate, silica gel, basic aluminium phosphate, activated alumina, and titania gel. A reduced nickel-aluminium silicate gave no ethylbenzene, but small amounts of toluene (cf. Komarewsky, *J. Amer. Chem. Soc.*, 1937, **59**, 2715). Of the other catalysts, bauxite was by far the best; aluminium silicate was also reasonably active. At 450°, under the most favourable conditions, *i.e.*, slow rates of flow of benzene and approximately equimolecular proportions of the reactants, yields of 8.2% of ethylbenzene could be obtained with bauxite (yields are calculated as moles per 100 moles of benzene used). The other catalysts tried gave very small or negligible amounts of alkylated products.

Undesirable by-products were not obtained, and the unchanged reactants were recoverable in very good yield. The effective catalysts are easily handled and, with suitable reactivation, can be used indefinitely.

#### EXPERIMENTAL.

*Flow Apparatus.*—The vapourised reactants were passed at measured rates through a pre-heater at 250° into a "Pyrex" tube 93 cm. long enclosed in a box-type electric furnace. Ethylene (about 98% pure) was obtained from a cylinder of the compressed gas, and its rate measured by a calibrated flowmeter. Benzene ("AnalaR") was boiled electrically in a calibrated apparatus which gave rates of distillation dependent only on the current supplied (cf. Adkins, *J. Amer. Chem. Soc.*, 1922, **44**, 2175; Given and Hammick, *loc. cit.*). About 450 g. of catalyst, crushed and screened between 2/8 mesh, were used, and the free space in the furnace tube was approximately 300 c.c. The liquid products were condensed out, and the gaseous products collected for analysis when required.

*Catalysts.*—The bauxite was obtained from Messrs. Harrington Bros., and the aluminium silicate from Messrs. Peter Spence Ltd. The catalysts were dried thoroughly at 500° for several hours in the furnace before use, and had the compositions shown in Table I.

TABLE I.

Catalyst.	Loss on ignition,		Composition, %.				Traces of Cr, Mn, SO <sub>4</sub> Cr
	%.	Al <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub> .		
Bauxite .....	22.7	35.6	30.9	6.9	4.3		
Aluminium silicate .....	7	41—42	48	1	1—2		

The nickel-aluminium silicate was prepared by evaporating 450 g. of the aluminium silicate with a solution of 50 g. of nickel nitrate, drying the product in an air-oven at 200°, and decomposing it in the furnace tube at 400°. The nickel oxide was reduced in hydrogen at 350—400° for several hours, and the nickel-aluminium silicate catalyst finally heated at 500° in an atmosphere of hydrogen before use.

*Analysis of Products.*—Liquid products were analysed by fractional distillation in a Podbielniak type of still. Sharp separation of benzene and ethylbenzene (less than 0.5 c.c. distilled between the "plateaux") was easily obtained. The composition of gases was determined in a standard Bone and Wheeler apparatus.

*Characterisation of Aromatic Products.*—The hydrocarbon, b. p. 136°, obtained in an ethylation experiment was confirmed as ethylbenzene by refractive-index determinations with an Abbé refractometer, by quantitative analysis, and by bromination by the method of Friedel and Crafts (*Compt. rend.*, 1885, **101**, 1220) (see Table II).

TABLE II.

Hydrocarbon.	$n_D^{14.5^\circ}$ .	C, %.	H, %.	M. p. of Br <sub>5</sub> -derivative.	Mixed m. p. + authentic specimen.	Br, %, in Br <sub>5</sub> -derivative.
B. p. 136° .....	1.4976	90.0	9.2	141—142° ( <i>ex EtOH</i> )	140—143°	79.8
Authentic ethylbenzene.....	1.4980	90.6	9.4	141°	—	80.0

The suspected toluene obtained over nickel-aluminium silicate was converted into a pentabromo-derivative with bromine and aluminium chloride. This on recrystallisation from toluene melted at 277—279°. Pentabromotoluene prepared from authentic toluene melted at 279—281°, and a mixed m. p. with the bromo-derivative showed no depression.

*Results.*—(a) *Aluminium silicate.* A series of experiments with this catalyst showed that fair yields of ethylbenzene could be obtained by using slow rates of benzene flow. In the two final runs (Table IIIa), benzene and ethylene were passed over the catalyst in approximately equimolecular proportion. Deactivation of the catalyst is clearly shown by runs 1 and 2 carried out consecutively under identical conditions. For this reason, oxygen was passed over the aluminium silicate at 500° before each subsequent experiment (see below in connection with bauxite). The products were pale yellow, slightly cloudy liquids. Higher homologues of ethylbenzene were not formed in measurable amount.

TABLE III.

Expt.	Temp.	Rate C <sub>2</sub> H <sub>4</sub> , l./hr.	Rate C <sub>6</sub> H <sub>6</sub> , g./hr.	Time of expt. (hrs.).	Yield of EtPh, c.c.	Yield of EtPh, % (on C <sub>6</sub> H <sub>6</sub> ).
(a) <i>Aluminium silicate.</i>						
1	450°	1.0	21.7	3.0	1.4	1.4
2	450	1.0	21.7	3.0	0.8	0.8
3	450	1.0	21.7	3.0	1.3	1.3
4	500	2.3	17.0	4.0	2.6	2.5
5	500	3.6	17.0	4.0	3.0	2.8
6	450	3.6	13.5	3.75	3.1	4.0
7	500	3.6	13.5	3.75	3.1	4.0
(b) <i>Bauxite.</i>						
8	450	3.6	17.0	3.5	5.5	6.0
9	450	5.0	17.0	3.5	5.6	6.1
10	450	5.0	13.5	4.0	6.9	8.2

(b) *Bauxite.* Similar results were obtained with bauxite (for composition, see above), but percentage yields were approximately double. Again, reactivation of the used catalyst in oxygen at 500° was carried out before each experiment. Products were slightly cloudy, pale yellow liquids. Typical figures are given in Table IIIb.

(c) *Nickel-aluminium silicate.* This catalyst gave no yield of ethylbenzene, but instead a small fraction boiling at 110°. Toluene was shown here to be the only alkylated product (Table IV).

TABLE IV.

Expt.	Temp.	Rate C <sub>2</sub> H <sub>4</sub> , l./hr.	Rate C <sub>6</sub> H <sub>6</sub> , g./hr.	Time of expt. (hrs.).	Yield of MePh, c.c.	Yield of EtPh, c.c.
11	450°	3.6	17.0	3.7	1.4	0
12	450	3.6	17.0	3.7	1.2	0

(d) *Recovery of the reactants.* Benzene and other aromatic compounds are unchanged in the presence of metallic oxides below at least 600° (cf. Beilstein, "Handbuch," Bd. V, 185). The existing data on ethylene are contradictory (cf. Egloff, "Reactions of Pure Hydrocarbons," 1937, p. 260), but decomposition should be slight below 500°. This was confirmed for aluminium silicate and bauxite, over which ethylene was passed and the gaseous products collected and analysed (Table V). Over nickel-aluminium silicate, decomposition was considerable, with formation of much methane and hydrogen.

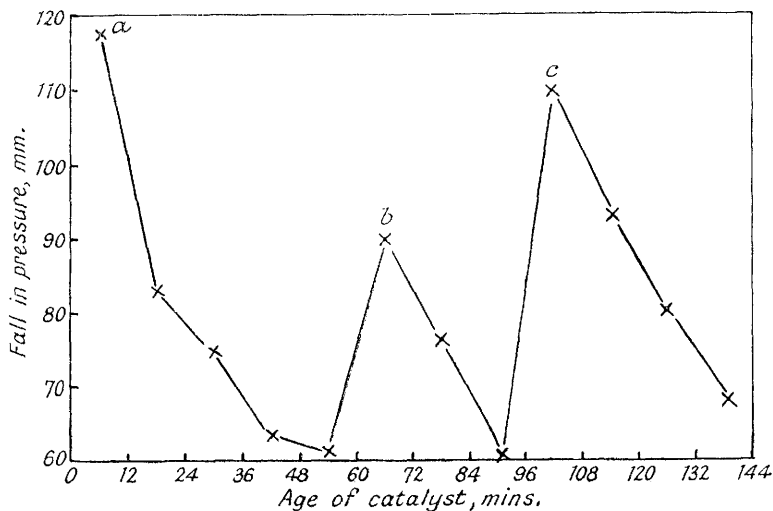
TABLE V.

Conditions.	Higher olefins.	CO <sub>2</sub> .	C <sub>2</sub> H <sub>2</sub> .	C <sub>2</sub> H <sub>4</sub> .	Products, %.			Paraffins. N <sub>2</sub> , etc.	Residue, N <sub>2</sub> , etc.
					H <sub>2</sub> .	O <sub>2</sub> .	CO.		
C <sub>2</sub> H <sub>4</sub> at 3.6 l./hr. over Al silicate at 500° .....	1.2	1.1	—	84.9	—	1.1	—	—	11.7
C <sub>2</sub> H <sub>4</sub> at 3 l./hr. over bauxite at 450° .....	1.2	1.2	—	91.5	1.5	0.6	—	—	4.0
C <sub>2</sub> H <sub>4</sub> at 3.6 l./hr. over Ni-Al silicate at 450° .....	1.1	1.3	0.8	62.7	14.3	1.0	1.1	14.9	2.8
Original C <sub>2</sub> H <sub>4</sub> from cylinder...	0.7	—	—	97.5	—	—	—	(n = 1.6)	1.8

(e) *Deactivation and reactivation of bauxite.* Bauxite and other catalysts used in the benzene-ethylene reaction were found to undergo considerable deactivation during the course of an ethylation experiment (cf. runs 1 and 2, Table III). Investigations in an apparatus of the type used for studying the kinetics of gaseous reactions showed this to be caused by deposition of carbon (presumably from the decomposition C<sub>2</sub>H<sub>4</sub> → 2C + 2H<sub>2</sub>). Complete reactivation could be brought about by passing a stream of oxygen over the catalyst at 500°.

A series of experiments with approximately 150 mm. of benzene and 280 mm. of ethylene were carried out over bauxite at 448°. The figure shows the fall in pressure during an arbitrary period of 10 minutes plotted against the total life of the catalyst. At each point on the graph, the reaction tube was evacuated, the reactants admitted, and the fall in pressure in 10 minutes observed. The total times of each experi-

ment, about 12 minutes, were added together to give the age of the catalyst. The decomposition of ethylene alone (also involving a decrease of pressure) was small compared with the reaction between ethylene and benzene, so the fall in pressure observed was a rough measure of the rate of ethylation.



Point *a* refers to fresh bauxite; point *b* was obtained after air had been admitted to the catalyst at 500°, and *c* after oxygen had been kept in contact with it for a few hours at 500°.

The residual gas left after passing oxygen over the deactivated bauxite at 500° was proved to contain a high proportion of carbon dioxide.

A grant from the D.S.I.R. in support of the above work is gratefully acknowledged by one of us (M. R.).

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[Received, February 14th, 1947.]