381. *Some Catalysed Gas-phase Reactions of Aromatic Hydrocarbons. Part V. Interconversion of Alkylbenzenes. Disproportionation and Cracking Reactions.*

By P. H. Given and D. Ll. Hammick.

Previous work (Parts I—IV, *J.*, 1947, 928; 1948, 73, 1700, 2154) is extended by a study of the reactions of ethyl- and *n*-propyl-benzene with dimethyl ether, and of the same hydrocarbons and toluene and *p*-xylene when passed slowly (liquid hourly space velocities of 0·06—0·10 hour^{-1}) in the absence of the ether over a silica–alumina catalyst at 450°. Scission of alkyl groups is the main reaction of ethyl- and propyl-benzene, whether or not the ether is present, and disproportionation is very slight, whereas the principal reactions of methylbenzenes are methylation in the presence of dimethyl ether, and disproportionation in its absence; isomerisation of *p*-xylene occurs concurrently in either case. The silica–alumina catalyst is shown to be particularly active in the synthesis of ethylbenzene from benzene and ethylene. The yields of the products of the various reactions are compared with those thermodynamically possible.

We have shown previously (Given and Hammick, Part IV, *J.*, 1948, 2154) that, when a single xylene isomer is passed with dimethyl ether over a silica–alumina catalyst at 450°, about 22% is converted into trimethylbenzenes; isomerisation of the xylene occurs at the same time. We now find that, under the same conditions, only small yields of methylethyl- and methylpropyl-benzene are obtained from ethyl- and *n*-propyl-benzene respectively; the principal reaction in both cases is cracking, the main products containing fewer carbon atoms than did the original hydrocarbons. Thus there is a distinction between the behaviour of methyl- and other alkyl-benzenes; and it is clear that under the conditions used the methylation of alkylbenzenes, whatever the nature of the alkyl groups, is accompanied by various side-reactions (*e.g.*, isomerisation and cracking). We have therefore studied the reactions of a series of representative hydrocarbons (toluene, *p*-xylene, a xylene mixture, and ethyl- and *n*-propylbenzene) on passage over a silica–alumina catalyst in the absence of any alkylating agent, in order to gain further information concerning these side-reactions and to elaborate the distinction in behaviour between the various classes of hydrocarbons in their catalytic reactions. We have also determined the yield of ethylbenzene formed from benzene and ethylene at the same temperature and over the same catalyst.

As far as we are aware, the methylation of ethyl- and propyl-benzene by a gas-phase method has not previously been reported; the ethylation of benzene is, of course, well known (see, *e.g.*, O'Kelly, Kellett, and Plucker, *Ind. Eng. Chem.*, 1947, **39**, 154, who give full references to earlier work; also Hammick and Roberts, *J.*, 1948, 73). The reactions of pure hydrocarbons (*i.e.*, in the absence of an alkylating agent) over silica–alumina catalysts have attracted attention recently, since the collection of data relating to single compounds is important as a background to the industrial cracking and chemical refining of petroleum. Natanson and Kagan (*J. Phys. Chem. U.S.S.R.*, 1943, **17**, 381) passed toluene over a silica–alumina catalyst at a temperature (430°) and space rate of flow (0·05 hour^{-1}) comparable with those we have used, and found 25% of disproportionation to benzene and xylenes. Hansford, Myers, and Sachanen (*Ind. Eng. Chem.*, 1945, **37**, 671) report a similar disproportionation of *m*-xylene on the same type of catalyst at 538° and a liquid hourly space velocity (L.H.S.V.) of 1·05 hour^{-1}. On the other hand, Greensfelder, Voge, and Good (*Ind. Eng. Chem.*, 1945, **37**, 1168) state that *p*-xylene at 550° and L.H.S.V. 0·5 hour^{-1} suffers considerable cracking as well as disproportionation and report further that the composition of the recovered xylene approximates to that of the equilibrium mixture (calculated by Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803). These authors also record that for ethyl- and *n*-propyl-benzene under similar conditions (L.H.S.V., 1·7—1·9) removal of the alkyl groups, without disproportionation, is the main reaction. Thomas, Hoekstra, and Pinkston (*J. Amer. Chem. Soc.*, 1944, **66**, 1694) reached the same conclusions for ethylbenzene at 500° and L.H.S.V. 1·7—1·9 hour^{-1}.

Of this work, all but that of Natanson and Kagan was performed at temperatures and space rates of flow higher than those we used in our studies of reactions with dimethyl ether. In extending our work to the reactions of the hydrocarbons in the absence of ether, we have therefore restricted ourselves to the temperature (450°) and space rates of flow (L.H.S.V., 0·05—0·10 hour^{-1}) which we used in its presence.

We have compared the experimental yields of many of the reactions investigated with those theoretically possible, as calculated from equilibrium data. The extension of available information in the direction of lower rates of flow is of interest in this connection.

EXPERIMENTAL.

Materials.—The preparations of pure benzene, toluene, and *p*-xylene have already been described (Given and Hammick, *loc. cit.*). The xylene mixture was prepared by the methylation of benzene with dimethyl ether; its composition (*J.*, 1948, 2154) was ethylbenzene 0·4, *p*- 24·2, *m*- 54·3, and *o*-xylene 21·1%. The 1 : 4 alumina–silica catalyst, prepared by Messrs. Peter Spence Ltd., was that used in the earlier work.

The ethylbenzene was prepared by Clemmensen reduction of acetophenone. The product was heated under reflux with sodium to remove unsaturated compounds, and distilled; b. p. 136°, $n_D^{20°}$ 1·4959.

TABLE I.

Run no.	1	2	3	4	5	6	7	8
Hydrocarbon	toluene	*p*-xylene	xylene mixture	ethyl-benzene	ethyl-benzene	benzene	*n*-propyl-benzene	*n*-propyl-benzene
Alkylating agent	none	none	none	Me_2O	none	C_2H_4	Me_2O	none
Rate of flow, hydrocarbon, g./hr.	25·3	58	35·3	30	38·5	27·7	42	41
Space rate of flow, vol. liquid/vol. catalyst space/hr.	0·061	0·141	0·086	0·073	0·093	0·067	0·010	0·010
Rate of flow of alkylating agent, g./hr.	—	—	—	13·3	—	21·2	20·2	—
Molar ratio, hydrocarbon/other reactant	—	—	—	0·98	—	0·47	0·80	—
Yield, moles %, C_6	9·8	—	—	12·7	36·4	73·4	29·2	53·3
C_7	77·7	11·8	25·7	11·1	3·1 [a]	1·7 [a]	12·8	5·6
C_8	8·1	73·4 [b]	52·9	39·7	38·6	22·0	6·9	3·2 [a]
C_9	nil	11·7 [c]	16·9 [c]	8·9 [d]	2·4 [a]	nil	23·5	6·2
C_{10}	—	—	—	3·0 [a]	3·6 [a]	1·9 [a]	nil	nil
Total moles, liquid product	99·0	96·9	95·5	75·4	84·1	99·0	72·4	72·4

[a] These figures are less reliable than the others in the table, as the volumes of the cuts were small; they may be in error by 15% of the values quoted, whereas the rest are reliable to ±3—5%.

[b] The composition is given in Table III. We are indebted to Dr. Powell of Anglo-Iranian Oil Co. Ltd. for the analysis, which was made by the ultra-violet-spectroscopical method (Gordon and Powell, *J. Inst. Petrol.*, 1945, **31**, 428).

[c] These fractions distilled in the trimethylbenzene range, and the distillation curves, together with the refractive indices of successive portions of the distillates, indicated that *ψ*-cumene was the main component with small amounts (20% or less of each) of mesitylene and hemimellitene.

[d] Distilled entirely in the ethyltoluene range.

n-Propylbenzene was prepared by Clemmensen reduction of propiophenone; the partly unsaturated product was hydrogenated over Raney nickel; the material was fractionated in the Podbialniak still; b. p. 159°, $n_{\mathrm{D}}^{20^\circ}$ 1·4919.

The ethylene and nitrogen were cylinder gases used as supplied by the British Oxygen Company.

The apparatus, the Podbialniak still used in the analysis of the products, and the experimental methods, have been described previously (Part I, *J.*, 1947, 925; Part IV, *J.*, 1948, 2154). A slow stream of nitrogen (1—3 l. hour^{-1}) was used as a carrier gas in the experiments in which the reactions of a hydrocarbon in the absence of an alkylating agent were investigated.

Results.—All the reactions were performed at 450° over the silica–alumina catalyst. The rates of flow of the reactants and the yields of products are given in Table I. The contact times, calculated from the free space in the catalyst chamber (*i.e.*, volume of voids) and the volume of hydrocarbon vapour (at 450°/1 atm.) passed per hour, averaged about 45 seconds.

The yields are expressed as moles of product per 100 moles of aromatic hydrocarbon passed.

In runs 7 and 8 (*n*-propylbenzene) small cuts boiling near 60° were found; their refractive indices (material incompletely separated from benzene had $n_{\mathrm{D}}^{20^\circ}$ 1·4501) showed that they contained aliphatic hydrocarbons, presumably hexenes formed by polymerisation of propene. The yields calculated on the assumption that 2 moles of propylbenzene gave 1 mole of hexene, were 2·7% and 3·3%, respectively. The gaseous products of run 5 (ethylbenzene) contained an alkene of more than two carbon atoms (see analysis in Table II below), and the liquid products of the run also contained a little low-boiling material; thus some butenes may have been formed.

There was no evidence of the presence of any C_{12} hydrocarbons in the products of the propylbenzene experiments.

Analyses of 60—100-c.c. samples of the gaseous products of the reactions are given in Table II. The samples were collected at approximately the middle of the reaction periods.

TABLE II.

Run.	Aromatic hydrocarbon passed.	Alkylating agent.	Percentage by volume of gaseous products.						
			Me_2O.	C_nH_{2m}.	CO_2.	CO.	H_2.	C_nH_{2n+2}.	*n*.
4	Ethylbenzene	Me_2O	0·1	9·0	0·9	8·5	4·2	77·4	1·2
5	Ethylbenzene	none	nil	37·5	nil	1·2	30·8	30·6	2·35
7	*n*-Propylbenzene	Me_2O	0·5	20·7	1·2	5·2	8·9	63·6	1·5
8	*n*-Propylbenzene	none	nil	14·6	nil	1·3	26·2	57·8	3·1

CONCLUSIONS.

Disproportionation of Methylbenzenes.—The results of experiments 1—3 (Table I) show that disproportionation has occurred, but very little cracking; the disproportionated products are formed in nearly equivalent amount, and the total of these products and unchanged starting material is 95—99% in each case. Our yields resemble those of Hansford, Myers, and Sachanen (*loc. cit.*), and Greensfelder, Voge, and Good (*loc. cit.*), which is perhaps surprising in view of the wide difference between their working temperature and rates of flow, and ours (see Introduction). However, we do not find the extensive cracking of *p*-xylene reported by the latter authors.

In spite of the low L.H.S.V. we have used, the disproportionation of neither toluene nor the xylenes proceeds to equilibrium in a single pass. The equilibrium constants of the reactions in the vapour state at 450° (Pitzer and Scott, and Taylor *et al.*, *locc. cit.*) are :

$$2\mathrm{PhMe} \rightleftharpoons C_6H_6 + \underset{\substack{\text{(equilibrium}\\\text{mixture)}}}{C_6H_4Me_2} \qquad K_p = 0{\cdot}29 \quad . \; . \; . \; . \; . \; . \quad (1)$$

$$\underset{\substack{\text{(equilibrium}\\\text{mixture)}}}{2C_6H_4Me_2} \rightleftharpoons \mathrm{PhMe} + \underset{\substack{\text{(equilibrium}\\\text{mixture)}}}{C_6H_3Me_3} \qquad K_p = 1{\cdot}07 \quad . \; . \; . \; . \; . \; . \quad (2)$$

At equilibrium the products of reaction (1) should, therefore, consist of 47% toluene and 26·5% each of benzene and xylenes, whilst those of reaction (2) should contain 44·4% of C_8 aromatics, and 27·8% each of toluene and trimethylbenzenes. It appears that in our experiments the disproportionation of the xylene mixture approaches the equilibrium state, but the corresponding reactions of toluene and *p*-xylene have stopped some way short of equilibrium. (The actual composition of the C_8 and C_9 products were near enough to the equilibrium values for the comparisons to be fair; it should be noted that in the *p*-xylene experiment (run 2 in Table I) it is a C_8-mixture and not *p*-xylene which is involved in the equilibrium with toluene and trimethylbenzenes, since the single isomer rearranges in the course of the reaction.)

Isomerisation of Xylene.—The xylene recovered from run 2, in which *p*-xylene was passed over the catalyst, contained only 35·7% of the *para*-isomer, so that isomerisation occurs as well as disproportionation. The composition of this recovered xylene (Table III) is very nearly the same as that of the xylene recovered from our methylation of the *para*-isomer with dimethyl ether (see Part IV, *loc. cit.*, Table II, p. 2154), and both analyses are close to the equilibrium composition

(Taylor, Wagman, Williams, Pitzer, and Rossini, *J. Res. Nat. Bur. Stds.*, 1946, **37**, 95). The two analyses are reported in Table III, together with the equilibrium concentrations, and the analysis of Greensfelder *et al.* (*loc. cit.*), who have also observed the catalytic isomerisation of *p*-xylene.

TABLE III.

	Temp., ° c.	Ethyl-benzene.	Xylene.		
			para-.	*meta-*.	*ortho-*.
Isomerisation of *p*-xylene (run 2, this paper)	450	0·0%	35·7%	45·5%	18·8%
Methylation of *p*-xylene (Part IV)	450	0·4	33·8	46·1	19·3
Equilibrium (Taylor *et al.*)	450	9·0	21·2	47·3	22·5
,, ,, ...	550	11·0	23·0	45·5	20·5
,, (Pitzer and Scott)	450	—	21	59	19
,, ,, ...	550	—	21	58	21
Isomerisation of *p*-xylene (Greensfelder *et al.*)	550	—	27·4	47·3	25·3

We showed in Part IV (*loc. cit.*) that, when the other xylene isomers are passed with dimethyl ether over the catalyst, the composition of the xylene isolated from the products approximated to that of the equilibrium mixture. Considered with the figures quoted above, this shows that the isomerisation occurs independently of an alkylation reaction which may be proceeding simultaneously; *i.e.*, the presence of dimethyl ether is not an essential factor for isomerisation.

Reactions of Ethyl- and Propyl-benzenes.—From the analyses of the products of runs 5 and 8 (see Table I) it is seen that, when either ethyl- or propyl-benzene is passed alone over the silica–alumina catalyst, the principal reaction is scission of the whole side-chain, although some cracking in the middle of the chain evidently also occurs; it will be noted that the diethyl- and dipropyl-benzene formed in runs 5 and 8 respectively are far less than equivalent to the benzene produced, which confirms the conclusion that the reaction is indeed cracking and not disproportionation. The analyses of the gaseous products support the same conclusion (see below). The results quoted here are qualitatively similar to those of the experiments, already referred to in the introduction, of Greensfelder, Voge, and Good (*loc. cit.*) and Thomas, Hoekstra, and Pinkston (*loc. cit.*), although we find more extensive cracking at 450° than they did at 500—550°, presumably because of the much lower L.H.S.W. we have used.

The rapid cracking of C_2 and C_3 side-chains is clearly an important factor in determining the products of the reactions of ethyl- and *n*-propyl-benzene with dimethyl ether; in runs 4 and 7 (Table I), the yields of monomethylated products from ethyl- and propyl-benzene were 8·9% and nil, respectively, whilst substantial amounts of benzene and toluene were formed (together with some C_8 hydrocarbons from the propylbenzene). In contradistinction to this situation, we have found (Part IV, *loc. cit.*) that more than 20% of the monomethylated derivative, but very small amounts of demethylated products, are formed in the reaction of toluene or a xylene with dimethyl ether under the same conditions. Thus in the reactions of methylbenzenes, removal of methyl groups by cracking is much slower than methylation by dimethyl ether, or disproportionation in its absence; isomerisation of xylenes occurs freely whether the ether is present or not. On the other hand, the cracking of the side-chains of ethyl- and *n*-propyl-benzenes is much faster than the methylation, disproportionation, or isomerisation of the same compounds (the two last-named were found to occur to only a slight extent, if at all). Clearly the relative velocities of the various reactions depend markedly on the size of the alkyl side-chain attached to the benzene nucleus.

Gaseous Products of the Reactions of Ethyl- and n-*Propylbenzene.*—The principal gaseous products of the reactions of these two hydrocarbons, in the absence of dimethyl ether, are hydrogen, alkene, and alkane (see Table II); the alkane contains approximately the same number of carbon atoms as the side-chain of the hydrocarbon from which it was derived. In addition, there was some evidence (see Experimental section) of dimerization of the ethylene and propene to butenes and hexenes. One would expect the formation of some of the corresponding alkene in the cracking of an alkylbenzene, *e.g.*, $PhEt = C_6H_6 + C_2H_4$, and some dimerization might well occur; but one would not expect either hydrogen or an alkane to be formed. Greensfelder *et al.* (*loc. cit.*) found propane and propene, but no hydrogen, in the gaseous products of the cracking of *n*-propylbenzene. Thomas (*J. Amer. Chem. Soc.*, 1944, **66**, 1586) has reported an apparent gain in hydrogen during cracking of octenes on a silica–alumina catalyst at 375° and accounted for it by establishing that part of his products were hydrogenated with the simultaneous formation of a carbonaceous deposit poor in hydrogen; a carbonaceous deposit was also formed in our experiments, so that the " gain " of hydrogen we observe may be due to a disproportionation of similar type. The gases formed in the reactions of the alkylbenzenes with dimethyl ether have the compositions one would expect of a mixture of the decomposition products of the ether (see Given and Hammick, Part I, *loc. cit.*) with those of the hydrocarbons.

Reaction of Benzene and Ethylene.—The conversion of benzene and ethylene into ethylbenzene was 22% per pass (see run 6, Table I). This is much higher than the yield achieved by Hammick and Roberts (Part III, *J.*, 1948, 73), whose maximum conversion was 6·8%, using a bauxitic clay at a similar temperature and rate of flow. O'Kelly, Kellett, and Plucker (*loc. cit.*) obtained only 6—14% of ethylbenzene when they passed benzene and ethylene over a silica–alumina catalyst at 450—500° and 50—75 lb. per sq. in., but they used a space velocity some thirty times ours. Our catalyst would appear to be particularly active for this reaction.

Equilibrium between Benzene, Ethylene, and Ethylbenzene.—Since we have performed this reaction in both directions, we were interested to compare the experimental results with the calculated equilibrium compositions.

The equilibrium constant of the vapour-phase reaction, $C_6H_6 + C_2H_4 \rightleftharpoons PhEt$, is $K_p = 8{\cdot}61$ at 450° (Taylor *et al.*, *loc. cit.*), so that, if we start with benzene and ethylene in the ratio used in experiment 6 (Table I), the equilibrium mixture should contain 7·4% of benzene, 56·5% of ethylene, and 36·1% of ethylbenzene. We were not able to determine the total ethylene in the products, but from the above figures we see that at equilibrium the liquid products should consist of 17% of benzene and 83% of ethylbenzene, whereas our product contained 77% of benzene and 23% of ethylbenzene, so that our relatively high conversion is still some way short of that theoretically possible. If an equal number of molecules of benzene and ethylene is present in the equilibrium mixture (*i.e.*, when synthesis is performed with a 1 : 1 mixture, or when ethylbenzene is cracked), the mixture should contain 24·4% each of benzene and ethylene, and 51·2% of ethylbenzene, and the liquid products should consist of 32·3% of benzene and 67·7% of ethylbenzene. The mixture of the two liquids given by the experimental cracking of ethylbenzene contained 46·5% of benzene, and 53·6% of ethylbenzene, apparently beyond equilibrium; but the agreement is probably satisfactory, in view of the occurrence of side-reactions. A similar comparison of the cracking of propylbenzene with the corresponding theoretical equilibrium leads to the same conclusion.

The authors wish to express their gratitude to the Department of Scientific and Industrial Research for a grant to one of them (P. H. G.).

DYSON PERRINS LABORATORY, OXFORD. [*Received, December* 10*th*, 1948.]