21. *The Isomerisation of* p-*Xylene.*

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The presence of a third component such as hydrogen halide is shown to be an essential feature of the interaction of an aromatic hydrocarbon and an aluminium halide at room temperature. Mixtures of aluminium bromide and *m*- or *p*-xylene are shown to absorb hydrogen bromide until the relationship $HBr : AlBr_3 = 1 : 1$ obtains. Ternary complexes of the type $(ArH)_x(HBr,AlBr_3)_y$ have been obtained for the first time, and an almost colourless crystalline complex which provides analytical data compatible with the formula $(m\text{-Xylene})_3(HBr,AlBr_3)_2$ has been obtained from *m*-xylene and also from *p*-xylene.

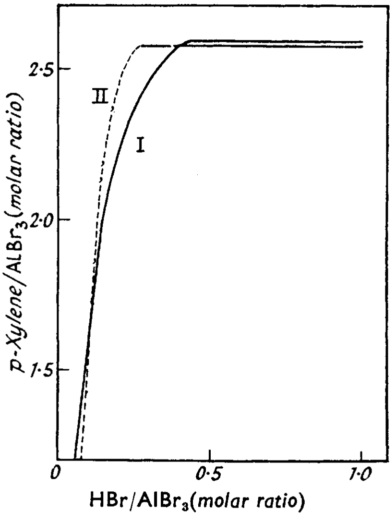
Although the rate of isomerisation of the xylenes in the presence of aluminium chloride is reported to be unaffected by the presence of hydrogen chloride (Norris and Vaala, *J. Amer. Chem. Soc.*, 1939, **61**, 2131), one of us has demonstrated that hydrogen chloride is necessary in the isomerisation of phenols, aromatic ketones, and hydroxy-aromatic ketones (*J.*, 1950, 994). This contradiction led us to reinvestigate the interaction of aluminium bromide with *p*-xylene and other aromatic hydrocarbons; the bromide was selected because it is readily soluble in the hydrocarbons.

Evaporation causes precipitation of the bromide from a solution of aluminium bromide in toluene (Norris and Rubinstein, *J. Amer. Chem. Soc.*, 1939, **61**, 1163), and Korshak, Lebedev, and Fedoseev (*Chem. Abs.*, 1948, **42**, 1217) have deduced, from the strict additivity of the molar refractivities of solutions of the bromide in both benzene and toluene, that no definite complexes are formed. Van Dyke (*J. Amer. Chem. Soc.*, 1950, **72**, 3619), using freezing-point data, has shown that aluminium bromide exists as Al_2Br_6 in solution in benzene; he claims that the more concentrated solutions provide a solid phase of $Al_2Br_6,2C_6H_6$ and suggests that this is the form in which the bromide is present in solution (cf. Plotnikov and Gratsianskiv, *Chem. Abs.*, 1939, **33**, 243). Gustavson (*Ber.*, 1878, **11**, 2151; 1879, **12**, 593) showed that aluminium chloride combines with benzene and toluene in the presence of hydrogen chloride to provide orange-coloured oils which regenerate the hydrocarbon on addition of water. Norris and Ingraham (*J. Amer. Chem. Soc.*, 1940, **62**, 1298) obtained complexes of the type $(ArH)_n,Al_2Br_6,HBr$ by bubbling hydrogen bromide into solutions of aluminium bromide in aromatic hydrocarbon; several complexes are listed in Table 1 and similar ones have been obtained with aluminium and hydrogen chlorides. The products obtained by reducing the pressure are given in the last column; they show that the stability of these complexes is a minimum for benzene and increases progressively as alkyl groups are introduced.

TABLE 1. *Products of interaction of hydrogen bromide, aluminium bromide, and aromatic hydrocarbons.*

Hydrocarbon	Complex	Description	Effect of diminished pressure Press. (mm.)	Residue
Benzene	$(C_6H_6)_6,Al_2Br_6,HBr$	Oil	12	Al_2Br_6
Toluene	$(C_7H_8)_6,Al_2Br_6,HBr$	Oil	12	$C_7H_8Al_2Br_6$
			0·002	mainly Al_2Br_6
Mesitylene	$(C_9H_{12})_3,Al_2Br_6,HBr$	Solid	0·002	C_9H_{12},Al_2Br_6
s-Triethylbenzene	$(C_{12}H_{18})_2,Al_2Br_6,HBr$	Solid	0·002	$C_{12}H_{18},Al_2Br_6$

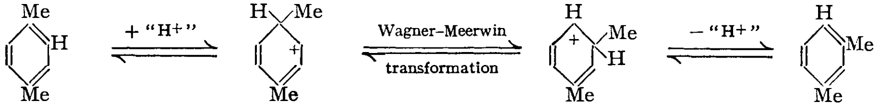
The literature does not contain the relevant data for the xylenes; Campbell and Hetherington (*Nature*, 1945, **156**, 389) have shown, however, that *m*-xylene forms a more stable complex with aluminium chloride than does *p*-xylene, and Campbell and Eley (*ibid.*, 1944, **154**, 85) have recorded the following heats of complex formation of aluminium chloride with benzene homologues: xylene, 22; mesitylene, 8; toluene, 0 kcal. Unfortunately, these authors do not refer to the presence of hydrogen chloride.



Our investigation of the effect of hydrogen bromide on the rate of isomerisation of *p*-xylene required homogeneous reaction mixtures and therefore entailed a preliminary study of ternary systems of *p*-xylene, aluminium bromide, and hydrogen bromide. Curve I (see figure) shows the composition of the dark oil deposited when various amounts of hydrogen bromide were dissolved in a solution of aluminium bromide in *p*-xylene (5 mols., based on the formula $AlBr_3$ for aluminium bromide) at 17·0°. The system was saturated with hydrogen bromide when the ratio $HBr : AlBr_3 = 1 : 1$ was reached and the complex now contained *ca.* 2·7 mols. of *p*-xylene; this was only little more than the amount of *p*-xylene (2·5 mols.) present in the complex when much less hydrogen bromide (*e.g.*, 0·30 mol.) was present. Curve II was obtained with *p*-xylene (2·56 mols.); the system was completely homogeneous when the amount of hydrogen bromide exceeded

0·25 mol. and, once again, could absorb up to 1·00 mol. of hydrogen bromide. Systems represented by the broken part of the curve contain undissolved aluminium bromide.

Isomerisation of p-*xylene*. This hydrocarbon remained unchanged after contact with excess of aluminium bromide at room temperature for a day. After a day at room temperature, two homogeneous reaction mixtures containing aluminium bromide, *p*-xylene (2·56 mols.), and hydrogen bromide (0·33 and 0·52 mol., respectively) provided hydrocarbon which was analysed by infra-red and ultra-violet spectroscopy; the data are assembled in Table 2, which also presents the results of four experiments in which a greater variation in concentration of hydrogen bromide was made and in which the reaction mixtures were placed in a thermostat at 25·0°. *All these data show that the rate of isomerisation of* p-*xylene increases with the concentration of hydrogen bromide.* The absence of any considerable disproportionation shows that isomerisation is not due to demethylation and subsequent remethylation and supports the mechanism proposed by one of us (*loc. cit.*) :



Ternary complexes of aromatic hydrocarbon, aluminium bromide, and hydrogen bromide in which the ratio HBr : AlBr$_3$ = 1 : 1 obtains are novel, only complexes in which the ratio HBr : Al$_2$Br$_6$ = 1 : 1 obtains having been described previously, and we have now measured the solubility of hydrogen bromide in mixtures of aluminium bromide with benzene, toluene, and *m*- and *p*-xylene, severally. The data are assembled in Table 3 and are in agreement with a decrease in basicity of these hydrocarbons in the order xylene > toluene > benzene, basicity being defined in the Lewis sense as ability to donate a pair of electrons.

TABLE 2. *Extent of isomerisation in ternary complexes of* p-*xylene, aluminium bromide, and hydrogen bromide after* 24 *hours.*

At room temperature.

p-Xylene (mols.)	AlBr$_3$ (mol.)	HBr (mol.)	Products, %			
			PhMe	*o*-Xylene	*m*-Xylene	*p*-Xylene
2·56	1·00	0·33	<1·0	0·8	38	61
2·56	1·00	0·52	<1·0	1·6	53	45
At 25·0°.						
2·50	1·00	0·43	1·5	1·5	45	46
2·50	1·00	0·64	<1·0	2·5	58	37
2·50	1·00	1·00	<1·0	3·0	66	28
2·50	1·00	1·00	1·0	2·0	67	27

TABLE 3. *Solubility of hydrogen bromide in mixtures of aluminium bromide and aromatic hydrocarbon at* 17·0°.

Expt.	Hydrocarbon	(mole)	AlBr$_3$ (mole)	HBr (mole)	HBr/AlBr$_3$
1	*p*-Xylene	0·071	0·028	0·029	1·0
2	,,	0·080	0·032	0·031	1·0
3	,,	0·096	0·038	0·038	1·0
4	*m*-Xylene	0·086	0·048	0·047	1·0
5	,,	0·150	0·034	0·033	1·0
6	Toluene	0·084	0·027	0·021	0·8
7	Benzene	0·140	0·039	0·022	0·6

A crystalline complex was obtained from *m*-xylene. In Expt. 4 the initial dark oil soon changed into a mass of small, pale brown, tetrahedral crystals. A larger proportion of *m*-xylene was used in Expt. 5 and large (*ca.* 1 cm.) tetrahedral crystals (m. p. 52—54°) were slowly deposited, having a composition compatible with the formula (*m*-Xylene)$_3$(AlBr$_3$,HBr)$_2$. The loss of colour accompanying crystallisation is very remarkable: it is obviously related to Norris and Ingraham's observation (*loc. cit.*) that the complex (1 : 3 : 5-Et$_3$C$_6$H$_3$)$_2$,Al$_2$Br$_6$,HBr is a red oil which changes into yellow crystals, and should be borne in mind when attempting to explain the colour of liquid complexes of aromatic hydrocarbons with aluminium and hydrogen halide and of solutions of toluene and higher benzene homologues in anhydrous hydrogen fluoride (Klatt, *Z. anorg. Chem.*, 1937, **234**, 189; see Dewar, " Electronic Theory of Organic Chemistry," Oxford, 1949, p. 169).

The homogeneous mixtures obtained in Expts. 1, 2, and 3 had separated into three phases after 4 days at 17° : a top layer of hydrocarbon, a middle layer of dark oil, and a bottom layer of large and almost colourless tetrahedral crystals (m. p. 52—54°) which did not depress the melting point of those obtained from *m*-xylene. The three phases were separated and analysed; the results are assembled in Table 4, and are compatible with the formulæ (*m*-Xylene)$_3$(AlBr$_3$,HBr)$_2$ and (Xylene)$_3$(AlBr$_3$,HBr) for the crystalline complex and the liquid complex, respectively.

TABLE 4.

	Crystalline complex : Expt. 1	Crystalline complex : Expt. 2	$(C_8H_{10})_3(AlBr_3,HBr)_2$ requires	Liquid complex : Expt. 1	Liquid complex : Expt. 2	$(C_8H_{10})_3AlBr_3,HBr$ requires
Hydrocarbon, %	30·0	30·9	31·4	47·0	47·2	47·7
Br, %	63·9	63·6	63·1	47·3	47·8	48·0
Al, %	5·6	5·4	5·3	4·1	4·1	4·05

Composition of the hydrocarbons obtained from the three phases.

	Crystalline complex	Liquid complex	Supernatant hydrocarbon
o-Xylene, %	0·5	5·3	3·6
m-Xylene, %	96·0 *	66·5	39·0
p-Xylene, %	3·5	26·0	58·0
Toluene, %........................	<1·0	2·5	<0·5
Total	100·0	100·3	100·6

* The impurities in the *m*-xylene are probably due to slight contamination of the crystalline complex by the liquid complex.

All the ternary complexes listed in Table 3 were stable only in an atmosphere of hydrogen bromide and lost part of this component when subjected to a stream of dry nitrogen; *e.g.*, the crystalline complex (*m*-Xylene)$_3$(AlBr$_3$,HBr)$_2$ and the liquid complex (*p*-Xylene)$_{2.5}$(AlBr$_3$,HBr) readily lost half their hydrogen bromide and provided homogeneous dark oils of composition (ArH)$_x$Al$_2$Br$_6$,HBr; these correspond to those obtained previously by other investigators. The complex from benzene readily lost most of its hydrogen bromide (75%) and separated into benzene and a solid phase (see Van Dyke, *loc. cit.*).

Ethylbenzene, propylbenzene, naphthalene, and tetralin suffered only little change in the presence of aluminium bromide at room temperature; in each instance reaction occurred when hydrogen bromide was also present. Ethylbenzene and propylbenzene suffered disproportionation into benzene and higher homologues, and ββ-dinaphthyl and *s*-octahydroanthracene were identified among the products obtained from naphthalene and tetralin, respectively.

EXPERIMENTAL

Freshly redistilled aluminium bromide (4·70 g.) was dissolved in *p*-xylene (10·60 g.; m. p. 11·3°) in a graduated cylinder fitted with a ground-joint stopper carrying inlet and outlet tubes fitted with taps. The inlet tube reached to the *bottom* of the cylinder. Hydrogen bromide was gradually bubbled into the mixture from a drying tower packed with phosphoric oxide. The mixture was shaken in a thermostat at 17·0° and the weight of hydrogen bromide absorbed and the volume of ternary complex and of supernatant hydrocarbon were determined after selected intervals of time. The results were as follows :

HBr (g.)	HBr/AlBr$_3$	Ternary complex (c.c.)	Supernatant hydrocarbon (c.c.)	$C_6H_4Me_2$ in complex/AlBr$_3$
0·079	0·055	4·6	9·7	1·2
0·137	0·096	5·6	8·7	1·7
0·299	0·209	7·0	7·3	2·3
0·467	0·327	7·5	6·8	2·5
0·627	0·439	7·6	6·7	2·6
0·910	0·636	7·7	6·7	2·6
1·200	0·839	7·8	6·7	2·6
1·430	1·00	7·8	6·7	2·6

The above experiment was repeated with aluminium bromide (8·40 g.) and *p*-xylene (8·60 g.). The bromide was not wholly in solution until the supernatant hydrocarbon had disappeared :

HBr (g.)	HBr/AlBr$_3$	Ternary complex (c.c.)	Supernatant hydrocarbon (c.c.)	C$_6$H$_4$Me$_2$ in complex/AlBr$_3$
0·128	0·051	6·6	6·6	0·9
0·239	0·094	8·6	4·6	1·4
0·305	0·118	9·9	3·3	1·7
0·468	0·184	12·5	0·7	2·4
0·687	0·271	13·2	0·0	2·58
2·550	1·00	13·4	0·0	2·58

After 4 days at 18°, large tetrahedral crystals and supernatant hydrocarbon (1·5 c.c.) had separated. These are described more fully below.

After 4 days at 18°, a homogeneous mixture of *p*-xylene (10·2 g.), aluminium bromide (10·2 g.), and hydrogen bromide (3·2 g.) had separated into three phases : supernatant hydrocarbon, dark brown oil, and large, pale brown, tetrahedral crystals. The reaction vessel was fitted with a separating funnel into which, after 7 days, the liquid phases were decanted by inverting the apparatus. The crystals (m. p. 52—54°) did not depress the m. p. of the ternary crystalline complex obtained from *m*-xylene, aluminium bromide, and hydrogen bromide. The three phases were separated and weighed amounts of the solid and of the liquid complex were decomposed with ice and water without loss of hydrogen bromide. In each instance, the hydrocarbon was isolated and its composition determined by infra-red and ultra-violet spectroscopy. The bromide and the aluminium content were determined respectively by titration with 0·2N-alkali and by precipitation with 8-hydroxyquinoline. The results are presented in Table 4.

Effect of Hydrogen Bromide on the Rate of Isomerisation of p-*Xylene.*—The hydrocarbon (9·5 g. ; m. p. 11·3°) was added to aluminium bromide (11·6 g.) in a flask fitted with a ground-glass stopper. A part of the bromide dissolved and the mixture provided *p*-xylene (8·7 g. ; m. p. 9·5°) after a day at 17°. The same result was obtained when potassium bromide was also present.

p-Xylene (17·4 g.) was added to aluminium bromide (17·1 g.), and hydrogen bromide (1·70 g.) was added until the mixture was homogeneous. Half this mixture was transferred to a second vessel and hydrogen bromide (0·50 g.) was added. Both mixtures were decomposed with water after 24 hours at 17°. Four mixtures were decomposed after 24 hours at 25·0°; they had contained the following weights of *p*-xylene, aluminium bromide, and hydrogen bromide, respectively : (*a*) 7·95, 8·01, and 1·05 g. ; (*b*) 10·17, 10·15, and 2·02 g. ; (*c*) 6·20, 6·13, and 1·86 g. ; (*d*) 5·30, 5·08, and 1·54 g. The composition of the recovered hydrocarbons was determined (see Table 2).

Solubility of Hydrogen Bromide in Mixtures of Aluminium Bromide and Aromatic Hydrocarbon.—*Benzene.* Benzene (10·9 g.), which had been shaken several times with concentrated sulphuric acid and finally distilled from sodium, was added to freshly distilled aluminium bromide (10·5 g.) at 17·0°. Much of the bromide did not dissolve until hydrogen bromide was added; the mixture absorbed 1·85 g. and provided a dark brown oil. A stream of dry (P_2O_5) nitrogen (50 c.c./min.) was passed in turn through a bubbler containing benzene, the mixture, a closely packed plug of glass wool, and finally an absorption vessel containing water which was neutralised periodically with 0·1N-alkali. In 24 hours, alkali (170 c.c.; equivalent to 1·38 g. of hydrogen bromide) was required. The initially homogeneous mixture had partly decomposed into a surface layer of benzene and a crystalline bottom layer (cf. Van Dyke, *loc. cit.*).

Toluene. This hydrocarbon (7·7 g.) and aluminium bromide (7·3 g.) absorbed hydrogen bromide (1·75 g.) and provided a homogeneous brown oil from which, after 24 hours at 17·0°, the toluene was recovered quantitatively.

p-*Xylene.* *p*-Xylene (7·5 g. ; m. p. 11·3°) and aluminium bromide (7·5 g.) provided a mixture which absorbed hydrogen bromide (2·3 g.). A stream of dry nitrogen (50 c.c./min.), in 24 hours, removed hydrogen bromide (1·05 g.) which neutralised 130 c.c. of 0·1N-alkali. The mixture was decomposed with dilute hydrochloric acid and provided hydrocarbon (6·6 g. ; m. p. −6°) which apparently contained 85% of *p*-xylene.

m-*Xylene.* This isomer (9·1 g.) was added to aluminium bromide (12·9 g.) ; most of the bromide dissolved and the rest soon dissolved on addition of dry hydrogen bromide. The mixture absorbed hydrogen bromide (3·85 g.) and pale brown crystals were deposited until only a trace of dark brown oil remained. A stream of dry nitrogen (50 c.c./min.) swept out hydrogen bromide (2·00 g.) in 2 days and a dark oil remained. The experiment was repeated with *m*-xylene (16·2 g.) and aluminium bromide (9·0 g.); the mixture absorbed hydrogen bromide (2·7 g.) and formed a dark brown oil with a supernatant layer of colourless hydrocarbon. This layer increased in volume during 12 hours at 17·0° and large, pale brown, tetrahedral crystals (m. p. 52—54°) were deposited from the dark brown oil.

Effect of Hydrogen Bromide on the Interaction of Other Hydrocarbons with Aluminium Bromide.—*Ethylbenzene.* This hydrocarbon (8·5 g.) was added to aluminium bromide (11·4 g.), and the mixture kept at 17° for 2 days. Ethylbenzene (b. p. 134—134·5°; 6·8 g.) was recovered. Ethylbenzene (10·9 g.), aluminium bromide (10·1 g.), and hydrogen bromide (0·9 g.) provided a homogeneous dark oil which was not saturated with hydrogen bromide and, after 2 days at 17°, provided the following fractions: (i) benzene (b. p. 80—85°; 0·5 g.), (ii) ethylbenzene (b. p. 134—136°; 1·0 g.), (iii) *m*- and *p*-diethylbenzene (b. p. 170—180°; 6·5 g.), (iv) higher homologues (b. p. 205—210°; 1·8 g.); (v) residue (0·5 g.) (see Heise and Töhl, *Annalen*, 1872, **270**, 158).

Propylbenzene. (i) This (b. p. 160°; 6·0 g.) was recovered from a mixture of propylbenzene (7·1 g.) and aluminium bromide (9·4 g.) which had been kept at 17° for 24 hours. (ii) Propylbenzene (9·6 g.), aluminium bromide (9·9 g.), and hydrogen bromide (0·8 g.) formed a homogeneous dark red oil which provided fractions containing benzene (0·8 g.), propylbenzene (0·7 g.), dipropylbenzene (4·8 g.), and higher-boiling products (2·2 g.) (see Heise and Töhl, *loc. cit.*).

Tetralin. This hydrocarbon (15·8 g.) was recovered from a mixture of tetralin (18·3 g.) and aluminium bromide (7·6 g.) which had been kept at 17° for 12 hours. Tetralin (10·8 g.), aluminium bromide (11·1 g.), and hydrogen bromide (2·1 g.) formed a homogeneous deep red oil which, after 12 hours at 17°, provided the following hydrocarbon fractions upon distillation under 15 mm.: (i) tetralin (b. p. 85—88°; 1·8 g.); (ii) mainly octahydroanthracene (m. p. and mixed m. p. 72—73°; b. p. 160—170°; 2·9 g.), (iii) 190—200° (2·8 g.); (iv) residue (2·4 g.) (see Schroeter, *Ber.*, 1924, **57**, 1990).

Naphthalene. Naphthalene (4·8 g.) and aluminium bromide (6·8 g.) in chlorobenzene (30 c.c.) provided a blood-red solution from which naphthalene (4·2 g.) was recovered after 12 hours at 17°. Naphthalene (4·5 g.), aluminium bromide (7·3 g.), and hydrogen bromide (0·5 g.) in chlorobenzene (30 c.c.) provided a very dark solution from which no naphthalene and a little ββ-dinaphthyl were obtained after 12 hours at 17°.

We thank Imperial Chemical Industries Limited, Dyestuffs Division, for infra-red and ultra-violet spectroscopic analyses.

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