

970. *The System Benzene-Hydrogen Bromide-Aluminium Bromide. Part II.\**

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A complex,  $(C_6H_6)_n, Al_2Br_6$ , has been detected in solution by its characteristic absorption band at 2785 Å. A similar complex has been detected for  $Al_2I_6$ , and possibly exists for  $Al_2Cl_6$  where the concentration at saturation was too low for detection. It is probable that  $n = 1$ , and that the complex  $C_6H_6, Al_2X_6$  is analogous to Benesi and Hildebrand's  $C_6H_6, I_2$  complex discussed recently by Mulliken. The 2785 Å line, therefore, probably arises as a charge-transfer spectrum, *i.e.*, for the transition  $C_6H_6, Al_2X_6 \longrightarrow C_6H_6^+, Al_2X_6^-$ . On introduction of hydrogen halide a new band appears at 3300 Å which with increasing concentration spreads up to 5500 Å and is responsible for the characteristic colour of the complex. In the presence of excess of hydrogen halide the 2785 Å band disappears, as may be seen from experiments with very low concentrations of aluminium bromide. A band at 3400 Å is also observed with  $C_6H_6, Fe_2Cl_6$ . We assume we have to deal with a singlet-triplet transition in the benzene molecule, perturbed in the first case by the electrical forces in the ternary system, and in the second by the magnetic moment of the ferric chloride.

WHEREAS an absolutely pure solution of aluminium bromide in benzene is colourless, addition of hydrogen bromide causes the solution to become orange, and eventually to split into two liquid phases, the lower of which is orange-red. Evidence presented previously (Eley and King, Part I\*) gave a composition of the lower phase approximating to  $Al_2Br_6, HBr, 6C_6H_6$ , and showed it to be highly ionic. The nature of these ions is still in doubt. It seemed possible that a study of the absorption spectra might help and this view was supported by a personal communication from Professor J. H. Hildebrand. He pointed out that the conclusion that there was some solvation of  $Al_2Br_6$  molecules by benzene which comes from solubility measurements (Eley and King, *Trans. Faraday Soc.*, 1951, **47**, 1287) might be further investigated by ultra-violet absorption studies along the line pursued for iodine-benzene by Benesi and Hildebrand (*J. Amer. Chem. Soc.*, 1949, **71**, 2703). These authors found an intense absorption peak at 2970 Å, which may be ascribed to an  $I_2, C_6H_6$  complex. Mulliken (*J. Amer. Chem. Soc.*, 1950, **72**, 600; 1952, **74**, 811) suggests that the 2970 Å band is due to an increase in the transition probability of the forbidden 2600 Å transition of benzene owing to interaction of excited states of the two components or that it is a charge-transfer spectrum due to  $C_6H_6, I_2 \longrightarrow C_6H_6^+, I_2^-$ .

EXPERIMENTAL

All solutions were made up in a high vacuum, by a technique similar to that used previously (Eley and King, *J.*, 1952, 2517). The concentration of aluminium bromide in benzene was

\* Part I, *J.*, 1952, 2517.

determined by weighing. Where hydrogen bromide was subsequently admitted to the system, its pressure was measured, and its concentration in the solution calculated by using the Henry's law constant for pure benzene (Kapustinskii and Mal'tsev, *Chem. Abs.*, 1941, **35**, 957; Saylor, *J. Amer. Chem. Soc.*, 1940, **62**, 3228). This constant is not an exact quantity.

The solutions, or pure solvent, were filled into 1-cm. quartz absorption cells by a "dry box" technique and transferred to the Unicam S.P. 500 spectrophotometer as quickly as possible. The housing of the cells was kept dry by phosphoric oxide. The light transmitted by the solution was plotted as a fraction of the light transmitted by the pure solvent over the range 2740—10,000 Å. With care the "dry-box" technique was satisfactory.

The materials used in this research were purified as before (Eley and King, *loc. cit.*).

A few experiments were also made with cyclohexane and ferric chloride.

*Aluminium Halide-Benzene.*—The molar extinction coefficient  $\epsilon$  calculated on the molecule  $Al_2X_6$  is plotted as a function of wave-length,  $\lambda$ , in Fig. 1 for aluminium bromide and aluminium

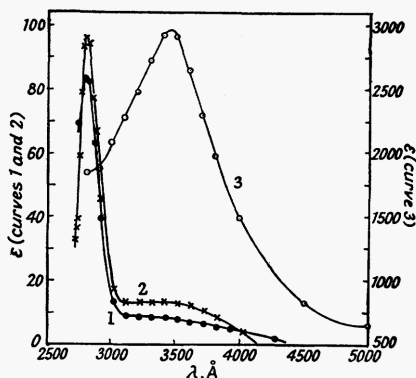


FIG. 1. Absorption spectra. 1, Aluminium iodide in benzene. 2, Aluminium bromide in benzene (the path length is in cm. and the concn. in moles of  $Al_2X_6$  per l.). 3, Ferric chloride in benzene (the concn. is in moles of  $FeCl_3$  per l. Ferric chloride in cyclohexane shows no absorption over this range of wave-lengths).

iodide. The strong band at 2785 Å obeys Beer's law while the weak band at 3300 Å does not, as shown by the results in Table 1.

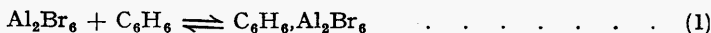
It is considered that the band at 3300 Å arises from the products of hydrolysis of the aluminium halide by traces of moisture. A saturated solution of aluminium chloride gave

TABLE 1.

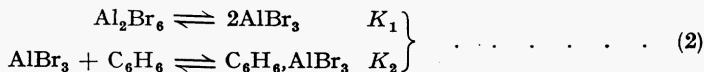
<i>Aluminium bromide in benzene.</i>			<i>Aluminium iodide in benzene.</i>		
Concn., $10^{-4}$ moles/l.	$\epsilon(\lambda 2785)$	$\epsilon(\lambda 3300)$	Concn., $10^{-4}$ moles/l.	$\epsilon(\lambda 2785)$	$\epsilon(\lambda 3300)$
48.4	96.3	13.7	28.1	83.8	23.3
123.5	99.5	18.6	113.9	85.2	8.6
153	97.5	—	320.2	84.3	4.05
231	99.0	—			
462	—	2.58			

no measurable absorption in the 1-cm. cell at 2740—10,000 Å, compared with pure benzene. We consider that this is not due to a difference in behaviour, but rather to the low solubility of aluminium chloride, which may well be measurable with a longer path.

We consider two possible equilibria



and



Since Beer's law is obeyed at 2785 Å with respect to the concentration of aluminium halide in benzene, then, if the absorption at 2785 Å is attributed to the complex, as seems likely, the concentration of complex is directly proportional to the concentration of aluminium bromide. This proves mechanism (1), except that the number of benzene molecules entering the equilibrium is not necessarily one. For mechanism (2) at high dilution the concentration of complex would vary as the square root of the halide concentration.

*Aluminium Bromide-cycloHexane.*—A freshly prepared solution of aluminium bromide in cyclohexane (dry-box technique) was always slightly cloudy, but the cloud vanished if the

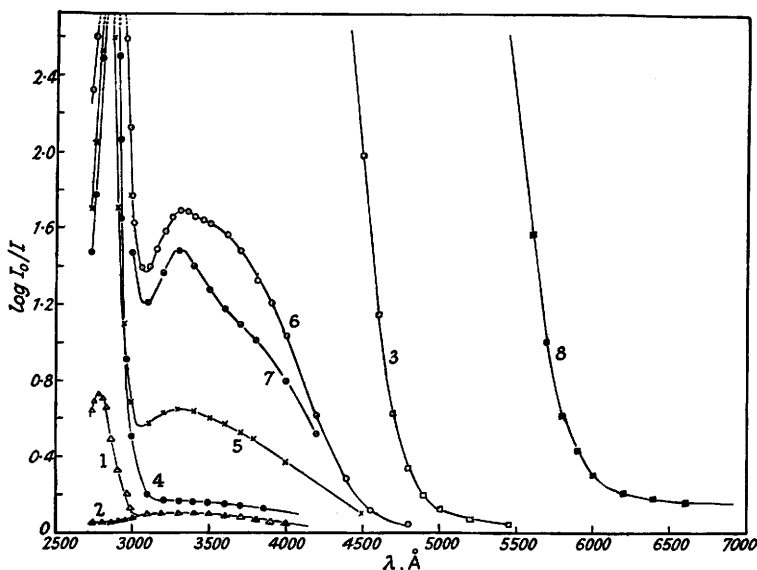
solution contained in the absorption cell was kept overnight in a desiccator, and the solution could be examined in the spectrophotometer. The result was no measurable absorption at 2740–10,000 Å. A series of bands below 2740 Å are thought to be associated with the aluminium bromide molecule.

*Hydrogen Bromide-Benzene.*—A solution of 0.250 mole of hydrogen bromide per l., corresponding to a pressure of 200 mm., gave no measurable absorption at 2740–10,000 Å.

*Aluminium Bromide-Hydrogen Bromide-Benzene.*—The results for this system are listed in Table 2. The concentration of hydrogen bromide was calculated from the Henry's law coefficient for pure benzene, and is therefore only approximate.

The full absorption curves are given in Fig. 2. Expts. 1 and 2 were made with *dilute* solutions of aluminium bromide and show that the addition of hydrogen bromide suppresses the characteristic band at 2785 Å. Subsequent experiments were on more concentrated solutions, where it was found impossible to suppress the 2785 Å band. These results show in a general way, however, that the 3300 Å band is definitely associated with the ternary system  $\text{Al}_2\text{Br}_6, \text{HBr}, \text{C}_6\text{H}_6$ , and not with any of the components taken singly or in pairs.

FIG. 2. Absorption spectra of the system aluminium bromide-hydrogen bromide-benzene. The numbers refer to expts. in Table 2.



All the solutions described in the Table were clear, and varied from nearly colourless (expt. 1) to dark yellow (expt. 3). No separation of a second liquid layer occurred. In a further experiment conditions were adjusted to allow separation of a lower orange-red layer

TABLE 2.

Expt.	$C_{\text{H}}$ , $10^{-4}$ mole/l.	$p_{\text{HBr}}$ , mm.	$C_{\text{HBr}}$ , $10^{-4}$ mole/l.	$\log I_0/I$ ; $\lambda = 2785 \text{ \AA}$	$\log I_0/I$ ; $\lambda = 3300 \text{ \AA}$
1	60.4	5	63	0.7212	0.1013
2	60.4	200	2500	~0	0.1020
3	3550	300	3750	*	*
4	651	5	63	*	0.1662
5	434	100	1250	*	0.6383
6	1340	43	540	*	1.6968
7	1340	13	163	*	1.4660

\* Too strong for measurement.

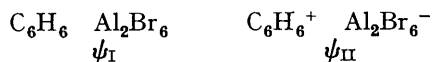
and the spectrum was taken (Fig. 2, curve 8). Absorption was strong at all wave-lengths below 5500 Å. This absorption may be compared with the curve observed with the yellow solution, expt. 3, where absorption is strong below 4500 Å.

*Ferric Chloride.*—The spectrum of a solution of ferric chloride in benzene is shown in Fig. 1. Ferric chloride in *cyclohexane* shows no absorption over this range.

The benzene solution is yellow and the colour is immediately destroyed on shaking with water. The concentration of ferric chloride in benzene was 0.05 g./l. A comparable amount of ferric chloride dissolved in cyclohexane, according to a silver nitrate turbidity test.

## DISCUSSION

*Aluminium Bromide-Benzene.*—It seems probable that the 2785 Å band arises from a molecular complex,  $\text{Al}_2\text{Br}_6 + n\text{C}_6\text{H}_6 \rightleftharpoons n\text{C}_6\text{H}_6 \cdot \text{Al}_2\text{Br}_6$ , where  $n$  is probably 1, as in the case of iodine. Experiments on the equilibrium in an inert solvent would allow this point to be settled, but with our present technique we have failed to secure accurate results with cyclohexane owing to the cloudiness already mentioned. If we adopt the Mulliken description, we have to consider two canonical structures



If  $a$  is the coefficient of I and  $b$  that of II, we have for the ground state

$$\psi_{\text{N}} = a\psi_{\text{I}} + b\psi_{\text{II}}$$

and for the excited state

$$\psi_{\text{E}} = a\psi_{\text{II}} - b\psi_{\text{I}}$$

and since for a loosely bound complex  $a \gg b$ , the ground state is largely  $\psi_{\text{I}}$  and the excited state  $\psi_{\text{II}}$ , the 2800 Å band corresponding to the charge transfer  $\psi_{\text{N}} \rightarrow \psi_{\text{E}}$ , *i.e.*, largely  $\psi_{\text{I}} \rightarrow \psi_{\text{II}}$ . The stability of the complex is largely due to the (small) resonance energy between I and II. There is also the possibility of some bonding by donation of an electron pair from the  $d$ -shell of the bromine atoms to the antibonding  $\pi$ -orbitals of the benzene molecules, along the lines indicated by Dewar for  $\text{Ag}^+$  (*Bull. Soc. chim.*, 1951, 79c).

The predominance of  $\psi_{\text{I}}$  would agree with the small dipole moment, 2–3 D, of aluminium bromide in relatively concentrated benzene solution (0.01M) (Nespal, *Z. physikal. Chem.*, 1932, 16, B, 153). Eley has pointed out that the small dipole moments of molecular complexes (compared with the expected value for complete electron transfer) may be explained in terms of the participation of non-bonded states in a resonance structure (Conference on Cationic Polymerisation, Stoke on Trent, March, 1952, to be published).

The complex  $\text{C}_6\text{H}_6 \cdot \text{Al}_2\text{Br}_6$  is to be distinguished from the complex  $\text{C}_6\text{H}_6 \cdot \text{AlBr}_3$ , which is a lattice complex (Eley and King, *Trans. Faraday Soc.*, 1951, 47, 1287). This is most noticeable in the case of aluminium iodide, where  $\text{C}_6\text{H}_6 \cdot \text{Al}_2\text{I}_6$  exists in solution, but there is no lattice complex  $\text{C}_6\text{H}_6 \cdot \text{AlI}_3$ , probably because of stereochemical factors.

*Aluminium Bromide-Hydrogen Bromide-Benzene.*—The 3300 Å band which appears in this system spreads as the concentration increases, and is responsible for the colour of the system. The spreading is probably mainly a solvent effect—the solution fades somewhat when cooled in liquid air. This band may be distinguished very clearly from the 2785 Å band associated with  $\text{C}_6\text{H}_6 \cdot \text{Al}_2\text{Br}_6$ , which disappears eventually as more of the ternary system is formed.

We consider that this band is probably associated with the transition from the ground singlet to the lower triplet state of benzene. The presence of a very weak band in pure benzene has been noted at 3400 Å for absorption (Sklar, *J. Chem. Physics*, 1937, 5, 669) and emission (Shull, *ibid.*, 1949, 17, 295). The exact assignment of the triplet state is still under discussion (*cf.*, *e.g.*, Shull, *loc. cit.*; McCline, *ibid.*, p. 665; Mizushima and Koide, *ibid.*, 1952, 20, 765), but the main point is that, because of the change in multiplicity, the transition probability is normally very small. In the ternary system benzene-aluminium bromide-hydrogen bromide conductivity measurements have shown a very strong dissociation into ions, possibly  $\text{H}^+$  and  $\text{Al}_2\text{Br}_7^-$ , but not yet identified with certainty. It would seem probable that the strong electrical forces arising from the ions will act so as to "catalyse" this transition. It seemed to us that the perturbing effect of the ions is similar to that suggested earlier for the radiationless transition involved in the quenching of fluorescence of organic molecules by ions (Eley, *Trans. Faraday Soc.*, 1939, 35, 37). The suggestion that the 3300 Å band arose from an electrical perturbation would be confirmed if the band were obtained by a magnetic perturbation. This may be supposed to be the

situation with ferric chloride, which in benzene in the absence of hydrogen halide may be expected to be largely homopolar  $\text{Fe}_2\text{Cl}_6$  molecules. The paramagnetism of these molecules in the gaseous state was established by Lallemand (*Ann. Physique*, 1935, **3**, 97) and we expect a similar behaviour in solution. The band observed is not to be ascribed to the  $\text{Fe}_2\text{Cl}_6$  molecule itself, since it is not observed in *cyclohexane* solution. It is reasonable therefore to ascribe the band to a magnetic "catalysis" of the singlet-triplet transition.

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