Solid Complexes of Aluminum Bromide with Aromatic Hydrocarbons[1-3]

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Abstract: Vapor pressure–composition phase studies have been made on a number of aluminum bromide–aromatic hydrocarbon systems at 0° and lower temperatures. In the case of the more volatile aromatics, the pressures above the system were measured by the usual manometric methods. For less volatile aromatics and for measurements at low temperatures, the pressures were measured by a convenient spectrometric technique developed for the purpose. The results indicate the existence of the following solid complexes: $ArH \cdot Al_2Br_6$ (1:2 complex) with benzene, toluene, *p*-, *o*-, and *m*-xylenes, and mesitylene, and $ArH \cdot AlBr_3$ (1:1 complex) with *m*-xylene and mesitylene. These complexes (I and II, in text) are presumed to be π complexes. The heats of dissociation, the standard free energies of dissociation, and the standard entropies of dissociation of the complexes have also been determined. From these results, the following order is established for the increasing stability of the corresponding aluminum bromide complexes: benzene < toluene < *m*-xylene < mesitylene. This is consistent with the relative basicity of the aromatics involved. The difference in complexing ability observed among the three isomeric xylenes indicates their relative abilities to complex with aluminum bromide to be as follows: *p*- and *o*-xylenes < *m*-xylene.

A considerable amount of research has been carried out by a number of workers on the complexes formed between aluminum bromide and aromatic hydrocarbons.[6] However, several conflicting formulations of the complexes have appeared in the literature.

As a result of melting point–composition phase studies, Menshutkin[7] concluded that no complex was formed between aluminum bromide and benzene, toluene, or *p*-xylene. However, Norris and his co-workers[8] reported that liquid complexes of the type $ArH \cdot Al_2Br_6$ were formed when the ternary complexes of aluminum bromide–hydrogen bromide with toluene or other aromatics were subjected to evaporation at reduced pressure. On the other hand, a number of authors claimed the existence of solid complexes of aluminum bromide with aromatics. For example, as a result of their melting point–composition phase studies, Plotnikov and Gratsianskii[9] concluded that aluminum bromide formed solid complexes of the type $ArH \cdot AlBr_3$ with benzene, *p*-xylene, and *m*-xylene, melting incongruently. Eley and King[10] substantiated Plotnikov and Gratsianskii's conclusion on the benzene–aluminum bromide system through a similar study. Van Dyke[11] likewise reported evidence for the existence of a solid complex containing 1 mole of benzene combined with 1 mole of aluminum bromide monomer from his vapor pressure–composition phase study at 15°. However, he claimed that the complex should be formulated as $(C_6H_6)_2 \cdot Al_2Br_6$, since the molecular weight of aluminum bromide in benzene solution corresponds to the presence of the dimer.

Thus, the literature contains a number of conflicting reports as to the existence and precise formulation of aluminum bromide–aromatic complexes. In our earlier paper,[12] direct evidence was presented for the existence of solid 1:2 π complexes, $ArH \cdot Al_2Br_6$,[13] formed between aluminum bromide and benzene or toluene. Recently, Eley and co-workers[14] also presented X-ray crystallographic evidence for the existence of the solid complex, $C_6H_6 \cdot Al_2Br_6$, formed between benzene and aluminum bromide.

Unfortunately, experimental difficulties had been encountered when we had attempted to extend the usual manometric methods to vapor pressure–composition phase studies involving *m*-xylene and mesitylene, because of the relatively low vapor pressures of these aromatics.[12] Accordingly, we undertook to develop a precise spectrometric technique suitable for the accurate measurement of low vapor pressures of the entire range of aromatic hydrocarbons of interest in this study. This technique is described in the Experimental Part. With the aid of this method, we were able to extend our vapor pressure–composition studies to *m*-xylene and mesitylene, as well as to other hydrocarbons at low temperatures.

In preceding papers of this series,[15,16] we described the existence of the 1:1 π complexes, $ArH \cdot HCl$ and $ArH \cdot HBr$, formed between the hydrogen halides and aromatic hydrocarbons, and discussed their relative stabilities. The following order was established for

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(1) The Catalytic Halides. XXIX.

(2) Based on a thesis submitted by S. U. Choi in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Presented in part at the XVIIth International Congress of Pure and Applied Chemistry, Munich, Germany, 1959.

(4) Research Assistant (1953–1956) on Project No. AT(11-1)-170, supported by the Atomic Energy Commission.

(5) Department of Chemistry, Hanyang University, Seoul, Korea.

(6) For detailed literature to early work, see L. J. Andrews, *Chem. Rev.*, **54**, 713 (1954).

(7) B. N. Menshutkin, *J. Russ. Phys. Chem. Soc.*, 41, 1089 (1908); *Chem. Abstr.*, **4**, 1488 (1910).

(8) J. F. Norris and D. Rubinstein, *J. Am. Chem. Soc.*, **61**, 1163 (1939); J. F. Norris and J. N. Ingraham, *ibid.*, **62**, 1298 (1940).

(9) V. A. Plotnikov and N. N. Gratsianskii, *Mem. Inst. Chem., Acad. Sci. Ukrain. SSR*, **5**, 213 (1938); *Chem. Abstr.*, **33**, 2432 (1939)); *J. Gen. Chem. USSR*, **15**, 596 (1945); *Chem. Abstr.*, **40**, 5656 (1946); *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 101 (1947); *Chem. Abstr.*, **42**, 4480 (1948).

(10) D. D. Eley and P. J. King, *Trans. Faraday Soc.*, **47**, 1287 (1951).

(11) R. E. Van Dyke, *J. Am. Chem. Soc.*, **72**, 3619 (1950).

(12) H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6265 (1953).

(13) The present study reveals that aluminum bromide forms solid complexes of the composition $ArH \cdot AlBr_3$ and $ArH \cdot Al_2Br_6$, with *m*-xylene or mesitylene at 0°. For convenience, these two types will be referred to as the 1:1 and 1:2 complexes, respectively.

(14) D. D. Eley, J. H. Taylor, and S. C. Wallwork, *J. Chem. Soc.*, 3867 (1961).

(15) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

(16) H. C. Brown and J. J. Melchiore, *ibid.*, **87**, 5269 (1965).

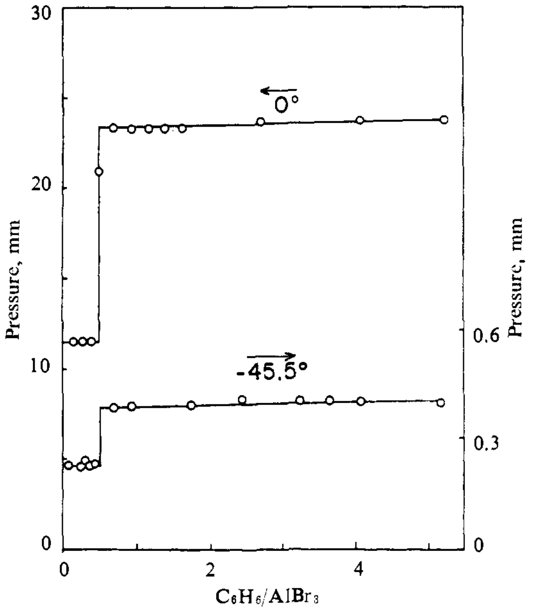

Figure 1. Vapor pressure–composition diagrams for the benzene–aluminum bromide system at 0 and −45.5°.

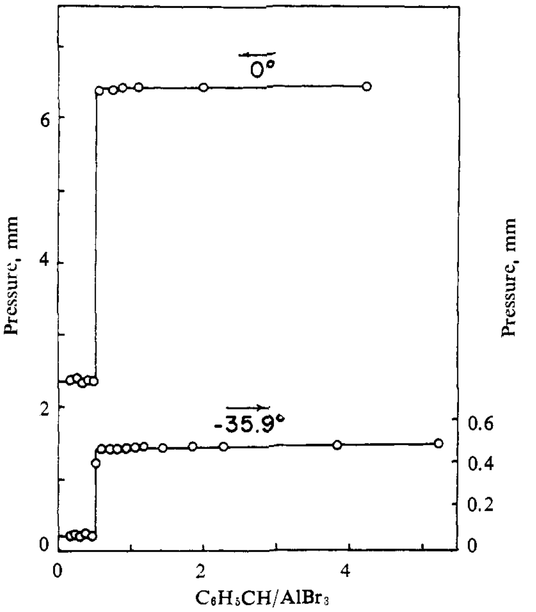

Figure 2. Vapor pressure–composition diagrams for the toluene–aluminum bromide system at 0 and −35.9°.

the increasing stability of the hydrogen halide–aromatic complexes: benzene < toluene < *m*-xylene < mesitylene. Thus, the relative stability of these hydrogen halide π complexes depends directly on the relative basicity of the aromatics involved.

It then appeared of interest to determine the thermodynamic stabilities of the complexes of aluminum bromide with a similar series of aromatic hydrocarbons, and to compare their behavior with that of the hydrogen halide–aromatic complexes. The present study involved the investigation of the nature and formulation of the complexes formed between aluminum bromide and the series of aromatic hydrocarbons: benzene, toluene, *p*-, *o*-, and *m*-xylenes, and mesitylene.

Results

Aluminum bromide dissolved readily in the aromatic hydrocarbons investigated, and the color of the resulting solutions was more intense in the more basic aromatics, *i.e.*, very faint yellow with benzene, lemon-yellow with toluene, yellow with *p*-, *o*-, and *m*-xylenes, and orange-yellow with mesitylene.

Spectrometric Technique for the Measurement of Low Vapor Pressures of Aromatic Hydrocarbons. After attempts to extend the usual manometric methods to *m*-xylene and mesitylene failed, we attempted to utilize sensitive glass sickle gauges and effusion methods to measure the low pressure of the aromatic vapor above the corresponding aluminum bromide complexes. However, we were unable to realize the desired precision. Consequently, we turned our attention to the possibility of utilizing the high ultraviolet molar absorbancy indices of aromatic hydrocarbons for this purpose.

In the procedure the aromatic vapor above the complex was permitted to come to equilibrium with a bulb of large volume. Then an intervening valve was closed and the trapped vapor was quantitatively condensed and dissolved in 95% ethyl alcohol. From the absorbancy of the resulting solution in the ultraviolet region, the amount of aromatic present could be calculated and translated into the original pressure of the aromatic above the complex.

The procedure was tested by determining the vapor pressures of pure benzene, toluene, *m*-xylene, and mesitylene at temperatures where the vapor pressure was in the range of 5.00 to 0.050 mm. The measured values gave excellent agreement, in many cases to better than 1%, with the corresponding vapor pressures calculated from vapor pressure equations in the literature (see Experimental Part).

The System Benzene–Aluminum Bromide. The benzene–aluminum bromide system was previously studied at 17.7°.[12] Examination of this system was extended to lower temperatures, 0 and −45.5°, in order to explore the possible existence of some solid complex other than the product $C_6H_6 \cdot Al_2Br_6$, previously identified. Data of the present study are shown graphically in Figure 1. The vapor pressure was sensibly constant over an extensive composition range of $C_6H_6/AlBr_3$ down to 0.5. It then dropped sharply to a new pressure plateau in the composition range of 0.5 to 0. This plateau is attributed to an equilibrium involving a solid 1:2 complex.

$$ArH \cdot Al_2Br_6(s) \rightleftharpoons Al_2Br_6(s) + ArH(g)$$

It appears, therefore, that aluminum bromide forms a solid 1:2 complex with benzene at 0 and −45.5° as well as at 17.7°, but no other solid complex exists under these conditions. The dissociation pressure of the solid 1:2 complex was 11.5 mm at 0°.

The System Toluene–Aluminum Bromide. This system was also previously studied at 17.7 and 0°.[12] The study was extended to the lower temperature for the same reasons given above. The vapor pressure–composition data (Figure 2) indicate the existence of only the 1:2 complex, $C_6H_5CH_3 \cdot Al_2Br_6$, at 0 and −35.9° as well as at 17.7°. The dissociation pressure of the solid complex observed was 2.37 mm at 0°. The pressure plateau over the composition range of $C_6H_5CH_3$ from 0.5 upwards at each temperature represents the

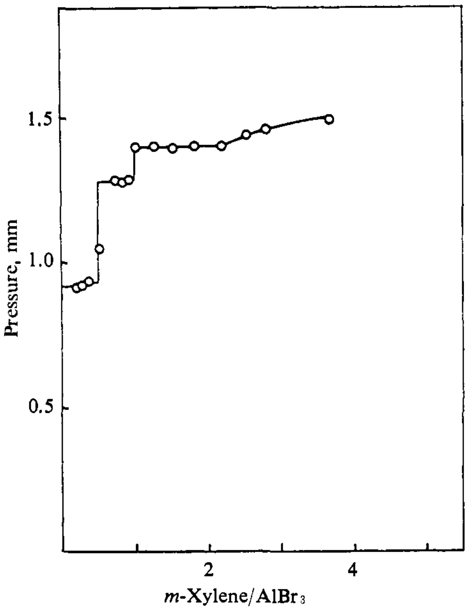

Figure 3. Vapor pressure–composition diagram for the m-xylene–aluminum bromide system at 0°.

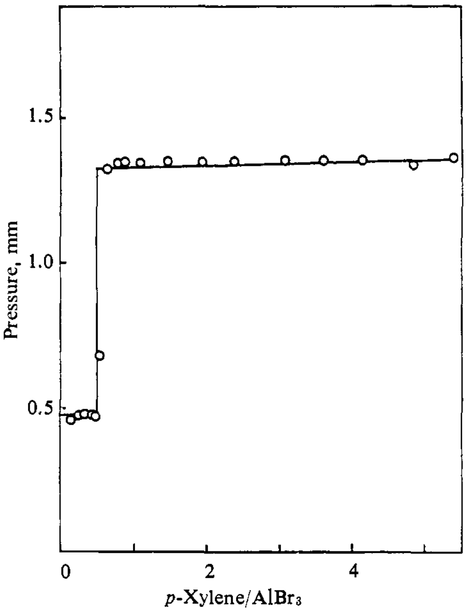

Figure 4. Vapor pressure–composition diagram for the p-xylene–aluminum bromide system at 0°.

coexistence of two phases: the solid 1:2 complex and the solution.

The System m-Xylene–Aluminum Bromide. Typical data for the vapor pressure–composition studies on this system are shown graphically in Figure 3. The two pressure plateaus in the composition ranges of m-xylene/AlBr$_3$ from 1.0 to 0.5 and from 0.5 to 0 are attributed to the following two equilibria involving the solid 1:1 complex, m-xylene·AlBr$_3$, and the solid 1:2 complex, m-xylene·Al$_2$Br$_6$, respectively.

$$2\text{ArH}\cdot\text{AlBr}_3(s) \rightleftharpoons \text{ArH}\cdot\text{Al}_2\text{Br}_6(s) + \text{ArH}(g)$$

$$\text{ArH}\cdot\text{Al}_2\text{Br}_6(s) \rightleftharpoons \text{Al}_2\text{Br}_6(s) + \text{ArH}(g)$$

The dissociation pressures of the 1:1 and 1:2 solid complexes at 0° were 1.29 and 0.93 mm, respectively. The pressure plateau in the composition range of m-xylene/AlBr$_3$ from 2.2 to 1.0 corresponds to the coexistence of two phases: the solid 1:1 complex and the solution.

The 1:1 complex observed can be formulated as (m-xylene)$_2$·Al$_2$Br$_6$, because this gives also the mole ratio, m-xylene/AlBr$_3$, of unity. However, we[17] have found the molecular weight of aluminum bromide in m-xylene at 0° to correspond to the monomeric aluminum bromide complexed with the aromatic. Therefore, it seems reasonable to formulate the complex with the mole ratio, m-xylene/AlBr$_3$, of unity, as m-xylene·AlBr$_3$.

Thus, we have observed that m-xylene forms both 1:1 and 1:2 complexes with aluminum bromide, whereas benzene and toluene form only the 1:2 complexes. This difference is attributed to the relative basicity of these aromatics.

The Systems p- and o-Xylenes–Aluminum Bromide. In view of the existence of both 1:1 and 1:2 solid complexes in the case of m-xylene, we undertook to examine the behavior of p- and o-xylenes. Data of the phase studies on the p-xylene–aluminum bromide and o-xylene–aluminum bromide systems at 0° are shown graphically in Figures 4 and 5, respectively. In both cases the data indicate the existence of 1:2 complexes only. The dissociation pressures of these solid complexes at 0° were 0.478 and 0.414 mm, respectively.

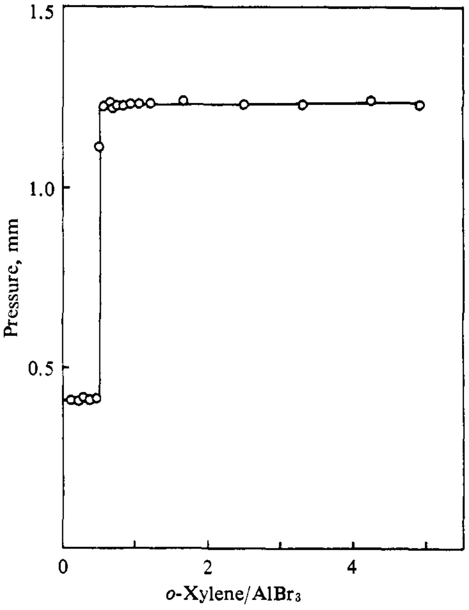

Figure 5. Vapor-pressure–composition diagram for the o-xylene–aluminum bromide system at 0°.

Thus, a significant difference exists between p- or o-xylene and m-xylene in their complexing ability with aluminum bromide, the *meta* isomer forming both 1:1 and 1:2 complexes at 0°, whereas the *ortho* and *para* derivatives yield only the 1:2 complexes at this temperature.

The System Mesitylene–Aluminum Bromide. Here again the vapor pressure–composition data indicate the existence of both 1:1 and 1:2 solid complexes, mesitylene·AlBr$_3$ and mesitylene·Al$_2$Br$_6$ (Figure 6). The dissociation pressures of these complexes at 0°

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(17) S. U. Choi, W. C. Frith, and H. C. Brown, manuscript in preparation.

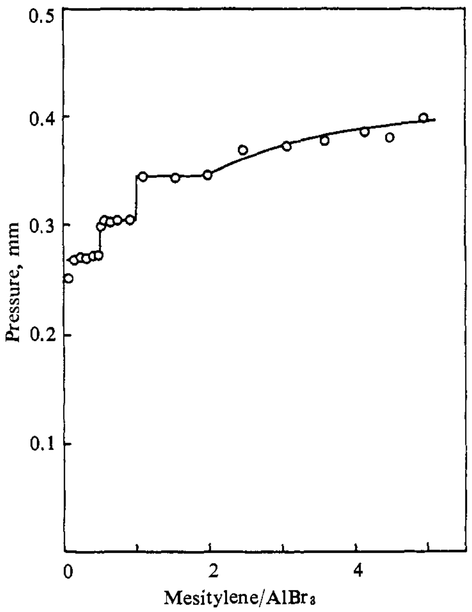


Figure 6. Vapor pressure–composition diagram for the mesitylene–aluminum bromide system at 0°.

were 0.304 and 0.271 mm, respectively. The pressure plateau in the composition range of mesitylene/$AlBr_3$ from 2.0 to 1.0 represents the coexistence of two phases: the solid 1:1 complex and the solution.

Discussion

As a result of the present investigation, the following solid complexes were found to exist at 0°.

$ArH \cdot Al_2Br_6$ (1:2 complex)	$ArH \cdot AlBr_3$ (1:1 complex)
benzene	...
toluene	...
p-xylene	...
o-xylene	...
m-xylene	*m*-xylene
mesitylene	mesitylene

It was then of interest to examine the relative thermodynamic stability of these solid complexes. The heats of dissociation, $\Delta H°$, of the 1:1 and 1:2 complexes were determined from the variation of dissociation pressures of the complexes with temperature. These determinations concerned the following two equilibria.

$$ArH \cdot AlBr_3(s) \rightleftharpoons {}^1/_2ArH \cdot Al_2Br_6(s) + {}^1/_2ArH(g)$$

$$ArH \cdot Al_2Br_6(s) \rightleftharpoons Al_2Br_6(s) + ArH(g)$$

The equilibrium constants, K_1 and K_2, for these reactions were given by the equations, $K_1 = (P_1)^{1/2}$ and $K_2 = P_2$, where P_1 and P_2 denote the vapor pressures (in atm) of the aromatics over the solids in the two equilibria given above. Therefore, the heats of dissociation of the complexes could be obtained from the slope of a plot of log P_1 or log P_2 *vs.* $1/T$. The standard free energies of dissociation, $\Delta F°$, of the complexes were calculated from the observed values of the dissociation pressures of the complexes at each temperature. Moreover, from a knowledge of $\Delta H°$, $\Delta F°$, and the temperature, the standard entropy changes, $\Delta S°$, for the dissociation of the complexes were calculated. The results of these calculations are summarized in Table I.

Table I. Thermodynamic Data for Dissociation of the Aromatic–Aluminum Bromide Solid Complexes

Aromatic	Temp, °C	Pressure, mm	$\Delta H°$, kcal/mole	$\Delta F°$ at 0°, kcal/mole	$\Delta S°$ at 0°, eu
		1:1 Complexes[a]			
m-Xylene	0	1.29	4.87	1.73	11
	−9.2	0.743			
	−23.6	0.237			
Mesitylene	0	0.304	5.33	2.13	12
	−9.3	0.166			
	−23.7	0.047			
		1:2 Complexes[b]			
Benzene	0	11.5	10.6	2.27	30
	−35.7	0.650			
	−45.5	0.233			
Toluene	0	2.37	11.7	3.14	31
	−35.9	0.083			
	−45.3	0.033			
p-Xylene	0	0.478	12.6	4.00	31
	−10.9	0.183			
	−23.3	0.055			
o-Xylene	0	0.414	11.6	4.08	28
	−10.9	0.197			
	−23.4	0.056			
m-Xylene	0	0.930	12.6	3.64	33
	−9.1	0.408			
	−23.7	0.103			
Mesitylene	0	0.271	12.4	4.31	30
	−9.4	0.119			
	−23.7	0.031			

[a] $ArH \cdot AlBr_3(s) \rightleftharpoons {}^1/_2ArH \cdot Al_2Br_6(s) + {}^1/_2ArH(g)$. [b] $ArH \cdot Al_2Br_6(s) \rightleftharpoons Al_2Br_6(s) + ArH(g)$.

The relative stability of the solid complexes can be expressed in terms of the free energy of dissociation of the complexes. The larger values of the free energy of dissociation at a given temperature correspond to the greater stability of the complexes. It is then evident from Table I that the relative stability of the 1:2 complexes increases in the following order of the aromatic hydrocarbons involved: benzene < toluene < *m*-xylene < mesitylene. The order of the relative stability thus observed is the same as that of the aromatic–hydrogen halide complexes in *n*-heptane solution.[15,16] For closer examination of a quantitative relationship between the stabilities of the two groups of complexes, the free energy of dissociation at −78.5° of the hydrogen halide π complexes[16] was plotted against the free energy of dissociation at 0° of the aromatic–aluminum bromide 1:2 complexes (Figure 7). A good linear relationship is observed, supporting the proposal that both groups of complexes are closely related, in accordance with the proposal that both types involve an interaction of the π-electron cloud with the acceptor molecule.

It must be considered that the relative stabilities of these solid aromatic–aluminum bromide complexes are affected also by the relative magnitude of the crystal lattice energies of the complexes. From the regularities observed, however, it would appear that differences in the crystal lattice energies are relatively small and do not play a major role in the relative stabilities of the complexes.

One exception should be noted to this correlation. In the present study, *p*- and *o*-xylenes were found to form slightly more stable 1:2 complexes with aluminum

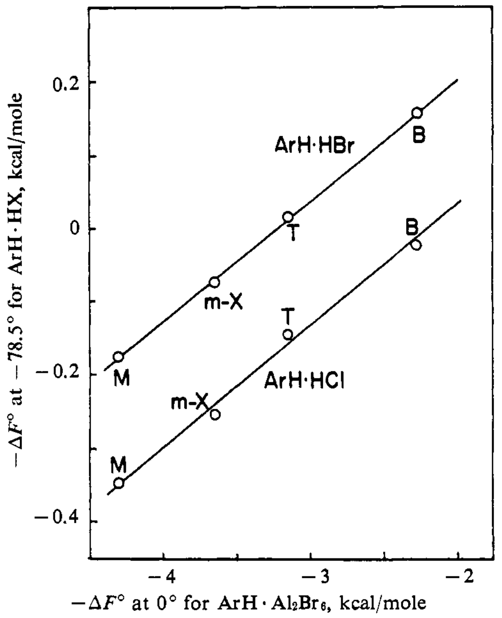


Figure 7. Correlation of the free energies of dissociation at 0° of the 1:2 aromatic–aluminum bromide complexes with those at −78.5° of the aromatic–hydrogen halide complexes. The upper line represents the correlation with the hydrogen bromide complexes and the lower with the hydrogen chloride complexes (B, benzene; T, toluene; m-X, *m*-xylene; and M, mesitylene).

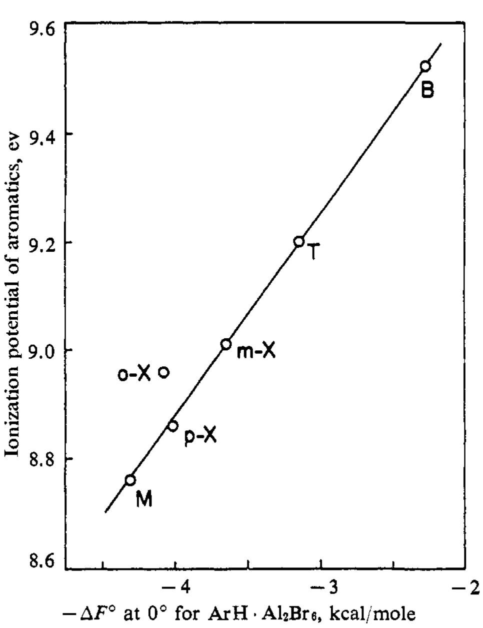


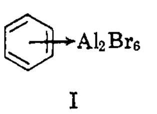
Figure 8. Correlation of the free energies of dissociation at 0° of the 1:2 aromatic–aluminum bromide complexes with ionization potentials of the corresponding aromatics: benzene (B), toluene (T), *p*-xylene (p-X), *o*-xylene (o-X), *m*-xylene (m-X), and mesitylene (M).

bromide than *m*-xylene,[18] whereas the reverse was observed previously[15] for the interaction of the three xylenes with hydrogen chloride in *n*-heptane solution.

A plot of the standard free energy of dissociation at 0° of the aromatic–aluminum bromide 1:2 complexes *vs.* the ionization potentials[19] of these aromatics reveals a good linear relationship between the two quantities, with only *o*-xylene exhibiting a significant deviation from the linear relationship (Figure 8).

This linear relationship suggests that the ionization potentials of aromatics may be taken as a measure of their relative abilities to form complexes with aluminum bromide and related Lewis acids. As discussed above, crystal lattice energies do not appear to vary significantly among the aromatic–aluminum bromide solid complexes. Hence, the relative magnitude of the ionization potentials of the aromatics appears to be a major factor determining the relative ability of formation of the solid aluminum bromide complexes by the aromatics. The fact that the *o*-xylene derivative is slightly more stable than predicted on the basis of the ionization potential suggests that the lower steric requirement of the two neighboring methyl groups may be a factor in the higher stability.[18]

Previously, the 1:2 complexes of aluminum bromide with benzene or toluene were proposed to be π complexes with structure I.[12,20] Similarly, the 1:1 complexes observed in the present study are also presumed to be π complexes with structure II. These π complexes are considered to be formed through an interaction of the π-electron cloud of the aromatic ring with the acceptor molecule, aluminum bromide. This interaction is presumed to be an electron donor–acceptor interaction, as is the case with other molecular complexes.[6,21,22] Hence, the relative stability of the aluminum bromide–aromatic complexes may be related directly to the relative basicity of the aromatics.



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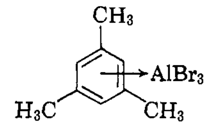


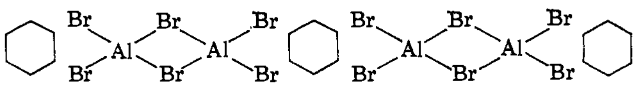
II

As mentioned above, the ΔF° values observed at 0° for the three xylene–aluminum bromide 1:2 complexes do not exhibit a linear correlation with their relative stability to form π complexes with hydrogen chloride in *n*-heptane solution. In the present study, however, it is observed that only the more basic aromatics are able to form the 1:1 solid π complexes with aluminum bromide. It is also observed that *m*-xylene is closer to mesitylene than to toluene in its π-complexing behavior with aluminum bromide, whereas *p*- and *o*-xylenes are similar to toluene rather than to mesitylene, since *m*-xylene and mesitylene form both the 1:1 and 1:2 solid complexes with aluminum bromide, but toluene and *p*- and *o*-xylenes form only the 1:2 solid complexes. Hence, it must be concluded that *m*-xylene has greater ability to form π complexes with aluminum bromide than the other xylenes, and therefore, the following would be

[18] The factor of the crystal lattice energies may be responsible for the relatively high stabilities of *p*- and *o*-xylene derivatives. We attempted to avoid this factor in a later study by examining complex formation in solutions of aluminum bromide in these aromatics (ref 17).

[19] H. Baba, I. Omura, and K. Higashi, *Bull. Chem. Soc. Japan*, **29**, 521 (1956). The following values (in ev) are reported as the ionization potentials: benzene, 9.52; toluene, 9.20; *p*-xylene, 8.86; *o*-xylene, 8.96; *m*-xylene, 9.01; and mesitylene, 8.76.

[20] Eley and his co-workers have reported the following crystal structure for the $C_6H_6 \cdot Al_2Br_6$ solid complex (ref 14)



[21] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952); R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

[22] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

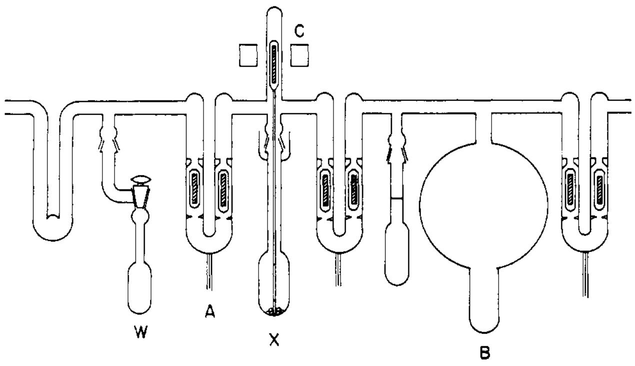


Figure 9. Apparatus for vapor pressure–composition phase studies.

the order of increasing π-complexing ability of the aromatics with aluminum bromide: *p*- and *o*-xylenes < *m*-xylene.

In the present study, dimeric aluminum bromide is observed to form solid π complexes with all of the aromatics studied, whereas monomeric aluminum bromide does so only with *m*-xylene and mesitylene. Since these π complexes are considered to be formed through an electron donor–acceptor interaction, it may be concluded that monomeric aluminum bromide behaves as a weaker acceptor than dimeric aluminum bromide in π-complex formation with aromatic hydrocarbons. This apparent anomaly may be rationalized as follows. For the formation of the 1:2 complexes, only one of the bridge bonds in the dimeric aluminum bromide molecule must be broken in order that π electrons in the aromatic nuclei can be shared with the aluminum atom. In order to form a 1:1 complex, both of the bridge bonds in the aluminum bromide dimer must be broken. Only a relatively basic aromatic will interact sufficiently strongly with the aluminum atom so as to provide the requisite energy to break both bridge bonds.

Experimental Part[23]

Apparatus. The apparatus for the present study is shown diagramatically in Figure 9. All experiments were carried out in a high-vacuum system where the material came in contact with glass and mercury, and more rarely with stopcock grease. The general vacuum line techniques were similar to those described by Sanderson.[24]

Materials. High purity samples of the aromatic hydrocarbons used in the present study were supplied by the National Bureau of Standards.[25] Aluminum bromide (Fisher Scientific Co.) was purified by successive sublimation *in vacuo* and stored in small ampoules with thin, fragile break-tips.[23]

Vapor Pressure–Composition Phase Studies. A known amount of aluminum bromide was introduced into the reaction vessel X by a method similar to that used previously.[12,23] The aromatic hydrocarbons to be studied were transferred from the weighing tube W to the reaction vessel by the usual vacuum line techniques. The reaction vessel contained a stirrer with a glass-enclosed iron core which was activated by a solenoid C and a timer. Several glass beads in the vessel greatly improved the efficiency of the agitation. The reaction vessel was kept in a constant temperature bath until thermal equilibrium was reached between the vapor and the condensed phase (an elapse of about 0.5 to 2 hr). The pressure was then measured by the indirect method based on the ultraviolet spectrophotometric determination of the aromatic present as vapor in the system under study. For the benzene–aluminum bromide and toluene–aluminum bromide systems both at 0°, the pressure was measured directly with a mercury manometer.

In order to vary the composition of the system, the valve A was opened and a small quantity of the aromatic was removed from the reaction vessel to the weighing tube. The pressure was measured again. The above-mentioned procedure was repeated until all of the aromatic was removed. Upon the completion of each series of experiments, the volume, V_R, of the reaction vessel including the bulb B was measured. The quantity of the aromatic present as vapor was then calculated from the ideal gas law and subtracted from the total quantity of the aromatic in the system, and the new value was then used in the calculation of the mole ratio, $ArH/AlBr_3$, for the condensed phase.

Data of the vapor pressure–composition phase studies on the benzene–aluminum bromide system at −45.5° are shown in Table II as a typical example of the present study.

Determination of Thermodynamic Quantities for the Dissociation of the Complexes. After a clear solution of aluminum bromide in an aromatic was prepared in the reaction vessel X, the aromatic was carefully removed from the vessel until the mole ratio $ArH/AlBr_3$ was slightly less than 0.5. Although the exact value of the mole ratio was known, it was not strictly necessary because a small change in the mole ratio did not produce any appreciable effect upon the pressure as long as the mole ratio was slightly less than 0.5. The removal of the aromatic was carried out at the lowest temperature used in each case. After keeping the reaction vessel in a constant temperature bath for a sufficient length of time (up to about 1 hr), the pressure was measured by the methods mentioned above. The bath was removed from the reaction vessel and replaced by a bath at the next higher temperature to be investigated. The above-mentioned procedure was then repeated. From the variation of dissociation pressure of the complex with bath temperature, the heat of dissociation of the 1:2 complex, $ArH \cdot Al_2Br_6$, was calculated.

In addition, for the *m*-xylene– and mesitylene–aluminum bromide systems, the mole ratio $ArH/AlBr_3$ was also adjusted to a value slightly below 1.0, and the same procedure was followed for the determination of the dissociation pressure of the 1:1 complexes, $ArH \cdot AlBr_3$.

Spectrometric Technique for the Measurement of Low Vapor Pressures of Aromatic Hydrocarbons. After the entire apparatus was thoroughly degassed, a small quantity of the aromatic hydrocarbon was introduced into the vessel X by the usual vacuum line techniques.[24] A cold bath maintained at the desired temperature was placed around the vessel X and the vapor allowed to expand into the large bulb B. (The cold baths were prepared from solid–liquid slushes of the following substances: ice–water, 0°; diethylene glycol, −10°; carbon tetrachloride, −23°; ethylene dichloride, −36°; and chlorobenzene, −45°. The temperatures were checked by means of a platinum resistance thermometer.) After an adequate time had elapsed for the system to come to equilibrium (usually 1 hr), the intervening valve was closed and the aromatic vapor in the bulb was condensed into the small removable tube to its left. (Condensation times of 15 to 30 min were used to ensure quantitative transfer.) Dry air was admitted, the tube removed from the line, and 95% ethyl alcohol added to the calibrated etched mark (volume, *V* ml). Then the absorbancy, *A*, of the solution was measured at the wavelength corresponding to to the maximum absorption of ultraviolet radiation by the aromatic, with a Beckman DU spectrophotometer.

Since the solutions of the aromatic hydrocarbons obeyed Beer's law over the range of concentrations used, the pressure *P* of the aromatic in the bulb B could be calculated by the following equation, assuming the vapor obeys the ideal gas equation

$$p = AVRT_B/(1000\ a_M b V_B)$$

where *R* is the gas constant, T_B the absolute temperature of the bulb, a_M the molar absorbancy index of the aromatic, *b* the thickness of the absorption cells in the spectrophotometer, and V_B the volume of the bulb including the small side tube.

The results of typical measurements of vapor pressures of benzene, toluene, *m*-xylene, and mesitylene at various temperatures are summarized in Table III. From the table it is seen that the observed values agree well with the values calculated from the vapor pressure equations available in the literature.[26] It is concluded therefore

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[23] For the numerical values of the vapor pressure–composition studies and for further details, consult S. U. Choi, Ph.D. Thesis, Purdue University Library.

[24] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[25] This supply is gratefully acknowledged.

Table II. Vapor Pressure–Composition Data for the Benzene–Aluminum Bromide System at −45.5°

Absorbancy at 2545 Å	Temp of bulb, °C	Pressure,[a] mm	Benzene[b] Total, mmoles	Benzene[b] Vapor, mmole	Mole ratio $C_6H_6/AlBr_3$[c]	Observation
0.303	25.6	0.407	14.82	0.015	11.0	Faint yellow solid over the entire range of the mole ratio
0.302	23.9	0.403	12.19	0.015	9.02	
0.297	24.4	0.397	10.64	0.015	7.87	
0.297	24.8	0.398	9.14	0.015	6.76	
0.299	24.5	0.400	7.01	0.015	5.18	
0.300	24.9	0.402	5.55	0.015	4.10	
0.302	24.9	0.404	4.99	0.015	3.68	
0.302	25.7	0.405	4.39	0.015	3.24	
0.301	24.8	0.403	3.37	0.015	2.49	
0.298	24.7	0.399	2.39	0.015	1.76	
0.296	24.8	0.396	1.32	0.015	0.97	
0.295	25.8	0.396	0.99	0.015	0.72	
0.173	26.1	0.233	0.66	0.009	0.48	
0.172	25.7	0.231	0.58	0.009	0.42	
0.175	25.7	0.235	0.49	0.009	0.36	
0.174	25.3	0.233	0.40	0.009	0.29	
0.173	24.8	0.232	0.15	0.009	0.10	

[a] $V = 10.0$ ml; $a_M = 216$; $b = 1.00$ cm; $V_R = 642.6$ cc. [b] $V_R = 702.8$ cc. [c] $AlBr_3 = 1.35$ mmoles.

Table III. Vapor Pressures of Aromatic Hydrocarbons

Aromatic	Temp of bath, °C	P, mm Obsd	P, mm Lit.
Benzene	0.0	24.4	24.2[a]
	−23.7	3.39	3.58[a]
	−35.5	1.18	1.18[a]
	−45.5	0.408	0.412[a]
Toluene	0.0	6.72	6.72[b]
	−23.7	1.22	1.22[b]
	−35.5	0.443	0.441[b]
	−45.5	0.171	0.168[b]
m-Xylene	0.0	1.61	1.62[c]
	−9.4	0.773	0.792[c]
	−24.2	0.207	0.223[c]
	−35.6	0.076	0.073[c]
Mesitylene	0.0	0.449	0.446[d]
	−9.4	0.201	0.202[d]
	−24.2	0.051	0.050[d]

[a] $\text{Log } P \text{ (mm)} = 9.0963 - 1882.0/(244.0 + t)$ (t in °C). [b] $\text{Log } P \text{ (mm)} = 6.95334 - 1343.943/(219.377 + t)$. [c] $\text{Log } P \text{ (mm)} = 7.00659 - 1460.498/(214.889 + t)$. [d] $\text{Log } P \text{ (mm)} = 7.04089 - 1567.10/(212.00 + t)$.

that this method can be successfully applied to the accurate measurement of low vapor pressures of the aromatic hydrocarbons investigated.

The plots of the logarithm of the observed vapor pressure, P, of each hydrocarbon *vs.* the reciprocal of the bath temperature, T, expressed on the absolute scale, indicated a good linearity over the range of temperature studied.

The molar absorbancy indices were determined in the following manner. A known quantity of the aromatic hydrocarbon was dissolved in 95% ethanol and diluted to a known volume. The absorbancies of several solutions prepared by successive dilution of this standard solution were then measured at the wavelength corresponding to maximum absorption of the hydrocarbon, using a Beckman DU spectrophotometer. The molar absorbancy indices of the aromatic hydrocarbons were then determined from the plots of the absorbancies *vs.* the concentrations of the solutions. The results of these measurements are summarized in Table IV. The solutions obeyed Beer's law over the range of concentration listed in the last column of Table IV.

Table IV. Molar Absorbancy Indices, a_M, of Aromatic Hydrocarbons at Wavelengths (λ_{max}) of Maximum Absorption in the Ultraviolet Region

Aromatic	a_M	λ_{max}, Å	Concn range,[a] 10^{-3} mole/l.
Benzene	216	2545	0.5–4.0
Toluene	259	2620	0.8–3.8
p-Xylene	582	2744	0.3–1.9
o-Xylene	277	2630	0.4–3.7
m-Xylene	315	2652	0.5–3.9
Mesitylene	307	2650	0.4–2.0

[a] Concentration range where the solutions obeyed Beer's law.

Typical calculations of the vapor pressure utilizing this procedure are summarized in Table V.

Table V. Vapor Pressure of Benzene

Temp of bath, °C	A at 2545 Å	V, ml	Temp of bulb, °C	V_B, cc	P, mm[a]
0.0	0.732	250	27.8	652.7	24.4
−23.7	0.508	50.0	28.6	652.7	3.39
−35.5	0.366	25.0	27.5	672.4	1.18
−45.5	0.309	10.0	27.4	657.0	0.408

[a] $a_M = 216$; $b = 1.00$ cm.

The procedure utilized to determine the vapor pressure of the aromatic hydrocarbon above the hydrocarbon–aluminum bromide system was entirely analogous, with the exception that the hydrocarbon–aluminum bromide mixture of known composition was present in the magnetically stirred vessel X, instead of the pure hydrocarbon as described above.

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(26) "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, Circular C 461, U. S. Government Printing Office, Washington, D. C., 1947.