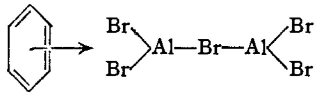
crease with increasing number of methyl groups.[16] The increase in intensity of the color of the solutions of aluminum bromide in these hydrocarbons (Table I) also supports the conclusion that these solutions must contain an increasing concentration of $ArH{\cdot}Al_2Br_6$ complexes as we proceed from benzene to toluene to *m*-xylene and to mesitylene.

We suggest that these complexes are probably π-complexes[16] with the structure



It has frequently been suggested that dimeric aluminum bromide does not itself react with aromatic hydrocarbons, but first dissociates into the monomer which exists associated with the aromatic hydrocarbon.[5] While this may occur, we know of no decisive evidence which requires this conclusion at the present time. Indeed, Eley and King's observation that solutions of aluminum bromide in benzene obey Beer's law over a wide range of concentration is strong evidence against such a dissociation.

As far as we can now ascertain these complexes do not have any significant role in Friedel–Crafts reactions.

Experimental Part[17]

Materials.—Phillips Research Grade aromatic hydrocarbons were treated with anhydrous aluminum chloride and then distilled through a column rated at 72 plates. A constant boiling center cut was collected and stored over calcium hydride. Commercial aluminum bromide (Eimer and Amend) was distilled three times in an evacuated all glass apparatus and collected in convenient samples (*ca.* 0.3 g.) in small ampoules which were drawn down into thin, fragile tips. These ampules were sealed under vacuum and the aluminum bromide was observed to be analytically pure and to remain in satisfactory condition for the experiments over long periods of time.

Introduction of Aluminum Bromide.—The aluminum bromide was introduced in the following manner. The tip of the weighed ampule was carefully scratched and the ampule placed in the side arm of an apparatus containing a glass-enclosed hammer. The side arm was closed and the entire apparatus sealed on to the lower end of the reaction tube. When the system was thoroughly degassed, the glass-enclosed hammer was lifted slightly with magnets and dropped onto the fragile, strained tip. The aluminum bromide was then distilled out of the ampule into position in the reaction tube. The section containing the ampule was then sealed at the constriction, removed from the remainder of the apparatus, and the ampule and tip removed and weighed. Experiment showed that we could in this way transfer samples of 0.2 to 0.3 g. of aluminum bromide with an uncertainty of only 0.0003 g. (*i.e.*, introduced by wt.: 0.2423, 0.2629, 0.2162 g.; found by analysis: 0.2419, 0.2625, 0.2160 g.). The samples thus transferred were analyzed for aluminum and bromide ions—they were analytically pure.

Phase Studies.—The aluminum bromide was introduced as described above into a tube with a magnetically operated stirrer. A weighed sample of the aromatic hydrocarbon was condensed into the tube and the tube maintained at constant temperature with stirring until no change in pressure was observed. Hydrocarbon was added or subtracted to obtain additional points. In all cases the solutions appeared to be stable and did not change with time.

The molecular weight measurements were made using similar methods. Two tubes, one containing the pure hydrocarbon and the other containing the solution of aluminum bromide, were connected to the two limbs of a manometer. The apparatus was designed so that the two tubes could be inserted into the same constant temperature bath. In this way the pressure lowering was measured directly and the effects of small variations in the temperature of the bath were thereby reduced.

The same differential procedure was utilized for the study of the interaction between mesitylene and aluminum bromide in cyclopentane solution.

LAFAYETTE, INDIANA

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[16] D. A. McCaulay and A. Lien, THIS JOURNAL, **73**, 2013 (1951); H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

[17] For the experimental values of the vapor pressure–composition studies and diagrams of the apparatus used in these studies consult W. J. Wallace's Ph.D. thesis, Purdue University Library.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Complexes of Hydrogen Bromide–Aluminum Bromide with Aromatic Hydrocarbons[1,2]

BY HERBERT C. BROWN AND WILLIAM J. WALLACE[3]

RECEIVED MARCH 11, 1953

Henry's law constants were determined for the solubility of hydrogen bromide in benzene, toluene, *m*-xylene and mesitylene. The solubility increases in the order listed. Aluminum bromide is slightly soluble in liquid hydrogen bromide at −78.5°; it appears to exist as a dimer in this solvent. Hydrogen bromide and aluminum bromide react with the aromatic hydrocarbons to form σ-complexes with the compositions: $ArH_2^+ Al_2Br_7^-$(ArH = benzene, toluene, *m*-xylene and mesitylene) and $ArH_2^+ AlBr_4^-$ (ArH = toluene, *m*-xylene, mesitylene). The stability of the complexes increases in the order: $ArH_2^+ AlBr_4^- < ArH_2^+ Al_2Br_7^-$. as well in the order: ArH = benzene < toluene < *m*-xylene < mesitylene. At −80° an unstable solid complex was prepared with the unusual composition: $toluene{\cdot}2HBr{\cdot}Al_2Br_6$. The precise formulation of this product is uncertain. At slightly higher temperatures one mole of hydrogen bromide is evolved. It may be that one mole of hydrogen bromide is held by crystal lattice forces. In the presence of excess hydrocarbon the products contain additional molecules of the aromatic component. The precise nature of the forces holding these additional aromatic components remains to be clarified.

Introduction

The alkylation of aromatic hydrocarbons by means of the Friedel–Crafts reaction is accompanied by the formation of highly colored (frequently red), hydrocarbon insoluble oils. These oils have usually been considered to be undesirable by-products, although Gustavson[4d] demonstrated that they have marked catalytic properties. In spite of a number of earlier studies,[5–7] the precise nature of

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[1] The Catalytic Halides. VI.

[2] Abstracted from a thesis presented by William J. Wallace in partial fulfillment of the requirements for the Ph.D. degree.

[3] Standard Oil Company (Indiana) Fellow, 1950–1952.

[4] (a) G. G. Gustavson, *Ber.*, **11**, 1841 (1878); (b) 2151 (1878); (c) **16**, 784 (1883); (d) *J. prakt. Chem.*, [2] **42**, 250 (1890); **68**, 209 (1903); (e) **72**, 57 (1905).

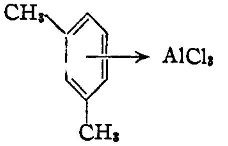
[5] B. N. Menshutkin, *J. Russ. Phys. Chem. Soc.*, **41**, 1089 (1909).

[6] J. F. Norris and D. Rubinstein, THIS JOURNAL, **61**, 1163 (1939).

[7] (a) H. Campbell and D. D. Eley, *Nature*, **154**, 85 (1944); (b) M. H. Dilke, D. D. Eley and M. J. Perry, *Research*, **2**, 538 (1949).

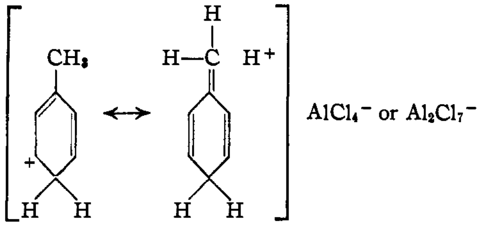
these complexes is only now becoming clear.[8–12]

The earlier workers noted that these "red oils" are formed from aluminum halides and aromatics only in the presence of hydrogen halides.[4–6] However, the formulations proposed for the products did not involve the hydrogen halides. Thus Gustavson[4] proposed the empirical formula $AlBr_3 \cdot 3ArH$ for the products, Norris suggested the formula $Al_2Br_6 \cdot 6C_6H_5CH_3$ for the toluene complex, while Eley and his co-workers[7b] considered the red oil that they obtained from aluminum chloride and *m*-xylene to be a π-complex



Norris later recognized that these Friedel–Crafts complexes contain hydrogen halide and reported the isolation of several crystalline products from mesitylene (Mes) and 1,3,5-triethylbenzene (TEB): $3Mes \cdot Al_2Br_6 \cdot HBr$,[8a] $2TEB \cdot Al_2Br_6 \cdot HBr$,[8a] $Mes \cdot Al_2Br_6 \cdot HBr$,[8b] $TEB \cdot Al_2Br_6 \cdot HBr$[8b]. He concluded that a third component was essential for the formation of complexes of aromatic hydrocarbons and aluminum halides.[8b,13]

As part of our program for examining the precise role of the catalytic halides in Friedel–Crafts reactions, we earlier examined the interaction of the catalyst couple, hydrogen chloride–aluminum chloride on toluene.[10] We observed that in the presence of excess hydrogen chloride at −80°, aluminum chloride dissolved to give a deeply colored solution. A 1:1 ratio of $AlCl_3$ to HCl absorbed was observed. At higher temperatures, −40°, and lower concentrations of hydrogen chloride, we observed a ratio of $AlCl_3$ to HCl of 2:1. We suggested that the products are to be considered as carbonium ion salts or σ-complexes[14]



In these experiments the hydrocarbon was present in excess. We were able, therefore, to fix only the $HCl/AlCl_3$ ratios. However, in another recent study involving the $HF–BF_3$ system, with hydrogen fluoride present in excess, the limiting ratio of ArH/BF_3 has been established as 1:1.[9]

The experiments involving aluminum chloride were exceedingly slow to reach equilibrium, presumably because of the low solubility of the metal halide. Accordingly, our study of the toluene–$HCl–AlCl_3$ system was very tedious. In continuing our studies of these systems, we decided to shift our attention to the more soluble aluminum bromide. As was anticipated, in these systems equilibrium is reached far more rapidly. In the present paper we wish to report our observations on the complexes of hydrogen bromide–aluminum bromide with benzene, toluene, *m*-xylene and mesitylene. Our studies were carried out in the presence of an excess of the aromatic component and attention was primarily devoted to establishing the ratios of hydrogen bromide to aluminum bromide in the complexes formed. Only in the case of toluene was the aromatic component systematically varied to establish its function in the complexes.

In the course of this study we also determined the solubility and molecular weight of aluminum bromide in liquid hydrogen bromide at −78.5° and the solubility of hydrogen bromide in the four aromatic hydrocarbons mentioned.

Baddeley and his co-workers[11] have recently reported the preparation of complexes of hydrogen bromide–aluminum bromide with *m*- and *p*-xylene. Moreover, Eley and King[12] have described a study of the corresponding system with benzene. It now appears possible to offer a simple interpretation of the great majority of the available observations on these systems.

Results and Discussion

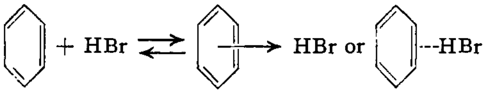
Solubility of Hydrogen Bromide in Aromatic Hydrocarbons.—The solubility of hydrogen bromide in benzene, toluene, *m*-xylene and mesitylene increases with increasing number of methyl groups (Table I, Fig. 1). The solubility is considerably greater than that estimated for an ideal solution.[15]

TABLE I

HENRY'S LAW CONSTANT FOR SOLUTIONS OF HYDROGEN BROMIDE IN AROMATIC HYDROCARBONS

Hydrocarbon	Temp., °C.	Henry's law constant (mm.) $k_{obsd.}$	k_{ideal}	$k_{obsd.}/k_{ideal}$
Benzene	5.7	5920	11850	0.500
Toluene	0.0	4440	10070	.441
	−78.5	100	404	
m-Xylene	0.0	3730	10070	.371
Mesitylene	0.0	3370	10070	.335

As in a previous study of the solubility of hydrogen chloride in aromatic hydrocarbons,[14] the high solubility is attributed to the formation of π-complexes, the stability of which increases with increasing basic properties of the aromatic nuclei.



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[8] (a) F. Norris and J. N. Ingraham, THIS JOURNAL, **62**, 1298 (1940): (b) J. F. Norris and J. E. Wood. *ibid.*, **62**, 1428 (1940).

[9] (a) D. A. McCaulay, B. H. Shoemaker and A. P. Lien. *Ind. Eng. Chem.*, **42**, 2103 (1950); (b) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

[10] H. C. Brown and H. W. Pearsall. *ibid.*, **74**, 191 (1952).

[11] G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952).

[12] D. D. Eley and P. J. King, *ibid.*, 2517 (1952).

[13] However, it now appears definitely established that somewhat less stable complexes involving Al_2Br_6 and aromatic hydrocarbons are capable of existence. For pertinent references see the previous paper in this series: H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6265 (1953).

[14] H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

[15] The Henry's law constant for an ideal solution was taken as the vapor pressure of hydrogen bromide at these temperatures. The vapor pressure was estimated from data reported by J. R. Bates, J. O. Halford and L. C. Anderson [*J. Chem. Phys.*, **3**, 531 (1935)]. Since the extrapolation is large, the error is probably considerable. However, the relative magnitude of the values of $k_{obsd.}/k_{ideal}$ is probably significant.

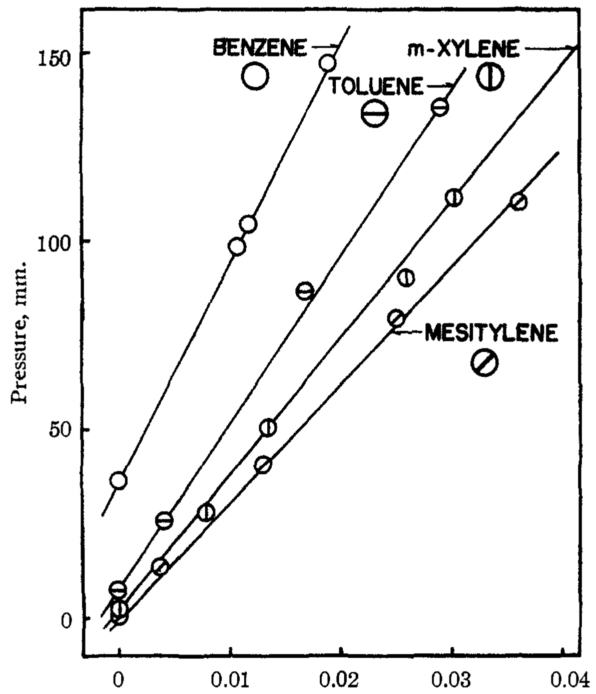


Fig. 1.—The solubility of hydrogen bromide in aromatic hydrocarbon.

At first sight this conclusion that the stability of the π-complexes increases from benzene to toluene to xylene appears to be in contradiction with the temperature–composition phase studies reported by Maass and his co-workers.[16] These investigators reported that toluene, *m*-xylene and mesitylene all form equimolar complexes with hydrogen bromide, whereas benzene and *p*-xylene do not. However, the compounds are relatively unstable, as indicated by very broad maxima in the phase diagrams and it is probable that the failure to isolate such compounds in the case of both benzene and *p*-xylene is primarily the result of the much higher melting points of these two hydrocarbons.

The System Hydrogen Bromide–Aluminum Bromide.—At 0° hydrogen bromide is not absorbed by aluminum bromide. The data in Table II reveal that the quantity of hydrogen bromide gas over a sample of freshly sublimed aluminum bromide is, within experimental error, identical with that introduced.

TABLE II

THE INTERACTION OF HYDROGEN BROMIDE WITH ALUMINUM BROMIDE AT 0°

BrH added mmole	Press. obsd., mm.	HBr present as gas, mmole	HBr absorbed, mmole
0.085	37.1	0.082	0.003
.412	191.0	.421	− .009
.708	325.2	.715	− .007
.984	452.3	.995	− .011

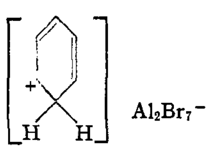
It was observed that the vapor pressure of liquid hydrogen bromide in contact with solid aluminum bromide at −78.51° decreased from the original value of 404.0 to 403.1. Applying Raoult's law to this solution results in an estimate of the solubility of aluminum bromide in liquid hydrogen bromide at −78.51° of 0.22 ± 0.04 mole %. A direct measurement of the solubility of aluminum bromide under these conditions indicated that 9.6 mg. (identified by m.p.) was soluble in 5.43 mmoles of hydrogen bromide, or 1.77 g. per mole of solvent. Thus, 1.77 g. is 0.0022 mole and the molecular weight is approximately 800.

The result is high for the dimeric formula (Al_2Br_6 = 534). However, the solubility is so low and the decrease in pressure so small, compared to the high vapor pressure of hydrogen bromide itself, that more precise measurements could not be obtained without considerable elaboration of the experimental techniques. Nevertheless, the solubility of aluminum bromide in liquid hydrogen bromide is definitely smaller than that estimated for an ideal solution. This result together with the molecular weight both support the conclusion that aluminum bromide does not coördinate with liquid hydrogen bromide.[17]

Eley and King[12] concluded from their vapor pressure measurements that aluminum bromide is not soluble in liquid hydrogen bromide at −78°. However, their pressure measurements were made only to the nearest mm. and the temperature is specified only to the nearest degree. A vapor pressure lowering of the magnitude we observed, 0.9 mm., might not have been noticeable under these conditions.

The System: Benzene–Hydrogen Bromide–Aluminum Bromide.—Aluminum bromide dissolved in excess benzene at 5.7° was treated with small amounts of hydrogen bromide. The original, almost colorless solution separated into two phases, the lower of which was orange-red in color. The data are shown graphically in Fig. 2.

It is apparent that a complex is formed with the composition *x* benzene·$HBr{\cdot}Al_2Br_6$. Eley and King have demonstrated that the colored lower phase is an excellent conductor of the electric current. In accordance with our previous discussions[10,14] we propose to formulate the product as a σ-complex



with the ions associated with a number of additional molecules of the aromatic. We shall defer discussion of this point to a later section.

In their recent paper Eley and King state: "His (Menshutkin[5]) view that there was not formed a compound of definite composition agrees with that advanced here." We are puzzled at this conclusion. The data certainly support the conclusion that a relatively unstable complex is formed with a ratio of one molecule of hydrogen bromide per aluminum bromide dimer. The complex is of low stability—hydrogen bromide is readily removed to reverse the reaction. However, it should be

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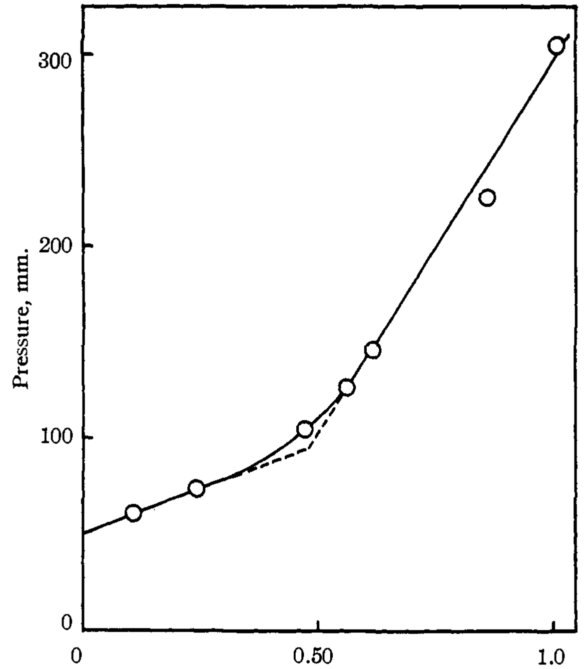
[16] O. Maass and J. Russell, THIS JOURNAL, **40**, 1561 (1918); O. Maass, E. H. Boomer and D. H. Morrisson, *ibid.*, **45**, 1433 (1923).

[17] C. M. Fontana and R. J. Herold, *ibid.*, **70**, 2881 (1948), reached the same conclusion through their observations on the solubility of hydrogen bromide in paraffin hydrocarbons in the presence and absence of dissolved aluminum bromide. See also ref. 12.

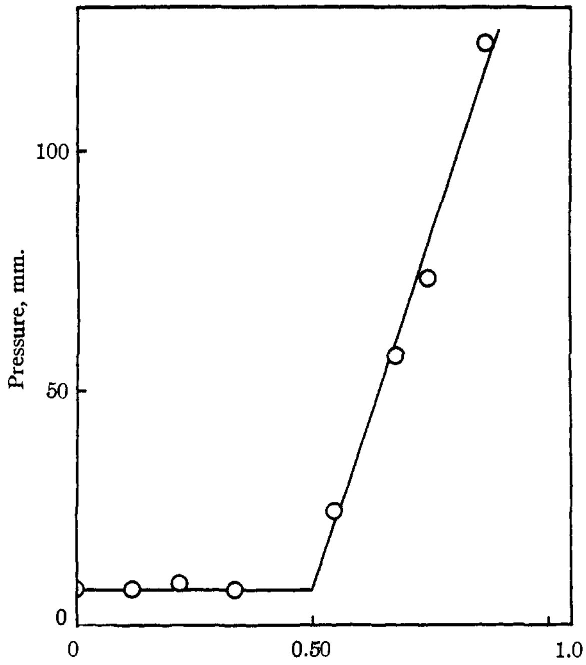


Mole ratio: $HBr/AlBr_3$ (benzene in excess).

Fig. 2.—Solubility of hydrogen bromide in a solution of aluminum bromide in benzene at 5.7°.

pointed out that the σ-complexes of benzene must be generally unstable. Thus, McCaulay and Lien[9b] report that benzene is too weak a base to react with $HF–BF_3$. To our knowledge the benzene–$HBr–Al_2Br_6$ σ-complex is the first such derivative to be isolated and points to an exceedingly high proton-transfer ability for the hydrogen bromide–aluminum bromide catalyst couple.

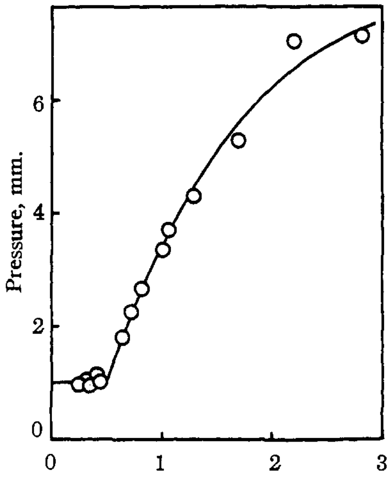
The System: Toluene–Hydrogen Bromide–Aluminum Bromide at 0°.—Addition of hydrogen bromide to a solution of aluminum bromide in excess toluene resulted in the separation of an intensely colored red lower layer. The complex is much more stable than the corresponding benzene derivative, since the pressure did not increase until the mole ratio of HBr/Al_2Br_6 exceeded unity (Fig. 3).



Mole ratio: $HBr/AlBr_3$ (toluene in excess).

Fig. 3.—Solubility of hydrogen bromide in a solution of aluminum bromide in toluene at 0°.

By reducing the pressure on the system it was observed that the excess hydrogen bromide and toluene could be removed, leaving the colored lower layer behind in the reaction vessel. By difference the composition of the lower layer was 6.28 toluene·$HBr·Al_2Br_6$. The vapor pressure was high, 7.15 mm. at 0°. Upon further distillation, only toluene was recovered until the composition dropped to toluene·Al_2Br_6·HBr and pressure dropped to 1.0 mm. At this stage the product was a light colored solid, m.p. 4°. The volatile material recovered from this point on consisted of an equimolar mixture of toluene and hydrogen bromide (Fig. 4).



Mole ratio: toluene/$AlBr_3$ (HBr/Al_2Br_6 = 1 with toluene/$AlBr_3$ = 0.5).

Fig. 4.—Vapor pressure–composition data for the toluene–$HBr–Al_2Br_6$ complex as a function of the toluene/$AlBr_3$ ratio.

The procedure was then reversed. A 1:1 mixture of HBr and Al_2Br_6 contained in a reaction vessel fitted with a manometer was treated with small measured quantities of toluene. The pressure dropped rapidly until one mole of toluene had been added, then it rose along the same smooth curve which had been obtained in the reverse process (Fig. 5).

This equimolar ternary compound was also formed by addition of hydrogen bromide to the binary compound, toluene·Al_2Br_6.[13] The yellow solid of the binary compound was first transformed into a red liquid and then, as more hydrogen bromide was added, the pressure remained sensibly constant and a solid product separated. After addition of one mole, the entire reaction mixture was a light colored solid and the pressure rose rapidly (Fig. 6).

It therefore appears that toluene forms a solid relatively stable σ-complex at 0° with the composition $CH_3C_6H_6^+$ $Al_2Br_7^-$. This product absorbs approximately 6 additional moles of toluene to form the highly colored oil characteristic of the "red oil"

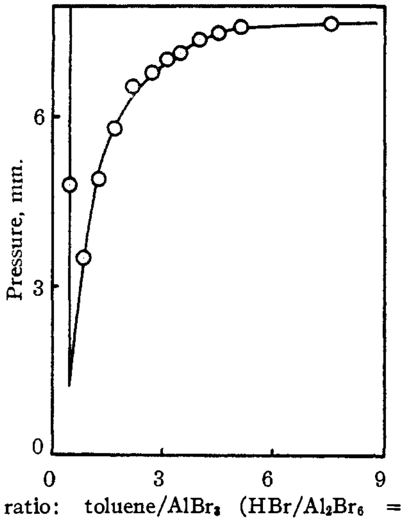


Fig. 5.—Pressure of ternary mixture, toluene–HBr–Al$_2$Br$_6$ as toluene is added to an equimolar mixture of HBr–Al$_2$Br$_6$.

complexes. In spite of the several different approaches described, we were unable to prepare at 0° a complex with a 1:1 ratio of HBr/AlBr$_3$. However, we did prepare such complexes with *m*-xylene and mesitylene and finally succeeded with toluene by operating at lower temperatures. These low temperature experiments revealed a number of other interesting phenomena and will be described in a later section.

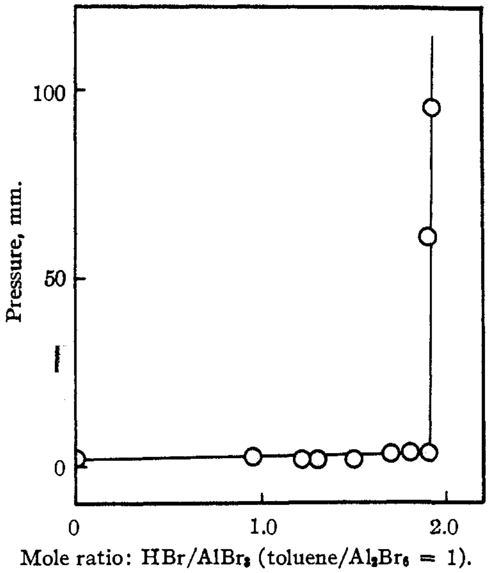


Fig. 6.—Pressure of system as hydrogen bromide is added to toluene·Al$_2$Br$_6$ at 0°.

The System: *m*-Xylene-Hydrogen Bromide–Aluminum Bromide.—At 0° a solution of aluminum bromide in excess *m*-xylene readily absorbs one mole of hydrogen bromide per mole of Al$_2$Br$_6$ to form a "red oil" similar to that described for toluene. However, the resulting product differs from the toluene derivative in readily absorbing a second mole of hydrogen bromide to form a crystalline, yellow solid.[11] Thus *m*-xylene forms complexes of two distinct series

$1,3\text{-}(CH_3)_2C_6H_5^+ AlBr_4^-$ $\quad$ $1,3\text{-}(CH_3)_2C_6H_5^+ Al_2Br_7^-$

As will be discussed later, these complexes contain additional molecules of aromatic hydrocarbon. However, there is little doubt that by adopting the procedures utilized in the toluene experiments the simple σ-complexes shown above could be obtained, free of the excess hydrocarbon. The data are presented in Fig. 7.

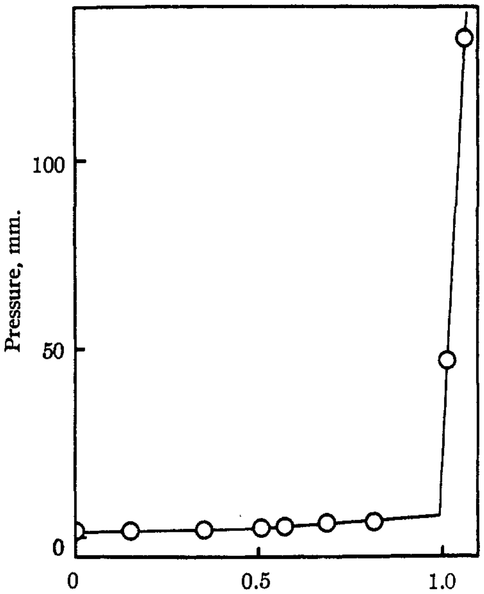


Fig. 7.—Solubility of hydrogen bromide in a solution of aluminum bromide in *m*-xylene at 0°.

The System: Mesitylene–Hydrogen Bromide–Aluminum Bromide.—The results with the mesitylene system were quite similar to those obtained with *m*-xylene. One mole of hydrogen bromide is absorbed by a mole of Al$_2$Br$_6$ in excess aromatic at 0° to form a red oil. A second mole of hydrogen

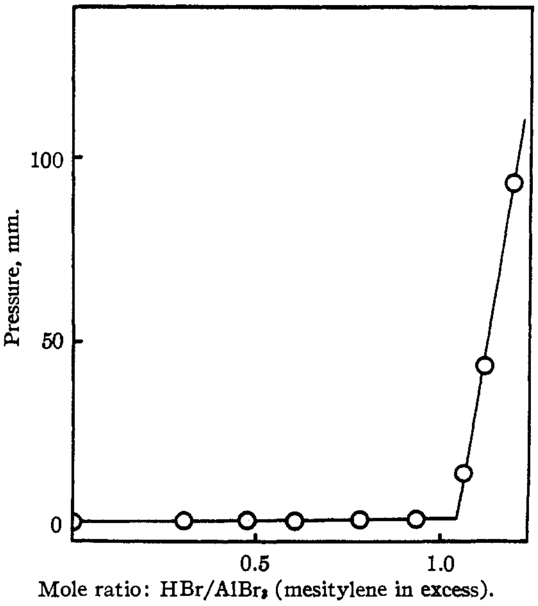


Fig. 8.—Solubility of hydrogen bromide in a solution of aluminum bromide mesitylene at 0°.

bromide is readily taken up to form a yellow crystalline product (Fig. 8).

Norris and his co-workers[8] had previously isolated complexes of mesitylene with the composition 3Mes·HBr·Al_2Br_6 (m.p. 47–48°)[8a] and Mes·HBr·Al_2Br_6.[8b] Thus, here also we have σ-complexes of two distinct series

$$ArH_2^+ \ AlBr_4^- \text{ and } ArH_2^+ \ Al_2Br_7^-$$

The System: Toluene–Hydrogen Bromide–Aluminum Bromide at −78.5°.—In view of our success in preparing complexes of *m*-xylene and mesitylene containing hydrogen bromide and aluminum bromide in ratios of HBr:$AlBr_3$ and HBr:Al_2Br_6, we decided to examine the possibility of preparing a HBr:$AlBr_3$ toluene derivative at lower temperatures. Accordingly we examined the action of hydrogen bromide and aluminum bromide on toluene at −78.5°.

An equimolar mixture of aluminum bromide dimer and toluene dissolved very slowly in excess liquid hydrogen bromide to give a slightly yellow solution at −78.5°. Hydrogen bromide was then removed in small portions. The pressure decreased in the normal manner until the composition of the mixture was one mole of toluene, one mole of aluminum bromide dimer and *two* moles of hydrogen bromide (Fig. 9).

This behavior was easily reproducible. There is, therefore, no doubt that at −78° a solid phase exists with the composition, toluene·2HBr·2$AlBr_3$.

The product is relatively unstable. On warming to −64.4° there was observed a sharp increase in pressure to 111 mm. and at 0° there was present in the gas phase one mole of hydrogen bromide (p = 196 mm.). This hydrogen bromide was not reabsorbed by cooling the mixture down to −78.5°. However, if sufficient liquid hydrogen bromide were present to dissolve the solid, the second mole of hydrogen bromide was reabsorbed and the original solid reformed.

It is difficult to formulate a reasonable structure for this toluene·2HBr·2$AlBr_3$ phase. The marked increase in pressure between −78.5 and −64.4° suggests that the second mole of hydrogen bromide is loosely held. Perhaps we have here the stable complex, $CH_3C_6H_6^+ \ Al_2Br_7^-$, containing a molecule of hydrogen bromide in the crystal lattice.

In a similar experiment in which the reaction mixture contained two moles of toluene, a stable solid containing two moles of hydrogen bromide was obtained. The product was stable at 0°. It exhibited dissociation pressures of 1.00 mm. at −79°, 2.50 mm. at −64.4° and 60.4 mm. at 0°, leading to a value for the heat of dissociation of 5.5 kcal.

Removal of the volatile components at 0° resulted in a smooth drop in pressure. The material recovered consisted of toluene and hydrogen bromide in equimolar amounts. The pressure drop continued until the residue possessed the composition, toluene·HBr·Al_2Br_6. It follows that the 1:1:1 complex is formed at −80° and exists at 0° with a moderate dissociation pressure. It readily loses toluene and hydrogen bromide to go over to the more stable 1:1:2 complex.

In view of the stability of the 1:1:1 complex at 0°, our failure to obtain it at that temperature is somewhat surprising. It is probable that this is a result of the high stability of the 1:1:2 complex and its existence as a solid which does not react with gaseous hydrogen bromide at any significant rate.

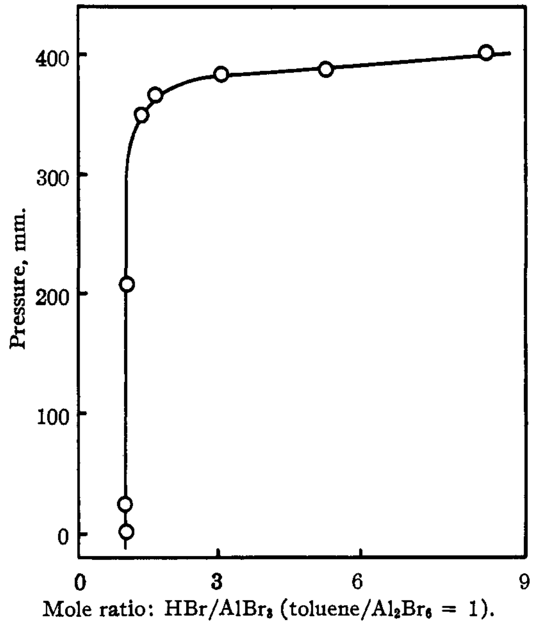


Fig. 9.—Pressure as hydrogen bromide was removed from a solution of toluene and Al_2Br_6 in liquid hydrogen bromide at −78.5°.

Norris and Ingraham[8a] reported that evacuation of the complexes 3Mes·HBr·Al_2Br_6 and 2TEB·HBr·Al_2Br_6 at 0.002 led to loss of hydrogen bromide and hydrocarbon to form the stable complexes Mes·Al_2Br_6 and TEB·Al_2Br_6. In our own studies of the toluene complexes we have observed that either excess toluene or excess hydrogen bromide may be removed to give the stable product, toluene·HBr·Al_2Br_6. Upon further evacuation both toluene and hydrogen bromide are simultaneously lost. In view of these results it appears desirable for the present to accept Norris' formulation of his products with some reservation.

The Hydrocarbon Component of Friedel–Crafts Complexes.—McCaulay and Lien[9b] have demonstrated that the stability of the σ-complexes (HF–BF_3) increases markedly in the order: benzene < toluene < *m*-xylene < mesitylene. Our results with the HBr–Al_2Br_6 system point to the same conclusion. Thus, benzene does not form a complex in the HBr–$AlBr_3$ series, and only an unstable one with HBr–Al_2Br_6. Toluene forms a relatively unstable complex with HBr–$AlBr_3$ and a more stable one with HBr–Al_2Br_6. Both *m*-xylene and mesitylene form stable complexes in both series. Not only do these results suggest an increase in the stability of the σ-complexes from benzene to toluene to *m*-xylene (and presumably to mesitylene) but it suggests that the proton transferring ability of HBr–Al_2Br_6 is considerably greater than that of HBr–$AlBr_3$.

These results may be summarized in the following chart.

increasing stability ↓	$ArH_2^+AlBr_4^-$	$ArH_2^+Al_2Br_7^-$	increasing stability ↓
	.....	benzene (unstable)	
	toluene (unstable)	toluene	
	m-xylene	*m*-xylene	
	mesitylene	mesitylene	
	increasing stability →		

There is little doubt that in these compounds one molecule of aromatic is united to a proton in the form of the σ-complex.[14] However, it appears that the simple product possesses a marked affinity for additional molecules of aromatic. For example, our results (Fig. 5) show that the toluene·HBr·Al_2Br_6 complex at 0° absorbed approximately six additional molecules of toluene, before a second phase appeared. Because of the instability of the corresponding benzene derivative, a similar phase study could not be made. However, qualitative observations indicate that the red oil phase in this case also contains approximately the same number of additional hydrocarbon molecules.

Unfortunately our techniques and experiments were developed primarily to establish the ratios of HBr to Al_2Br_6 in the complexes and were not well adapted to the determination of the precise number of molecules of hydrocarbon which were present in complexes prepared in the presence of excess hydrocarbon. If we assume that hydrogen bromide is not soluble in the solid complexes of *m*-xylene and mesitylene, we can utilize the Henry's law constants (Table I) to calculate the amount of free hydrocarbon present, and thereby the number of molecules of hydrocarbon present in the solid complexes. The results point to the compositions: 3.4 *m*-xylene·2HBr·Al_2Br_6, 3.4 mesitylene·2HBr·Al_2Br_6.

Baddeley[11] has recently reported the isolation of a crystalline complex (m.p. 52–54°) with the composition: 3 *m*-xylene·2HBr·Al_2Br_6. This product is presumably identical with the complex we prepared. Since the amount of the aromatic was established by a direct analysis in Baddeley's work, his value is doubtless more exact.

The precise manner in which these additional hydrocarbon molecules are held is uncertain. In the toluene case, the pressure increases smoothly with increasing content of toluene, until a separate hydrocarbon phase occurs. There is no evidence for a break in the curve and it, therefore, appears unlikely that the additional toluene molecules are held by simple valence forces. It is possible that the highly polarizable aromatic molecules serve to solvate the carbonium ion and the number present in the liquid red oils may not be an integral number, but vary considerably with the structure of the hydrocarbon and with the temperature. In the case of solid complexes, such as that isolated by Baddeley,[11] crystal lattice forces probably restrict the additional aromatics to a simple integral number.

Conclusions

As a result of these studies it now appears established that the Friedel–Crafts complexes ("red oils") are σ-complexes

$$ArH + HX + {}^1/_2M_2X_6 \rightleftarrows ArH_2^+ MX_4^-$$
$$ArH + HX + M_2X_6 \rightleftarrows ArH_2^+ M_2X_7^-$$

These σ-complexes are associated with additional molecules of aromatics. The complexes, as highly polar media which are good solvents for the metal halide, the alkyl halide and the aromatic, constitute a very favorable environment for the formation and reaction of ionic intermediates involved in the Friedel–Crafts reaction.

Experimental Part[18]

Apparatus.—All reactions were carried out in an all-glass high vacuum apparatus[19] in which the materials came in contact only with glass. In general the procedures were similar to those described in earlier papers of this series[10,13,14] and need not be described.

The phase studies involving hydrogen bromide were carried out in the following manner. A weighed amount of aluminum bromide was sublimed into the reaction tube and a corresponding weighed quantity of the aromatic hydrocarbon was then introduced into the vacuum apparatus and condensed in the tube. The tube was immersed in a bath at the desired temperature and small quantities of hydrogen bromide transferred from a calibrated bulb to the reaction tube. The amount of hydrogen bromide introduced was determined from the change in pressure of the calibrated bulb. The quantity in solution was obtained by correcting the quantity introduced by the small amount of hydrogen bromide contained in the vapor phase above the solution.

Materials.—The aluminum bromide and aromatic hydrocarbons were purified as described in the preceding paper.[13] Pure hydrogen bromide was most conveniently prepared by the following procedure. Distilled samples of aluminum bromide were permitted to stand in tubes open to the atmosphere (protected by a glass wool plug from dust particles) until the material was partially hydrated (approximately $AlBr_3·H_2O$). This material was then introduced into an evacuated tube in a section of the apparatus and gently heated with a smoky gas flame. Hydrogen bromide was evolved smoothly. Following a simple distillation from a −80° bath, the product was tensiometrically homogeneous, v.p. 404.0 mm. at −78.51°. The hydrogen bromide was stored as a liquid at −80°.

Solubility of Aluminum Bromide in Liquid Hydrogen Bromide.—A small tube was divided into two compartments by a sintered glass disk of medium porosity. The tube was connected to the high vacuum apparatus and a small quantity of aluminum bromide sublimed into one compartment. Then a known amount of liquid hydrogen bromide was condensed in the tube and it was sealed. The cell was placed in the −78.51° bath and frequently shaken to ensure good contact between the liquid hydrogen bromide and the solid. After 7 hours the cell was inverted and the solution permitted to filter into the second compartment. The tube was reattached to the line and the hydrogen bromide removed. The section of the cell containing the material which had dissolved was sealed off. The material was identified as aluminum bromide by its m.p. and the quantity established by weighing.

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[18] For the experimental values of the vapor pressure–composition studies and diagrams of the apparatus used in these studies consult W. J. Wallace's Ph.D. thesis, Purdue University Library.

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