stirrer, a reflux condenser and dropping funnel. The flask was flamed to remove water and the air displaced by nitrogen. The benzaldehyde (0.777 g., 7.33 mmoles) in 50.0 ml. of tetrahydrofuran was introduced into the flask and maintained at 0°. A solution of sodium trimethoxyborohydride (15.0 ml. containing 0.440 mmole/ml.) was added through the dropping funnel over a period of 2 min. Aliquot samples were removed at suitable intervals and analyzed for residual aldehyde using 2,4-dinitrophenylhydrazine[8] and for active hydride, using the procedure of Lyttle, Jensen and Struck.[9] The results are summarized in Table III.

**Reduction of Benzoyl Chloride at 0°.**—The experiment was carried out precisely as in the case of benzaldehyde described above, except that 1.00 g. (7.11 mmoles) of benzoyl chloride was used. The results of the aldehyde and hydride determinations are summarized in Table IV.

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[8] H. A. Iddles, A. W. Low, B. D. Rosen and R. T. Hart, *Anal. Ed.*, **11**, 103 (1939).

[9] D. A. Lyttle, E. H. Jensen and W. A. Struck, *ibid.*, **24**, 1843 (1952).

LAFAYETTE, INDIANA

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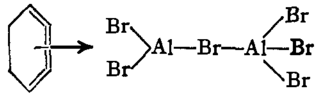
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

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

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

RECEIVED MARCH 11, 1953

Aluminum bromide possesses the dimeric formula, $Al_2Br_6$, in benzene solution. Vapor pressure–composition phase studies at 17.7° show the existence of solid compounds $Al_2Br_6\cdot ArH$ with benzene and toluene. Similar studies of the corresponding *m*-xylene and mesitylene systems did not indicate the formation of similar solid complexes. However, the color of the solutions as well as molecular weight determinations of solutions of mesitylene and aluminum bromide in cyclopentane support the existence of similar complexes in the case of the latter two hydrocarbons. It is proposed that these aromatic aluminum bromide compounds are π-complexes with the structure



## Introduction

Aluminum bromide is readily soluble in aromatic hydrocarbons, apparently with the formation of complexes. Unfortunately a number of serious conflicts exists in the observations and data recorded in the literature and unequivocable formulation of the complexes is not now possible.

For example, two groups of workers[4,5] agree that aluminum bromide possesses a high dipole moment in dilute benzene solutions. However, one group claims that the dipole moment drops to zero at higher concentrations[5] and differs, thereby, from the first group.[4] The change in dipole moment with concentration is attributed to the existence of aluminum bromide in dilute solutions in the monomeric form, $AlBr_3$, complexed with the aromatic hydrocarbon, and in the dimeric uncomplexed form in the more concentrated solutions. Parachor measurements[6] and molecular weight determinations by freezing point[4,7] and vapor pressure lowering[7] indicate a dimeric formula for aluminum bromide in benzene solution. Moreover, the dimeric formula is also supported by the observation that the molar refractivities of solutions of aluminum bromide in benzene and toluene exhibit strict additivity.[8] The parachor measurements[6] were made in dilute solution, comparable to those used in the dipole moment determinations.[5] A serious conflict exists between the respective conclusions of the two groups of authors.[5,6]

As a result of his study of the systems of aluminum bromide with benzene, toluene and *p*-xylene, Menshutkin[9] decided that complex formation did not occur. However, as a result of a similar study, Plotnikov and Gratsianskii[10,11] concluded that aluminum bromide does form complexes with benzene, *p*-xylene and *m*-xylene (m.p. 37, 31.2, 4.5°, respectively). The complexes melt incongruently. The arrests in the phase diagrams occurred on the hydrocarbon-rich side of equimolar proportions of aluminum bromide and hydrocarbon so that the complexes were assigned the empirical formula $AlBr_3\cdot ArH$. Moreover, a recent study of the benzene–aluminum bromide system has been considered to confirm Plotnikov's conclusion.[12] The authors also formulate the complex as $AlBr_3\cdot C_6H_6$ with an incongruent m.p. of 37°. However, Van Dyke concluded that the solid compound which separates from these solutions should be formulated as $Al_2Br_6\cdot 2C_6H_6$, since aluminum bromide exhibits the dimeric molecular weight in benzene solution.[7]

A different formulation for these complexes is indicated by data reported by Norris and Ingraham.[13] They prepared ternary complexes of aluminum bromide and hydrogen bromide with benzene, toluene, mesitylene and 1,3,5-triethylbenzene. At reduced pressures the ternary complexes lost both hydrogen bromide and hydrocarbon. The benzene

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[1] The Catalytic Halides. V.

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

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

[4] H. Ulich and W. Nespital, *Z. Elektrochem.*, **37**, 559 (1933); H. Ulich, *Z. physik. Chem.*, *A* (*Bodenstein Festband*), 423 (1931); W. Nespital, *Z. physik. Chem.*, **B 16**, 153 (1932).

[5] V. A. Plotnikov, I. A. Sheka and Z. A. Yankelewich, *Mem. Inst. Chem., Akad. Sci. Ukrain. S.S.R.*, **4**, 382 (1939).

[6] L. Poppick and A. Lehrman, THIS JOURNAL, **61**, 3237 (1939).

[7] R. E. Van Dyke, *ibid.*, **72**, 3619 (1950).

[8] V. V. Korshak, N. N. Lebedeev and S. D. Fedoseev, *J. Gen. Chem.* (*U.S.S.R*), **17**, 575 (1947).

[9] B. N. Menshutkin, *J. Russ. Phys. Chem. Soc.*, **41**, 1089 (1908).

[10] V. A. Plotnikov and N. N. Gratsianskii, *Mem. Inst. Chem., Akad. Sci., Ukrain S.S.R.*, **5**, 213 (1939).

[11] V. A. Plotnikov and N. N. Gratsianskii, *Bull. Acad. Sci. U.S.S.R., Classe sci. chim.*, 101 (1947).

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

[13] J. F. Norris and J. N. Ingraham, THIS JOURNAL, **62**, 1298 (1940).

derivative at 12 mm. (25°) yielded $Al_2Br_6$; whereas at 12 mm. (25°) the toluene derivative, and at 0.002 mm. (25°), the remaining substances all formed products formulated as $Al_2Br_6 \cdot ArH$.

In the hope of clarifying these conflicting reports we undertook a study of the interaction of aluminum bromide with benzene, toluene, *m*-xylene and mesitylene.

## Results and Discussion

Aluminum bromide dissolves readily in the four aromatic hydrocarbons listed and the colors of the solutions show a regular change from an almost colorless solution with a faint yellow tinge for the benzene solution to an orange-colored solution for mesitylene. Moreover, the solubilities of aluminum bromide in these aromatic hydrocarbons are appreciably greater than in typical non-aromatic hydrocarbons (Table I).

TABLE I

PHYSICAL PROPERTIES OF SOLUTIONS OF ALUMINUM BROMIDE IN HYDROCARBONS

| Hydrocarbon | Color | Solubility at 17.7° (mole fraction) |
|---|---|---|
| *n*-Hexane | Colorless | 0.034[a] |
| Cyclohexane | Colorless | .079[b] |
| Benzene | Faint yellow | .111[c] |
| Toluene | Lemon yellow | .086[c] |
| *m*-Xylene | Yellow-orange | .333[c] |
| Mesitylene | Orange | .398[c] |

[a] Extrapolated from data of E. R. Boedeker and A. G. Oblad, THIS JOURNAL, 69, 2036 (1947). [b] At 17.2°, P. A. Leighton and J. B. Wilkes, *ibid.*, 70, 2600 (1948). [c] Calculated from vapor pressure diagrams.

The gradation in color and the high solubility both point to complex formation of some kind between aluminum bromide and the aromatic hydrocarbons.

**The System: Benzene–Aluminum Bromide.**—The molecular weight of aluminum bromide in benzene solution was determined over a wide range of concentration from the decrease in vapor pressure. The solutions were clear and did not change observably with time. The data are summarized in Table II. The molecular weights were calculated assuming that the aluminum bromide was present in unsolvated form (A) and as a complex containing one mole of benzene (B).

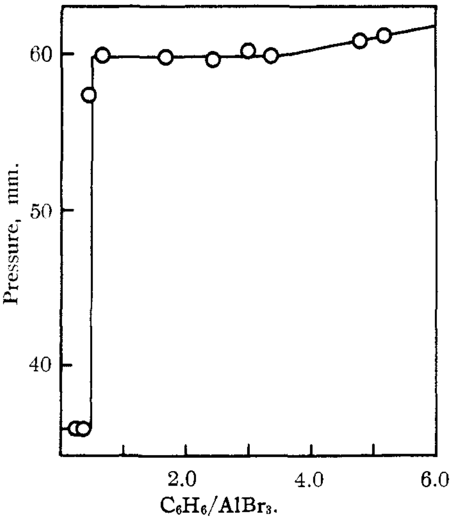

Fig. 1.—Vapor pressure–composition diagram for the aluminum bromide–benzene system at 17.7°.

TABLE II

MOLECULAR WEIGHT DATA FOR SOLUTIONS OF ALUMINUM BROMIDE IN BENZENE

| Temp., °C. | Press., mm. | Press.[a] decrease, mm. | $Al_2Br_6$ mmole | Benzene, mmole | Molecular weight[b] A. $Al_2Br_6$ | B. $Al_2Br_6 \cdot C_6H_6$ |
|---|---|---|---|---|---|---|
| 17.7 | 63.95 | 3.30 | 0.625 | 12.86 | 503 | 516 |
| 17.7 | 61.10 | 6.15 | .625 | 6.57 | 505 | 530 |
| 17.7 | 60.80 | 6.45 | .625 | 5.96 | 528 | 556 |

[a] Decrease observed directly by a differential method. [b] Theoretical for $Al_2Br_6$: 534.

The results are in somewhat better agreement with the conclusion that in benzene solution aluminum bromide exists primarily in the form of the unsolvated dimer, $Al_2Br_6$. If there is any tendency toward dissociation into monomer, it appears to be relatively small.

The vapor pressures of the benzene–aluminum bromide system were studied over a wide range of composition. Typical data are shown graphically in Fig. 1. The vapor pressure is sensibly constant at 59.9 mm. over the composition range of $C_6H_6/AlBr_3$ from 3.4 to 0.5. It then drops sharply to a new pressure plateau of 35.8 between the composition range of $C_6H_6/AlBr_3$ from 0.5 to 0. This last plateau corresponds to the existence of a solid phase $C_6H_6 \cdot Al_2Br_6$, with the first plateau corresponding to a saturated solution of this complex in benzene.

**The System: Toluene–Aluminum Bromide.**—Here also the vapor pressure–composition data (Fig. 2) show the existence of a solid phase $CH_3C_6H_5 \cdot Al_2Br_6$ with a dissociation pressure at 17.7° of

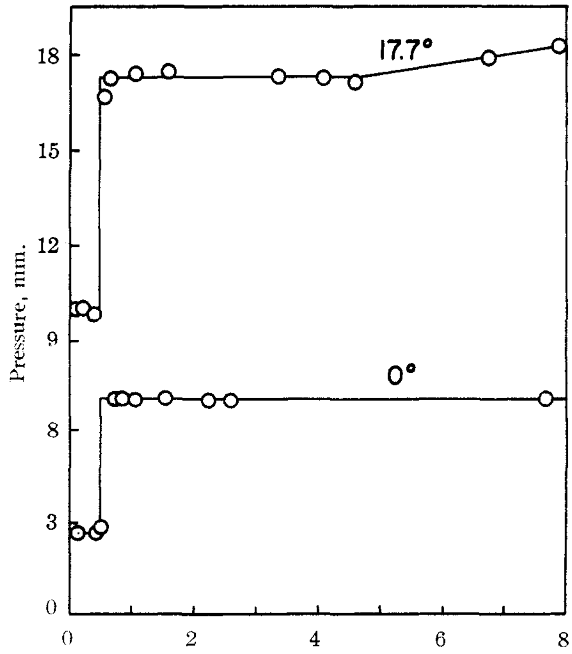

Fig. 2.—Vapor pressure–composition diagram for the aluminum bromide–toluene system at 17.7° and 0°.

9.9 mm., with a pressure plateau of 17.3 mm. between the compositions $CH_3C_6H_5/AlBr_3$ from 0.5 to 1.6 representing a saturated solution of the solid complex in toluene. At 0° the solid phase possesses the same composition with the dissociation pressure of the complex having the value 2.7 mm.

**Systems of Aluminum Bromide with *m*-Xylene and Mesitylene.**—We attempted to obtain similar vapor pressure–composition data for systems of aluminum bromide with *m*-xylene and mesitylene. Unfortunately, the low vapor pressure of these hydrocarbons rendered the studies relatively difficult and the data unsatisfactory. The results will therefore not be reported at this time.[14]

Since the vapor pressure technique, already poor for *m*-xylene, proved totally unsatisfactory for mesitylene, we utilized an indifferent solvent to examine complex formation between this hydrocarbon and aluminum bromide. A solution of 0.823 mmole of mesitylene in 27.41 mmoles of cyclopentane exhibited a lowering of the vapor pressure of 6.90 mm. as contrasted to 6.88 calculated for a perfect solution. Similarly 0.3526 g. of aluminum bromide in 27.41 mmoles of cyclopentane produced a vapor pressure lowering of 5.40 mm., corresponding to a molecular weight of 549 (calcd. for $Al_2Br_6$: 534). However, the lowering in vapor pressure observed for mixtures of aluminum bromide and mesitylene in the solvent was smaller than that calculated for the two reagents independently. The data are reported in Table III. The value of the equilibrium constant, $K_N$, was calculated assuming that the discrepancy in the vapor pressure lowering of the solvent was due to the reaction

$$\text{mesitylene} + Al_2Br_6 \rightleftarrows \text{mesitylene}\cdot Al_2Br_6$$

The excellent agreement in the values for $K_N$ at 0°, calculated for two different concentrations of mesitylene, supports this interpretation.

TABLE III

INTERACTION OF ALUMINUM BROMIDE AND MESITYLENE IN CYCLOPENTANE SOLUTION

| Temp., °C. | Press. decrease, mm. | Cyclopentane, mmole | Mole fraction, $N$ | | Degree of association, $\alpha$ | Equilibrium constant, $K_N$ |
|---|---|---|---|---|---|---|
| | | | $Al_2Br_6$ | Mesitylene | | |
| 0.0 | 9.65 | 28.07 | 0.0184 | 0.0721 | 0.1406 | 3.90 |
| 0.0 | 5.00 | 28.06 | .0205 | .0245 | .0962 | 3.91 |
| 17.7 | 11.25 | 28.85 | .0210 | .0250 | .0748 | 2.87 |
| 20.5 | 12.65 | 27.07 | .0211 | .0251 | .0713 | 2.74 |

**Relative Stability of the Aromatic Aluminum Bromide Complexes.**—It is of considerable interest to know how the stability of these aromatic aluminum bromide complexes varies with the structures of the aromatic component. Data which can be interpreted in terms of the stability of the complexes were obtained by preparing 1:1 products of $Al_2Br_6$ with benzene and toluene and observing the change in vapor pressure with temperature. The results are summarized in Table IV.

From these data it appears that the heat of formation of the solid complexes from solid aluminum bromide and liquid hydrocarbon is quite small, 2.0 kcal. for benzene and 3.1 kcal. for toluene. From the variation in the equilibrium constant ($K_N$) with temperature (Table VI), a heat of reaction of 2.7 kcal. is calculated for the reaction

$$\text{mesitylene}\cdot Al_2Br_6(\text{soln.}) = \text{mesitylene}(\text{soln.}) + Al_2Br_6(\text{soln.})$$

TABLE IV

VAPOR PRESSURES AND THERMODYNAMIC DATA FOR DISSOCIATION OF AROMATIC·$Al_2Br_6$ COMPLEXES

| | | | | | | kcal. | |
|---|---|---|---|---|---|---|---|
| | | | | | $\Delta H_D$[b] | $\Delta H_v$[c] | $\Delta H$[d] |
| Benzene·$Al_2Br_6$[a] | | | | | | | |
| Temp., °C. | 0.0 | 10.2 | 18.2 | | 10.13 | 8.09 | 2.0 |
| Press., mm. | 11.65 | 20.4 | 37.05 | | | | |
| Toluene·$Al_2Br_6$[a] | | | | | | | |
| Temp., °C. | 0.0 | 10.3 | 17.1 | 24.0 | 12.20 | 9.08 | 3.1 |
| Press., mm. | 2.35 | 5.50 | 9.3 | 15.15 | | | |

[a] Solid complex. [b] Heat of dissociation: $Al_2Br_6\cdot ArH(s) = Al_2Br_6(s) + ArH(g)$. [c] Heat of vaporization of hydrocarbon from "Selected Values of the Properties of Hydrocarbons," National Bureau of Standards, Circular C461, 1947, pp. 136. [d] Heat of reaction ($\Delta H = \Delta H_D - \Delta H_v$) $Al_2Br_6\cdot ArH(s) = Al_2Br_6(s) + ArH(l)$.

These results indicate that the complexes are all substances of a relatively low order of stability. Unfortunately, because of the characteristics of the different complexes, the data are not directly comparable and it is impossible to use the values to compare the effect of the structure of the hydrocarbon component upon the stability of the product. We are currently extending the inert solvent technique, used for mesitylene, to a number of additional hydrocarbons, in the hope of obtaining quantitative data of this kind.

**Nature of the Aromatic Aluminum Bromide Complexes.**—Eley and King[15] have recently reported a spectrometric investigation of solutions of aluminum bromide in benzene. They find a characteristic absorption band at 2785 Å., which they attribute to $Al_2Br_6\cdot n(C_6H_6)$, with $n$ probably having the value 1. They suggest that this complex is to be distinguished from the product $C_6H_6\cdot AlBr_3$ which both they[12] and Plotnikov[11] report from phase studies.

We do not agree with this interpretation. We believe that our vapor phase–composition studies definitely support the composition $ArH\cdot Al_2Br_6$ for the solid complexes isolated from the benzene- and toluene–aluminum bromide systems. We further propose that the proposed existence of solid complexes $C_6H_6\cdot AlBr_3$[11,12] and $2C_6H_6\cdot Al_2Br_6$[7] be accepted with caution until further confirmatory evidence is available.

In dilute cyclopentane solutions (0.02 mole fraction) mesitylene and aluminum bromide associate to complex to approximately 10% (Table III). Yet in benzene solution the molecular weight data indicate that there must be relatively little association between the aromatic and the halide—that is, the concentration of the $C_6H_6\cdot Al_2Br_6$ complex in the solution must be low. This suggests that there is an increased tendency for the formation of the $ArH\cdot Al_2Br_6$ complexes as one goes from benzene to mesitylene. Many other studies have shown that the basic properties of aromatic hydrocarbons in-

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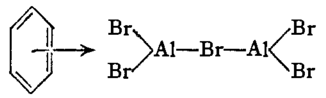
(14) Methods for making such vapor pressure–composition studies under conditions of low vapor pressure are now under development. We hope to be able to utilize these new techniques for a more complete study of the *m*-xylene and mesitylene systems. This work is being carried out in collaboration with Dr. William C. Frith.

(15) D. D. Eley and P. J. King, *J. Chem. Soc.*, 4972 (1952).

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.

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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.

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[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).