A SPECTROPHOTOMETRIC STUDY OF COMPLEXES OF BENZENE WITH FRIEDEL-CRAFTS CATALYSTS

By

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Friedel and Crafts discovered the catalytic effect of various metal halides in the alkylation and acylation of aromatic hydrocarbons. They recognized early that complexes involving the catalyst and other substances present were formed in their reaction mixtures. In the years that have followed, these complexes have been the object of a great amount of study, interest in them stemming, for the most part, from the desire of the investigators to elucidate the mechanism of this family of reactions and the role of the complexes therein.

This study is concerned with complexes involving certain metal halide catalysts and aromatic hydrocarbons. These are divided into two groups designated as pi and sigma complexes, the difference in the composition of the two being that a hydrogen halide molecule is also involved in the sigma complex. This research is further restricted to consideration of the pi complex variety.

Another important difference in the two complex types is the fact that the pi complex is very much less stable than is the sigma. Some pi complexes are thought to be insoluble oils or low-melting solids, as shown in Table 1. This research was an effort to investigate a few of these complexes by a method that has been little used to study them previously, spectrophotometry. On the surface it might appear that such a method is ideal for substances of low stability.

The specific objective of the research was to apply the method of continuous variations of Job to determine the composition of the

Representative Pi Complexes

Complex	Physical Form	Stability	Reference
$AlBr_3 \cdot C_6H_6$	Solid	m.p. 37°C	17, 52, 53
$AlBr_3 \cdot C_6H_6$	In Solution		68
$Al_2Br_6 \cdot (C_6H_6)_2$	In Solution		69
$AlBr_3 \cdot$ (p-xylene)	Solid	m.p. 31°C	54
$Al_2Br_6 \cdot$ (hexaethylbenzene)	Solid		34
$Sb_2Cl_6 \cdot C_6H_5CH_3$	Solid	m.p. 43°C	43
$Sb_2Cl_6 \cdot$ (m-xylene)	Solid	m.p. 38°C	44
$SbBr_3 \cdot C_6H_5CH_3$	Solid	m.p. 9°C	43
$Sb_2Br_6 \cdot C_6H_5CH_3$	Solid	m.p. 39°C	43
$SbBr_3 \cdot$ (m-xylene)	Solid	m.p. 14°C	44
$SbBr_3 \cdot$ (mesitylene)	Solid	m.p. 39°C	45
$Sb_2Br_6 \cdot$ (mesitylene)	Solid	m.p. 36°C	45

TABLE I

complexes of benzene with aluminum bromide, titanium tetrachloride, and possibly similar halides. The use of hydrocarbons other than benzene was also considered as an avenue of attack. The spectrophotometric data were to be used to determine the instability constants of the complexes found. The stabilities of the complexes of a particular hydrocarbon with different catalysts could then be compared. The use of toluene, m-xylene, and mesitylene with a particular catalyst would afford another interesting comparison, but this has already had some study.

Several limitations imposed not only by the method of study itself but by inherent characteristics of the systems under study became evident as the work progressed.

HISTORICAL

Through the years since they were first observed, complexes involving Friedel-Crafts catalysts and aromatic hydrocarbons have commanded much attention in the form of experimental work but also a vast amount of speculation. The speculation has dealt with their role in the catalysis of Friedel-Crafts reactions and, more recently, the isomerization and polymerization of hydrocarbons. The nature of the complexes from the standpoint of their bonding has also received much thought. These remarks are applicable to both the pi and sigma complex types, the distinction growing out of theories regarding their bonding, composition, and catalytic activity and the experimental evidence upon which these theories were based.

As early as 1903, Gustavson ($\overset{4}{2}$9) suggested that complexes between the catalyst and arenes might be intermediates in the Friedel-Crafts reactions. Later many investigators have postulated complex formation between the catalyst and the alkylating or acylating agent. Dougherty (16) suggested the following mechanism for the general reaction:

$$RX + MX_n \rightleftharpoons RX\cdot MX_n \rightleftharpoons R^{+}\ldots(XMX_n)^{-};$$

$$C_6H_6 + MX_n \rightleftharpoons C_6H_6\cdot MX_n \rightleftharpoons (C_6H_5MX_n)^{-}\ldots H^{+};$$

$$(C_6H_5MX_n)^{-}\ldots H^{+} + R^{+}\ldots(XMX_n)^{-} \rightleftharpoons (C_6H_5MX_n)^{-}\ldots R^{+} + H^{+}\ldots(XMX_n)^{-};$$

$$(C_6H_5MX_n)^{-}\ldots R^{+} \rightleftharpoons C_6H_5R\cdot MX_n \rightleftharpoons C_6H_5R + MX_n;$$

$$H^{+}\ldots(XMX_n)^{-} \rightleftharpoons HX\cdot MX_n \rightleftharpoons HX + MX_n.$$

MX_n represents the metal halide catalyst, RX the alkylating or acylating agent, and benzene the aromatic hydrocarbon. A similar mechanism was proposed by Wohl and Wertyporoch (74). The recent literature is replete with such proposals. As seen in the above, both the pi and sigma complexes may be visualized as being involved. Reports in the literature concerning the necessity for the presence of hydrogen halides for complexes involving the metal halide and arene are often conflicting. Recent work such as that employing tritium chloride to show hydrogen exchange between an aromatic hydrocarbon and hydrogen halide (13) indicates complex formation between these components (35, 37). This serves to point out the possible complexity of the ternary systems. Complexes between the metal halide and hydrogen halide, the remaining possibility for complication, have been found absent in inert solvents (9).

The early theories of complex formation were for various reasons inadequate for the purpose of explaining the pi complex in particular. The evolution of the modern concept of the bonding in these complexes began with the proposal by Weiss (1) of the ionic complex theory. His explanation involved the transfer of a single electron from the donor to the acceptor molecule producing an odd molecule and a complex product. The odd molecule accounted for the color in the complex systems. Brachman (5) improved this by a proposal that required only partial ionic character for the complex. According to this theory, the donor compound shares an electron pair with the acceptor, the complex structure being regarded as resonating between no-bond and dative structures. The color is simply a characteristic feature of the complex itself, not being determined by either component alone. These form the basis for the quantum-mechanical treatment in the revised Mulliken theory of complex bonding (46, 47, 48, 49, 50), which is considered to be the most adequate theory to date. Mulliken's conception of the bonding is similar to the Lewis theory of acid-base interaction but lacks the restriction that electron pairs must be shared or that a transferred electron must go from a particular atom in one molecule to a particular atom in the other. The visualization by Schuler (62) of the pi electrons of the aromatic nucleus behaving as a free electron gas responsible for complex formation is an interesting theory also.

Methods of study employed in the past to investigate both the pi and sigma complex systems, and representative references thereon, are: solubility determinations (6, 7, 17, 18, 19, 22, 64), distribution studies (38, 39), vapor pressure measurements (6, 7, 8, 10, 11, 12, 38, 39, 69), melting point-composition studies (30, 31, 43, 44, 45, 52, 53, 54, 61, 65), dipole moment measurements (55, 63, 66, 67, 68), conductivity measurements (4, 25, 35, 49, 51, 56, 72, 73, 74), viscosity measurements (14, 71), and spectrophotometry (13, 17, 21, 37, 57, 58, 59, 60).

The present review will deal only with studies of Friedel-Crafts catalyst-arene complexes in solution. This represents only a small fraction of the total work on binary systems. References cited below give conflicting reports concerning the existence of certain complexes, particularly those of benzene with aluminum bromide and aluminum chloride.

Working with solutions of aluminum bromide in aromatic hydrocarbons, Wertyporoch and Adamus (73) found that these were non-conducting. This may be taken as an indication that the interaction is at most weak. A few years later, Plotnikov and Gitman (51) found that xylene solutions of aluminum bromide do conduct, the conductance being a function of time up to about 20 days. They attributed this conductivity to the formation of a new complex electrolyte.

Viscosity measurements of solutions have also been applied to the study of binary systems. De Carli (14) found by this means that mixtures of stannic chloride and toluene show interaction. Although the data did not prove the existence of a compound, they did indicate that if one is formed its probable composition was $(CH_3C_6H_5)_4 \cdot SnCl_4$. Voskresenskaya, Ravich, and Shternina (71) detected the complex $C_6H_6 \cdot 2SbCl_3$ by viscosity measurements.

By consideration of molar refractions of solutions of aluminum bromide in benzene and toluene, Korshak, Lebedev, and Fedoseev (36) concluded that such solutions do not contain truly definite compounds. They describe the systems in terms of an equilibrium between components and complex which substantially favors the reactants.

Frith and Brown (24) have studied the molecular weight of aluminum bromide in benzene, toluene, m-xylene, and mesitylene. They interpret their results in terms of two reactions, both of which are complex formations. These are:

$$Al_2Br_6 + ArH \rightleftharpoons ArH \cdot Al_2Br_6;$$

$$ArH + ArH \cdot Al_2Br_6 \rightleftharpoons 2ArH \cdot AlBr_3.$$

They believe the dominant reaction in the case of benzene and toluene is the first above, the second appearing most important in the case of the more basic arenes. Brown and Wallace (12) made molecular weight determinations in solutions of mesitylene and aluminum bromide in cyclopentane. A complex having the composition $Al_2Br_6 \cdot ArH$ was indicated. On the basis of a colored solution they postulated the existence of a similar complex for m-xylene.

From vapor pressure measurements of solutions of aluminum bromide in benzene, Van Dyke (69) concluded that a complex is formed having the composition corresponding to one mole of arene per mole of aluminum bromide. The fact that the halide is dimeric in benzene led him to conclude that the addition compound is $Al_2Br_6 \cdot (C_6H_6)_2$. Brown and Wallace (12) also made vapor pressure measurements of this system and that of aluminum bromide-toluene as well. They agreed that complexes are formed but believed their composition is represented by $ArH \cdot Al_2Br_6$.

Solubility determinations have also been used to study the binary systems. Dilke, Eley, and Perry (15) found that a complex between aluminum chloride and xylene is formed very slowly in chlorobenzene solution. If the two components are kept in contact for 24 hours, a red oil is formed. Formation of the oil is slowed down if the vessel is stored in a desiccator over calcium chloride. It was found impossible to accelerate complex formation either by preliminary saturation of the diluent with hydrogen chloride or by the passage of moist nitrogen into the mixture. The complex was also formed only slowly in a high-vacuum apparatus using xylene that had been twice distilled from aluminum chloride. Solubility determinations by Eley and King (17, 18) show that aluminum chloride and aluminum bromide form ideal solutions in benzene, both halides being dimeric in solution. The solubility study of aluminum chloride in benzene by Swan and Garrett (64) is also relevant. They report that hydrogen chloride does not affect the solubility of the metal halide in benzene in the absence of water and oxygen. They describe the effect of water and oxygen as solubilizing agents for aluminum chloride in aromatic hydrocarbons. The conclusion of Schall (59) that water is necessary even for complex formation between benzene, aluminum bromide, and hydrogen bromide is in close agreement with the findings of Swan and Garrett above.

Comments on the solubility study of Fairbrother, Scott, and Prophet (22) will be found in a later section of this paper.

Spectrophotometry has had several recent applications to the study of solutions possibly containing binary complexes of metal halides and arenes. Priest and Schumb (57) used the spectrophotometric method to study the tungsten hexafluoride-benzene system. Solvents used were carbon tetrachloride, cyclohexane, and n-decane. Most liquids used were simply dried over anhydrous calcium sulfate and redistilled. Concentrations used ranged from 0.04 to 0.1 M. Absorbance measurements at selected wave lengths in the visible spectrum appeared to obey Beer's Law. A one-to-one ratio was proposed for the complex observed.

Eley and King (19) applied the spectrophotometric method to the study of complexes of benzene with aluminum bromide, aluminum chloride, aluminum iodide, and ferric chloride. The results they obtained were with solutions of the halides in benzene, the concentrations ranging from 0.005 to 0.05 M. Their use of cyclohexane was hampered by turbidity. They report a complex $(C_6H_6)_n \cdot Al_2Br_6$, in which n was thought to be unity, having a characteristic absorption band at 278.5 mμ. A similar complex was suggested as being possible for aluminum chloride also, though the concentration of this salt in the arene at saturation was too low for detection of the complex. Ferric chloride in benzene was found to have a strong band at about 347 mμ. In the aluminum bromide-benzene system a weak band was also observed at 330 mμ. The authors attributed this to a complex arising from partial hydrolysis of the salt by traces of water. These investigators employed a dry-box technique of cell filling that was found to be satisfactory if used with care.

Schall (59) studied the aluminum bromide-benzene system incidentally to his investigation of the ternary system involving hydrogen bromide also. Using a rather complex apparatus involving many greased joints and stopcocks, he was able to observe no evidence of complex formation between the metal halide and the arene. Since he employed Pyrex cells for his measurements, investigation of the ultraviolet spectrum was beyond his reach. Thus he could not have observed a complex that absorbed in that region.

Reid (58) found complexes of boron trifluoride with benzene and toluene at -80°C by spectrophotometry in hydrogen fluoride solutions. He attributed certain absorption bands to pi complexes and others to various ions in the system. Others report that this metal halide forms no complexes (26) with aromatic hydrocarbons. A difference in the temperatures at which the experiments were conducted may account for the different results, but the presence of hydrogen fluoride in the former experiments seems a highly important factor also.

Luther and Pockels (37) examined systems of aluminum bromide with benzene and toluene. They found an absorption maximum for the benzene solutions in perfect agreement with that found by Eley and King (19). From a consideration of the extinction at this wave length, they concluded that the absorption is due not to a complex but to the high ratio of scattered light to signal energy transmitted by the solutions near the absorption edge of the arene. They demonstrated that such a band could be caused by a difference in path length of 0.001 cm. with pure benzene in both cells.

Comyns, Howald, and Willard (13) have recently observed that toluene solutions of stannic chloride absorb ultraviolet light at higher wavelengths than do either of the components alone. They found the spectrum of such a solution to be unaltered by the addition of hydrogen chloride and by passage of time. They concluded on this basis that ternary complexes for this system either do not exist in appreciable concentrations or do not absorb appreciably above 360 mμ. The composition of the complex was not discussed.

Recently Fairbrother and Field (21), using techniques that should rigidly exclude even trace amounts of water, observed evidence that left "no doubt whatever" that a complex is formed between aluminum bromide and benzene. Their work employed benzene as the solvent. Their evidence for complex formation was a strong absorption edge in the ultraviolet below about 280 mμ. They were unable to read the maximum, however, the absorption below that wave length (280 mμ) increasing continuously into the region where benzene itself began to absorb strongly. They reported that the absorption was spurious and did not obey Beer's Law, the molar extinction increasing upon dilution. The absorption was found to disappear if the solution was diluted with cyclohexane. Evans (20) has explained the false absorption on the basis that such may be observed with photoelectric spectrophotometers having a single monochromator in the region where the solvent itself also absorbs. Experimental basis is cited indicating that this is indeed so. His interpretation of this maximum appears very similar to that of Luther and Pockels (37) regarding their own observations of the aluminum bromide-benzene absorption.

The account of the work of Fairbrother and Field (21) came too late to be of much value in this research. Their method of drying solvents was of particular interest, since something of the same nature had been tried here. A little thought revealed the superiority of their technique. Their drying was accomplished with the anhydrous salt as the final treatment, the solvent being vacuum-distilled from the metal halide solution into a cold trap at -195°C. Their apparatus was also excellent in that the cell was an integral part of it, imposing no problem of transfer from the solution flask.

The literature indicated that information concerning the composition of these complex types might be obtained from solutions in an inert solvent having no absorption in the ultraviolet spectrum if the turbidity encountered by Eley and King and by Schall could be eliminated.

EXPERIMENTAL METHODS

The method of study adopted required that solutions of the components to be complexed be made in an inert solvent. Any spectroscopic-grade aliphatic hydrocarbon would serve as solvent. It was thought desirable to obtain ultraviolet data for the systems to be investigated. This required the use of quartz spectrophotometer cells. The results of Schall (59) and of Eley and King (19) with the aluminum bromide-benzene system indicated that if a pi complex is formed from these its absorption is very near the benzene absorption edge. The plan was then to work with concentrations of this hydrocarbon that could be measured spectrophotometrically. Thus it would be possible to scan the entire ultraviolet region and observe any changes that might occur in the benzene spectrum.

The work with m-xylene, mesitylene, and with titanium tetrachloride-hydrocarbon systems was purely exploratory, no spectrophotometric data on these being available. Since the more stable complexes absorb at longer wave lengths, it was thought that complexes of the more basic aromatic hydrocarbons would have absorption bands more removed from the absorption of the hydrocarbon itself than would those of benzene. Other things being equal, they should thus more readily lend themselves to study by the method of continuous variations.

The Spectrophotometric Method

The Method of Continuous Variations. This method, first suggested by Job, has been widely used in the study of other complex systems. The method, its limitations, and its applications in terms of use with spectrophotometric data are well elaborated in the more recent literature by Vosburgh and Cooper (70) and by Harvey and Manning (32).

Consider the reaction

$$A + nB \rightleftharpoons ABn.$$

The problem with which we are concerned is the determination of the value of n. This can be accomplished by mixing solutions of A and B of the same concentration in varying proportions and measuring some property of the resultant mixture. This measured property must be quantitatively different for AB_n than for A plus nB. In the application of spectrophotometry to the method the measured quantity is light absorption. This requires that some wave length be found at which the absorption of the complex varies significantly from the sum of that of A and B. The difference between the actual extinction of mixed solutions of A and B and the calculated value assuming no interaction may be designated as Y. If this value Y is plotted against composition for a series of mixed solutions, the resulting curve will have a maximum if the extinction of the complex is larger than the sum of those of the components or a minimum if it is smaller. The concentration of the complex will be greatest at the maximum or minimum in the curve, and the value of n may be determined from the position of the highest concentration.

In the reaction shown let the equilibrium concentrations of A, B, and AB_n be c, c_2, and c_3 respectively. The equilibrium constant is then given by the expression

$$k = \frac{c_3}{c\ c_2^n} . \qquad (1)$$

Solutions of A and B in an inert solvent are made such that M and M_2 are the original concentrations of A and B. In preparing the mixed solution for complexing, let x liters of A and 1-x liters of B be used. The solutions are now mixed according to the above conditions so that the total volume of the mixture is constant throughout a particular series of solutions. The equilibrium concentrations may be expressed in terms of the original concentrations and volumes as below.

$$c = M\ (1-x) - c_3 \qquad (2)$$

$$c_2 = M_2x - nc_3 \qquad (3)$$

$$c_3 = kcc_2{}^n \qquad (4)$$

Differentiation of equations 2, 3, and 4 yields:

$$\frac{dc}{dx} = -M - \frac{dc_3}{dx}; \qquad (5)$$

$$\frac{dc_2}{dx} = M_2 - n\frac{dc_3}{dx}; \qquad (6)$$

$$\frac{dc_3}{dx} = kncc_2{}^{n-1}\,\frac{dc_2}{dx} + kc_2{}^n\,\frac{dc}{dx}. \qquad (7)$$

Substituting into equation 7 the values given in 5 and 6, one obtains

$$\frac{dc_3}{dx} = (kncc_2{}^{n-1})(M_2-n\frac{dc_3}{dx}) + (kc_2{}^n)(-M - \frac{dc_3}{dx}).$$

If c_3 is a maximum, dc_3/dx is zero. Imposing this condition yields

$$(kncc_2{}^{n-1})(M_2) - (kc_2{}^n)(M) = 0,$$

and

$$M_2ncc_2{}^{n-1} - Mc_2{}^n = 0.$$

Substituting into this the values of c and c_2, one obtains

$$nM_2\ (M(1-x)-c_3)(M_2x-nc_3)^{n-1} - (M_2x-nc_3)^n(M) = 0,$$

$$\frac{nM_2(M(1-x)-c_3)}{M_2x-nc_3} - M = 0,$$

$$\frac{nM_2(M(1-x)-c_3)}{M(M_2x-nc_3)} = 1,$$

and

$$nMM_2-nMM_2x-nM_2c_3 = MM_2x-nMc_3.$$

If x' is the value of x at which c_3 is a maximum as has been specified, and if M and M_2 are made equal to start, then

$$n(MM_2-MM_2x') = MM_2x'.$$

Solving for n then gives

$$n = \frac{x'}{1 - x'} .$$

From the definition of Y, it can be seen to be dependent only on c_3, so that when $dc_3/dx = 0$, $dY/dx = 0$ also. Thus from a plot of Y against x, the values of n can be calculated using that value of x for which Y is either maximum or minimum.

Determination of the Instability Constant. The method intended for use in this research is that of Foley and Anderson (23). It is based on changes in the degree of dissociation of the complex with changes in concentration. If a solution of A and B is prepared such that the ratio of B to A is n and this solution is then diluted with more solvent, the degree of dissociation increases. If a solution can be prepared such that the degree of dissociation is zero or very small, the extinction coefficient of the complex can be calculated. This quantity being known, it would then be possible to calculate the degree of dissociation at all other concentrations. Consequently, the instability constant can be determined.

In the equation for the reaction of A and B to give a complex AB_n, let c be the concentration of complex showing no dissociation. Let the degree of dissociation be a. Then at equilibrium

$$(1-a)\,c = \text{concentration of } AB_n,$$

$$ac = \text{concentration of } A,$$

and

$$nac = \text{concentration of } B.$$

Let E, E_2, and E_3 be the extinction coefficients of A, B, and AB_n

respectively; then from the definition of Y as being the actual extinction minus the calculated extinction for no reaction, it follows that

$$Y = acE + nacE_2 + (1-a)cE_3 - (cE + ncE_2),$$

and

$$Y = (1-a)\ c\ (E_3 - E - nE_2).$$

The value of the quantity $(E_3\text{-}E\text{-}nE_2)$ can be determined from the value of Y when a is equal to zero. The value of a at various concentrations may then be determined from the value of Y. The instability constant can then be calculated using the relationship

$$k = \frac{n^n\ a^{n+1}}{1 - a}\ c^n.$$

Other methods are available that accomplish the same end should this one prove troublesome. The situation can be complicated by the existence of two or more complexes in a solution at the same time. Such systems can still be treated, however, by making certain assumptions.

Preparation and Purification of Chemicals

Solvents. Cyclohexane and heptane both were used as solvents in the experiments. The cyclohexane used was Phillips spectro-grade and was subjected to no purification other than drying. The heptane used was initially Eastman Kodak practical-grade heptane from petroleum. This was purified by treatment with fuming sulfuric acid with vigorous stirring for several hours followed by three washings with aqueous sodium carbonate and an equal number of washings with water. It was then filtered through phosphorus pentoxide into a distilling flask and distilled from shreds of sodium metal. The distilled heptane was collected until samples gave spectral evidence of traces of some impurity absorbing below 250 mμ. The solvent remaining in the stillpot was recycled with the next batch treated.

Cyclohexane after use was shaken with a little water to destroy the remaining catalyst, the solid hydrolysis products were filtered off, and the solvent was treated with fuming sulfuric acid, etc. as described for the heptane above. Both the heptane and cyclohexane so treated were as transparent as, or slightly more than, the original spectroscopic-grade cyclohexane above 220 mμ. Since aromatic hydrocarbons are air-oxidized to phenols in trace amounts in the presence of metal halides such as those used, the distillation of the solvent from an alkali metal is an essential part of the purification of the used solvent. It may be so treated either before or after the sulfuric acid treatment. Distillation from sodium after the water washings, however, seems best since the solvent is thus partially dried in the final purification step.

In the early experiments attempts to dry the solvent by the action of the metal ketyl formed from sodium-potassium alloy and benzophenone were made. This was the method used by Schall (59) and should be most effective in the removal of water since the drying agent (a free radical) is actually in solution. This should greatly complement the drying action of the sodium-potassium alloy itself. Since measurements in the ultraviolet region of the spectrum were the aim of this research, it was imperative that the solvent come through the drying stage optically pure. The spectrum of the cyclohexane after treatment with the ketyl showed an appreciable amount of benzene to be present, the exact amount apparently depending upon the concentration of ketyl in the stillpot. This drying method was therefore abandoned, the solvents thereafter being simply stored over phosphorus pentoxide.

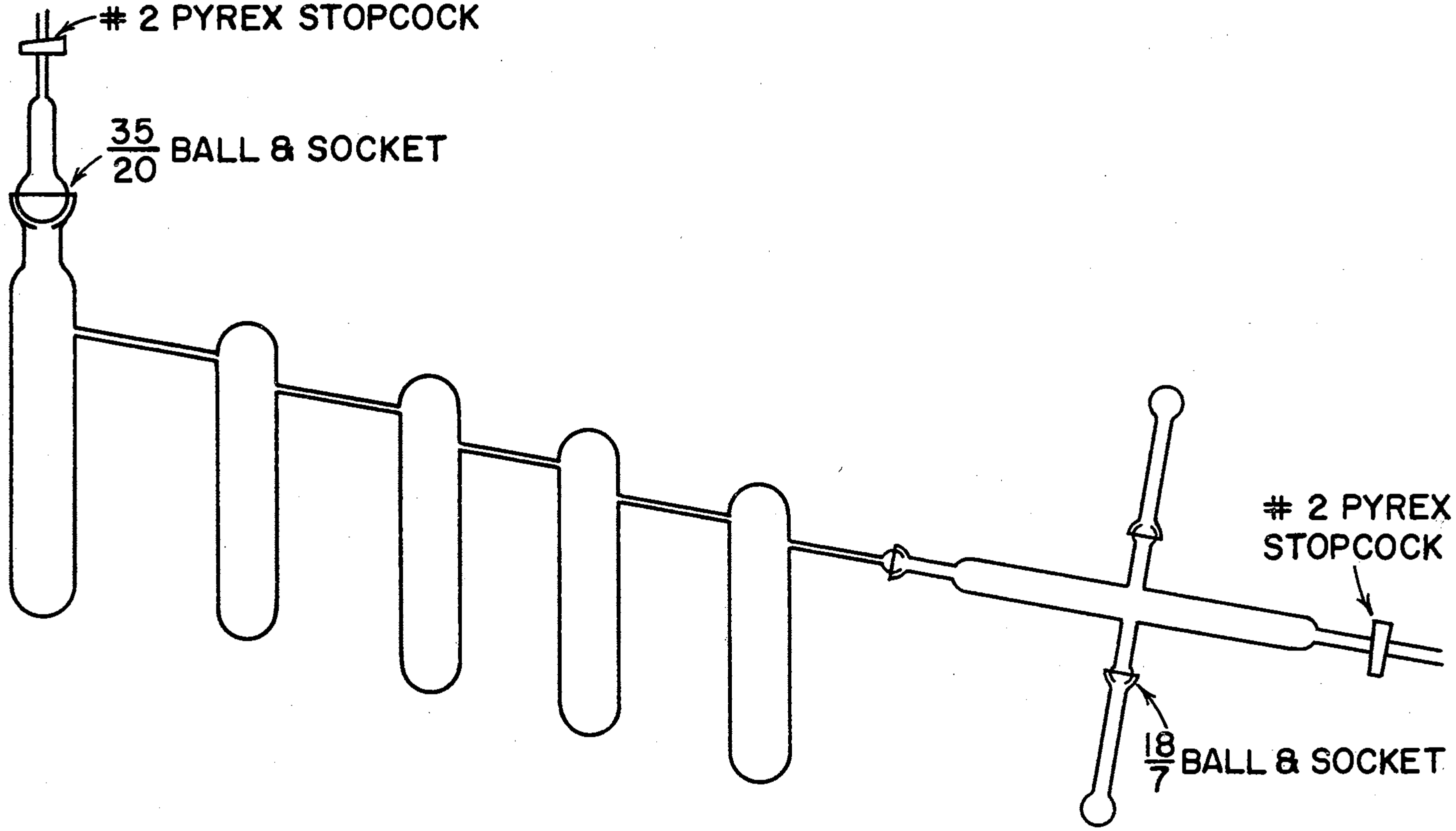
<u>Aromatic Hydrocarbons</u>. It was not thought that chemically pure grade aromatic hydrocarbons would contain sufficient impurities to

warrant purification for the purpose of this research. Thus the arenes used were subjected to no purification other than drying.

Merck reagent-grade thiophene-free benzene was used in the experiments. The m-xylene and mesitylene used were Matheson, Coleman, and Bell reagent-grade compounds. Drying of these was first attempted with phosphorus pentoxide. In the benzene the phosphorus pentoxide became slightly discolored, was more discolored in m-xylene, and became a mass of reddish-brown gum in mesitylene. No attempt was made to account for this. Complex formation might be suspected here also. The drying of the benzene was thereafter done with a very fine potassium sand, the m-xylene and mesitylene with sodium sand.

Catalysts. The aluminum bromide used was prepared in the laboratory by reaction of bromine and aluminum turnings in an atmosphere of dried nitrogen. The apparatus was constructed as shown in Figure 1. After bromine had been added to excess aluminum, the remaining bromine vapor was swept from the system by a stream of dried nitrogen. The product was then distilled through the four tubes and finally collected in ampoules which were sealed off for storage. These large ampoules contained about 5 grams of aluminum bromide each.

The apparatus for the preparation of the weighed aluminum bromide samples was similar to that shown in Figure 1 but was only large enough for handling the amount of catalyst contained in one of the large ampoules. The catalyst was again distilled five times and samples of varying sizes collected in the attached tubes which were accurately weighed previous to filling. After these ampoules had been sealed off, the stem of each was washed, dried by flaming, and weighed after cooling with the sealed ampoule, the weight of the metal halide being obtained by



ALUMINUM BROMIDE
PREPARATION AND PURIFICATION

FIGURE I

difference. The samples so prepared were white, crystalline aluminum bromide. Discolored samples were used only for practice solutions.

The titanium tetrachloride used was Fisher Scientific Company chemically-pure grade. It was distilled five times and collected in ampoules as was the aluminum bromide, the same apparatus being used. The samples of this halide were initially clear and colorless but became a little yellow in the ampoule after a few hours. The compound before distillation had been clear and colorless. Perhaps it would have been as well to inject the titanium tetrachloride directly from the stock bottle into the carefully dried ampoules with a hypodermic syringe and long needle. By using a 1-ml. syringe and teflon plug for the needle, it might also have been possible to weigh this catalyst directly into the solution flask from the syringe by difference, thus avoiding altogether the use of ampoules. Could this be done, solid halides might be handled in like manner by the use of concentrated solutions in the solvent employed for the study if their solubilities would permit the preparation of such concentrated solutions.

It was planned in the beginning that some experiments with aluminum chloride and ferric chloride as the Lewis acid would also be made. It was later decided that neither of these would be used because of their slight solubility in the inert hydrocarbon solvents, although this fact does not rule out the possibility of their use.

Nitrogen. The nitrogen used was ordinary Linde water-pumped nitrogen. It was purified and dried by passing it first through a fine glass frit at the bottom of a one-foot tower of pyrogallol, through fine frits into two one-foot towers of concentrated sulfuric acid, and finally through about an eight inch column of phosphorus pentoxide.

Apparatus and Procedure

The development of the apparatus used in this research began with efforts to simplify Schall's (59) apparatus. In order to avoid an analysis of the metal halide solutions, it was proposed to make them up to the desired concentrations volumetrically by using the weighed ampoules previously discussed. The solutions of the aromatic hydrocarbons were also prepared volumetrically. The error in concentrations of the resultant solutions so prepared was not thought serious enough to cause difficulty in interpretations of data for the method of continuous variations. The concentrations of the aromatic hydrocarbon could be checked spectrophotometrically for solutions from which equilibrium data were to be obtained.

Since the initial apparatus proved too complex and was ultimately very greatly simplified, it will merely be described rather than represented by diagram here. It consisted of a distillation apparatus, the stillpot of which could be charged either with the ketyl of sodium-potassium alloy and benzophenone or with phosphorus pentoxide. Two short condensers topped the stillpot, the first providing for refluxing, the second for condensing the solvent. This then drained through a 12/5 $ ball-and-socket joint into a 500-ml. solvent storage flask through a No. 2 Pyrex stopcock. Provision was made so that parts of the apparatus other than the stillpot could be flamed at reduced pressure to dry them and so that they could be filled with dried nitrogen while cooling. A constant pressure of nitrogen was maintained inside the apparatus during the cooling and during the distillation.

For the benzene solutions, the aromatic hydrocarbon and the solvent were distilled together in the apparatus above, the solvent in these solutions being cyclohexane. The vapor pressure curves of benzene and cyclohexane are so nearly identical that it was thought a dilute solution of benzene in cyclohexane could be distilled from the drying agent without significant change in concentration. This was shown to be the case. The solutions so distilled were stored in a 200-ml. flask.

Metal halide solutions were prepared by the use of a 50-ml. Pyrex burette. This was attached at the upper end by a 12/5 **S** ball joint to the solvent storage flask through a 7-mm. tube with a No. 2 Pyrex stopcock, this drain tube being ring-sealed into the storage flask near the top of the bulb to minimize contact of the solvent with the stopcock lubricant. At the bottom end the burette was attached through a 12/5 **S** ball joint to a 100-ml. catalyst solution flask. The top of this flask was a 35/20 **S** ball joint, the male or upper portion of which bore a No. 2 Pyrex stopcock through which the solvent entered. The tube through which the solvent passed from the flask into the measuring device was similar to that described for the aromatic hydrocarbon solution flask. The large joint allowed the ampoule to be placed in the flask. Drying was accomplished again by flaming at reduced pressure and cooling under a slight nitrogen pressure, the ampoule being placed in the flask after cooling. Solvent was then forced into the burette and metal halide solution flask by nitrogen pressure on the liquid in the solvent storage flask.

Mixing of solutions was accomplished by passing measured amounts of each into a mixing flask. A single 5-ml. burette fitted at the top with a Y bearing 12/5 **S** socket joints on its upper arms and at the bottom with a two-way diagonal opening capillary Pyrex stopcock was the measuring device. One arm of the stopcock led to the mixing flask, the other to a joint to which a waste flask was attached. The waste flask provided not only for disposal of excess solutions in the burette but also for drying the burette by rinsing with the salt solution. The mixing flask of about 200 ml. capacity was detachable through an 18/7 S ball joint above a No. 2 Pyrex stopcock. Provision was made also on the mixing flask for a means of cell filling.

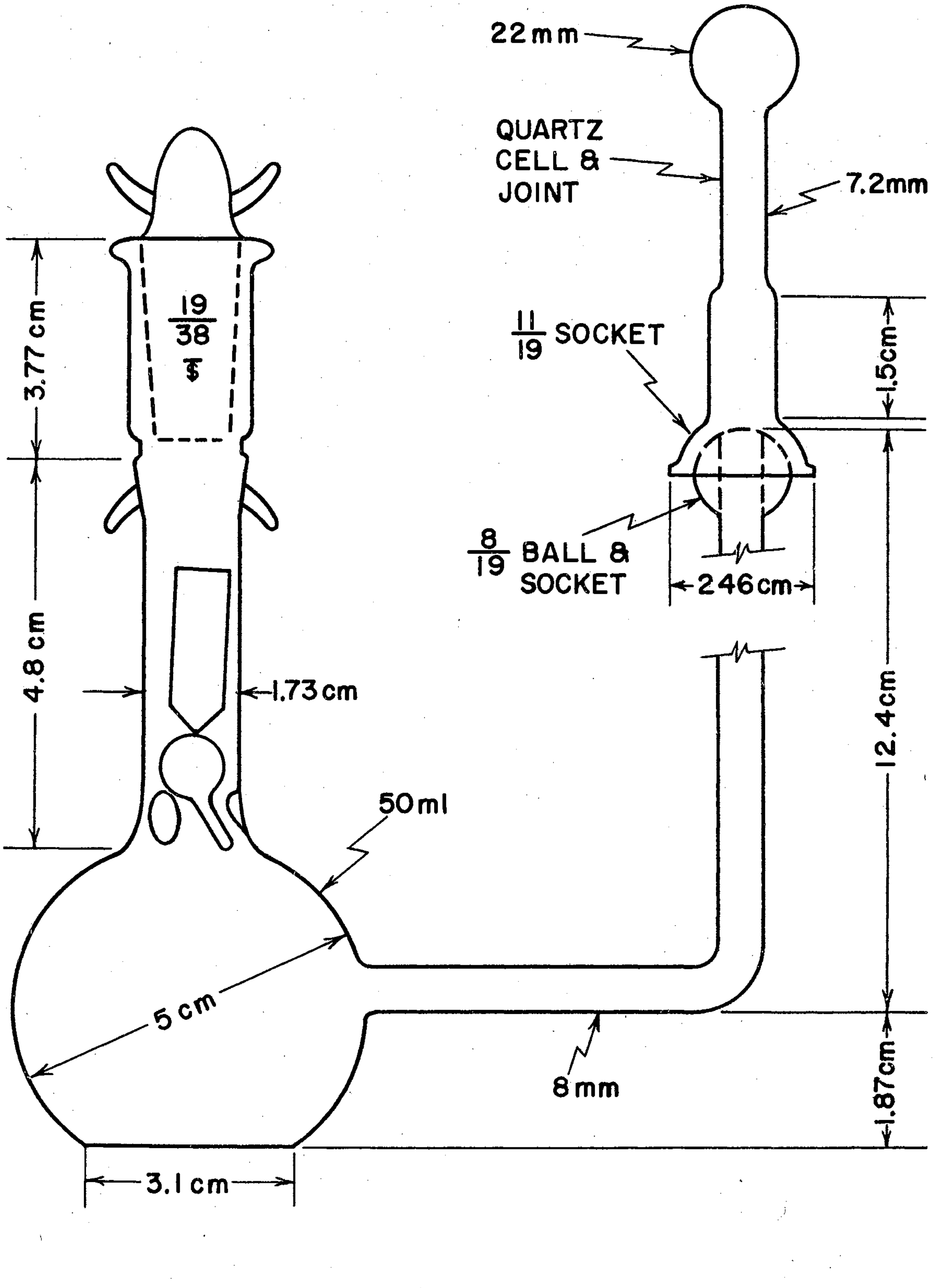
In the early experiments efforts were made to use an ordinary rectangular, open-top quartz cell for the solutions, employing various means of capping and drying. Since Eley and King (19) had reported some success with a dry-box technique of cell filling, a small dry-box was constructed for this work. No success was ever attained with the rectangular cells. A cell was then designed that could be attached to the mixing flask through an 18/7 S ball joint. This cell, having a path length of 1 cm., was constructed by Pyrocell Manufacturing Company, 207-11 E. 84th Street, New York 28, New York. In Figure 2 this cell is shown attached to a solution flask discussed later. Used with the apparatus just described, the new cell could be filled with a clear solution of the anhydrous salt, and this remained clear longer than necessary for the spectrophotometric measurements.

There remained at this stage only one apparent difficulty in the method. The metal halide solutions were always slightly yellow even when clear. At this time aluminum bromide was the only halide being used. Because of other observations this yellow color was attributed to the action of the metal salt upon the Dow-Corning High Vacuum Silicone Grease being used as stopcock and joint lubricant. Other lubricants were tried, but clear solutions then could not be obtained. The nitrogen atmosphere inside the apparatus had been abandoned by this time.

The procedure remained much the same as that described except that vacuum was now used to "pull" the liquids or solutions from one container to another, rather than nitrogen pressure to force them through. It was thought that this would eliminate a source of trace amounts of water vapor. The opposite effect may have been achieved in reality, the use of the vacuum increasing diffusion of water-bearing air into the system.

At this point a choice appeared to be necessary. The alternatives were to eliminate the necessity of stopcock and joint lubricant by drying and cooling in a stream of dried nitrogen and lubricating with just enough graphite to prevent sticking, or to revise the apparatus drastically. The latter route was chosen.

The results of this revision are shown in Figure 2. The new apparatus consisted of a single flask to which the cell was attached directly by means of the 18/7 ₷ ball joint on the side arm. The two joints on this flask were lubricated with graphite. Before use the flask was thoroughly cleaned with alcoholic potassium hydroxide cleaning solution, well rinsed several times with water, and dried in an oven at 150°C for 3-4 hours. The clean cell was dried in the oven along with the flask. When removed from the oven the cell and flask were attached to a fitting that permitted evacuation while both were being flamed. Immediately on completion of the flaming, dried nitrogen was allowed to fill the flask and a small nitrogen pressure was maintained while the flask and cell cooled. After cooling, the ball joints were detached and the cell very quickly clamped in place. The tapered stopper was then removed, the ampoule and breaker were quickly put in place, these being taken directly from an oven at 100°C, and the flask was stoppered. The flask was then clamped upright on a ring stand and dried solvent in the required amount



REACTION FLASK AND CELL

FIGURE 2

added by means of a well dried burette or hypodermic syringe through the tapered joint. The required amount of aromatic hydrocarbon was then added through this same joint by pipette. The joint cap was kept in place as much as possible during these additions. The volume of aromatic hydrocarbon was so small that it was best added in solution in the solvent. This made possible the use of a small syringe for this addition also. The syringe was superior to the burette or pipette in that it could be dried by rinsing with the halide solution, then with the solvent, before use.

After the components and metal halide ampoule were added to it, the flask was bounced so that the glass breaker crushed the bulb of the ampoule. The walls of the flask were then rinsed by splashing. After complete solution of the salt, enough solution was poured over into the cell to fill it, the whole assembly was fitted into the extended cell compartment of the spectrophotometer, and the desired measurements were made. The ratio of the reactants had to be changed for the next measurement. The hydrocarbon concentration could be adjusted upward to any desired value by simply adding more of it, either pure or in solution. The halide concentration, however, could be adjusted only downward to any desired concentration, this being done by dilution. The solution was thus made so that initially the ratio of the concentrations of metal halide to arene was high. The ratio was adjusted to lower values by simultaneously diluting with respect to the salt and increasing the concentration of the arene. Quantities needed were calculated and added through the tapered joint by pipette or syringe, dilutions being continued on a solution until turbidity developed. When this occurred, a new solution having the next lower ratio was prepared and diluted as needed until it became turbid also.

For the continuous variations data, the increment of concentration change was 0.001 M. The molecular weight of aluminum bromide was taken as 533.4 since it is widely reported to exist as the dimer in hydrocarbon solvents. Concentrations of solutions from which equilibrium data were sought depended upon quantitative indications from the continuous variations data concerning the extinction of the complex.

Spectrophotometers used were the Beckman Model DU with a photomultiplier attachment and the Beckman Model DK-1. The Model DK-1 is a recording instrument very useful for scanning. The Model DU was to be used for quantitative work at selected wave lengths.

Experimental Difficulties

To treat the most persistent difficulty first, turbidity will be discussed briefly. The early work was hampered by this continually. Schall (59) and Eley and King (19) also attest to the difficulty of preparing clear solutions of aluminum bromide in cyclohexane. The discovery of the contamination of the solvent by the ketyl mentioned previously came early in the work, so that no attempts were ever made to prepare a solution of the metal halide in the solvent so dried. Clear solutions with the old apparatus and solvent dried with phosphorus pentoxide were finally achieved but not consistently. Even the solutions that were usable were slightly turbid when fresh, this turbidity disappearing after two or three hours. Once the solution had cleared it could be run through the apparatus as indicated in the procedure and loaded into the cell without again becoming turbid at any point. This was taken as an indication that the turbidity did not result from hydrolysis by water absorbed on the glass but from inadequately dried solvent. The solvent was thereafter stored over phosphorus pentoxide even before distillation. Nevertheless, preparation of clear solutions remained uncertain.

It seemed that the best possible drying agent for the solvent should be the anhydrous salt itself. Consequently, an effort was made to use aluminum chloride to dry the cyclohexane. The apparatus for this was arranged so that a vacuum could be attained in all parts but the stillpot itself, this being attached to the rest of the apparatus through a large-bore Pyrex stopcock. After the rest of the apparatus had been evacuated, this stopcock was opened, allowing the air in the pot to be displaced by solvent vapor. The stopcock was again closed and the pumping resumed. This was repeated several times. Finally, the solvent was distilled by the application of a little heat and collected in a reservoir cooled in an acetone-dry ice bath. Some of the aluminum chloride sublimed into the solvent reservoir with the solvent. Similar results were obtained with aluminum bromide as the drying agent. The solvent in the reservoir after such a distillation was clear though contaminated with the metal halide, proving that it was dry. The contamination, however, caused abandonment of the method.

After revision of the apparatus, several clear solutions were made and used employing aluminum bromide and benzene. Turbidity was no longer a problem. Work was then started involving aluminum bromide and m-xylene. Turbidity again became troublesome. With this system the turbidity again disappeared on standing for a few hours. This time, however, a condensate in the form of an orange oil could be seen on the flask walls after the turbidity had disappeared. Careful examination of the freshly prepared turbid solutions revealed that the dispersed particles did not appear to be solid material. This was taken to mean that the complex in this system was insoluble in cyclohexane. This was shown spectrophotometrically in that the absorption attributed to the complex did not change quantitatively with changes in the concentrations of the components. The same situation was found to exist in the aluminum bromide-mesitylene system. In order to apply the method of continuous variations to these systems, the concentrations of the components would have to be decreased by a factor of ten at least. The concentrations for these solutions ranged from 0.01 to 0.001 M. Further reduction seemed inadvisable since hydrolysis would make these lower concentrations very uncertain at best.

Attention was turned at this point to the use of titanium tetrachloride as the Lewis acid. Turbidity returned to plague the experiments as never before. No solutions were obtained using this halide that could be used for spectrophotometric measurements.

Stopcock lubricants were the other point of difficulty in this research. It has been mentioned that Dow-Corning High Vacuum Silicone Grease apparently reacts with aluminum bromide. The lubricant, Non-aq, sold by Fisher Scientific Company was also tried. The apparatus could not be flamed well when this lubricant was used since it stiffened and charred upon the application of much heat. Otherwise, it appeared usable. It was shown not to react with aluminum bromide in solution. Graphite, graphite in mineral oil, and aluminum palmitate in mineral oil were also tried but found unsuitable. The problem was best dealt with by removal, as nearly as possible, of the need of a lubricant.

RESULTS AND THEIR INTERPRETATION

The Aluminum Bromide-Benzene System

This system was chosen for study first because some information concerning applications of spectrophotometry to it was available in the literature. This provided a means of comparing data with those of other workers and thus checking techniques.

In order to determine whether or not a complex was formed between these components in dilute solutions in an inert solvent, a 0.005 M metal halide solution was made in cyclohexane and its spectrum determined on the Beckman Model DK-1 from 2500-220 mμ. All aluminum bromide concentrations are in terms of the molecular weight of the dimer. Enough benzene was then added to make the solution 0.005 M in this component also. The spectrum was redetermined. The solution had no visible color. The metal halide was then destroyed and removed and the spectrum of the benzene alone in the solvent was obtained. No absorption bands appeared in the spectrum of the components together that indicated complex formation. The addition of curves showing the absorption of the components singly gave a curve that corresponded within the limits of experimental error to the curve obtained for the mixture. On this basis it was concluded that no complex absorbing light between the above wave length limits is formed between these components in solution at low concentrations in an inert solvent. This was considered in agreement with the finding of Fairbrother and Field (21) that the absorption exhibited by a solution of aluminum bromide in benzene disappeared upon dilution with cyclohexane. This may be due to dissociation of the complex, but it may also be due to the fact that after the solution is diluted the absorption edge of the benzene occurs at shorter wave lengths. This might effect the removal of the false absorption to which the peak at 278.5 mμ in the solutions in pure benzene has been attributed (20, 37).

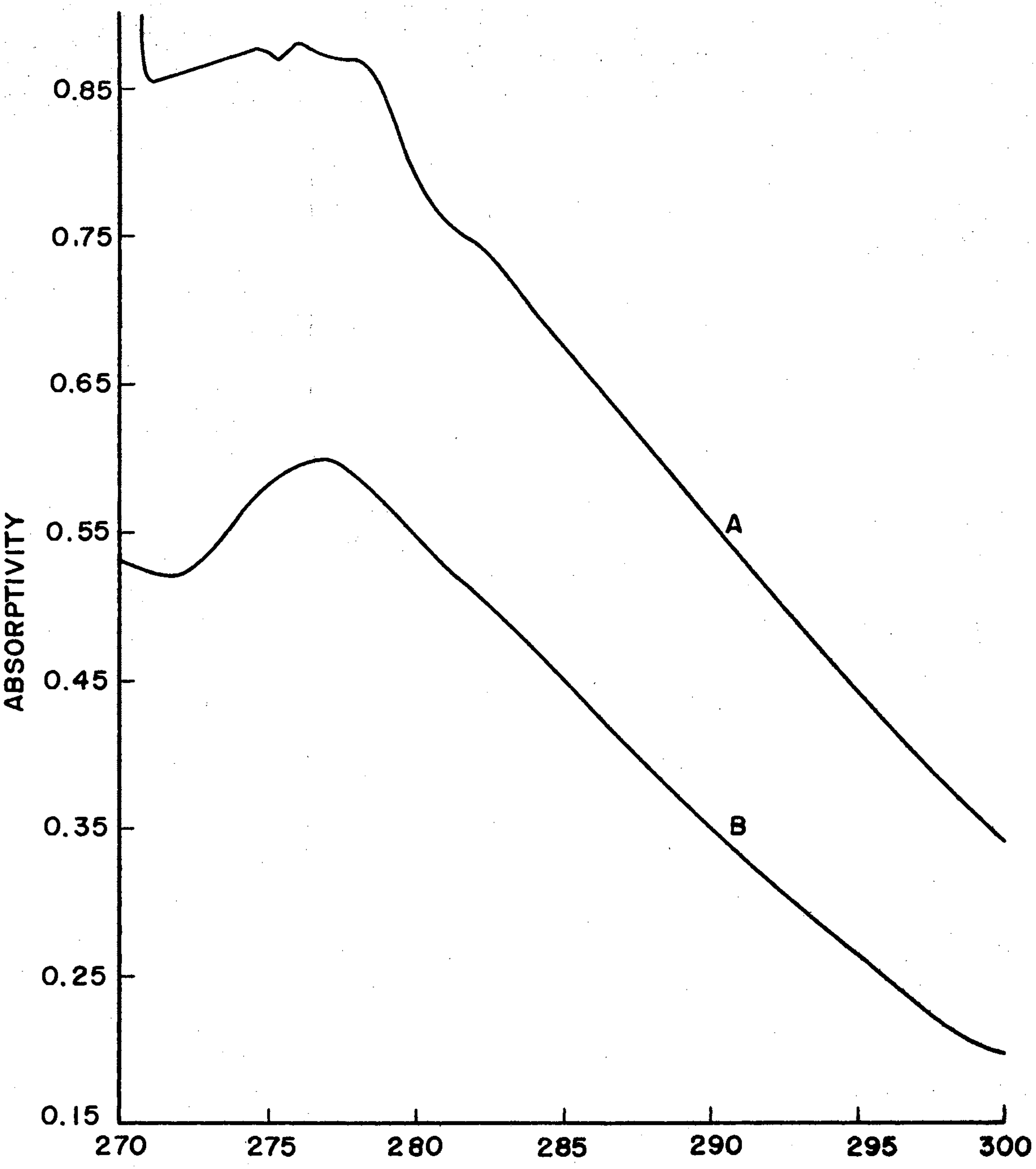
In the light of the above findings it was decided to experiment with more concentrated solutions. A clear 0.2 M solution of aluminum bromide was prepared and its spectrum determined. This showed an absorption maximum at about 304 mμ. Benzene was added to make the solution 0.8 M in this compound and the spectrum determined again. The band at 304 mμ then appeared shifted to a shorter wave length by about 3-4 mμ. There appeared also a weak absorption not attributable to either of the components singly at about 417 mμ, this showing up as a small plateau in the side of the aluminum bromide band having a maximum at 304 mμ. An approximate one-to-one dilution of this solution was made using cyclohexane and the spectrum redetermined. The decrease in the absorption at 417 mμ was proportional to the decrease in the benzene absorption maxima at 1654 and 2125 mμ. This plateau, coming as it did on the edge of the other absorption band, did not seem promising.

It was thought that some experiments should be run on aluminum bromide solutions in benzene in order to compare methods and data with those of Eley and King. The first step in doing this was the preparation of a 0.01 M solution of aluminum bromide in benzene. Its spectrum was scanned, pure benzene being used as the reference. The solution began to absorb strongly at about 360 mμ, and at 317 mμ the optical density exceeded 2. The solution did not transmit wave lengths shorter than this down to 260 mμ where measurement was stopped. No characteristic absorption was observed between 2500 and 360 mμ. Two indistinct plateaus were observed in the ultraviolet benzene absorption edge, one occurring at about 440 mμ and the other at about 530 mμ.

In order to observe the absorption maximum for the above edge, less concentrated solutions were obviously needed. The next solution prepared was approximately 0.005 M in aluminum bromide, no great care being taken with respect to concentrations in these exploratory experiments. The optical density did not exceed 2 this time until about 308 mμ was reached. The solution did not transmit light of wave lengths shorter than this down to 260 mμ where measurement ceased as before. The two plateaus mentioned above were still evident, the one at about 530 mμ having become still less distinct. Solutions still more dilute were needed. A 0.002 M solution was next prepared and its spectrum determined. This time the wave length of 300 mμ was reached before the optical density exceeded 2. The plateaus on the absorption edge of the metal halide still were visible, but they apparently did not obey Beer's Law.

The next solution prepared was 0.001 M in aluminum bromide. The spectrum revealed that the faint plateaus could no longer be seen and that the previously observed absorption edge had a maximum at 278 mμ, this being considered in agreement with the 2785 Å maximum for the absorption from the literature (19, 37). On the short wave length side of the maximum the absorption fell rather sharply until it reached the benzene absorption edge at about 273 mμ, where the benzene cut off light transmission altogether. The portion of this spectrum from 290 to 273 mμ is shown in curve A of Figure 3, the wave length axis being much expanded. Curve B in Figure 3 is the portion of the spectrum of the same solution after about 12 hours in the cell. This time, measurement was possible down to a wave length of about 261 mμ before the optical density exceeded 1. This difference was difficult to understand, particularly the cut-off value. The reference cell was always fitted into the cell compartment in a position subject to practically no variation from one measurement to another and could be filled to the same level for each measurement. Although this was not possible to nearly the same degree with the sample cell, it was not thought that the large difference in the spectra could be accounted for on this basis. The time necessary for the establishment of equilibrium in solution was considered as a possible factor, but the direction of the change with time was the reverse of what might be expected from this point of view. The quantitative change in absorption was thought to be due to the precipitation of a small amount of solid material that was observed on the bottom of the cell.

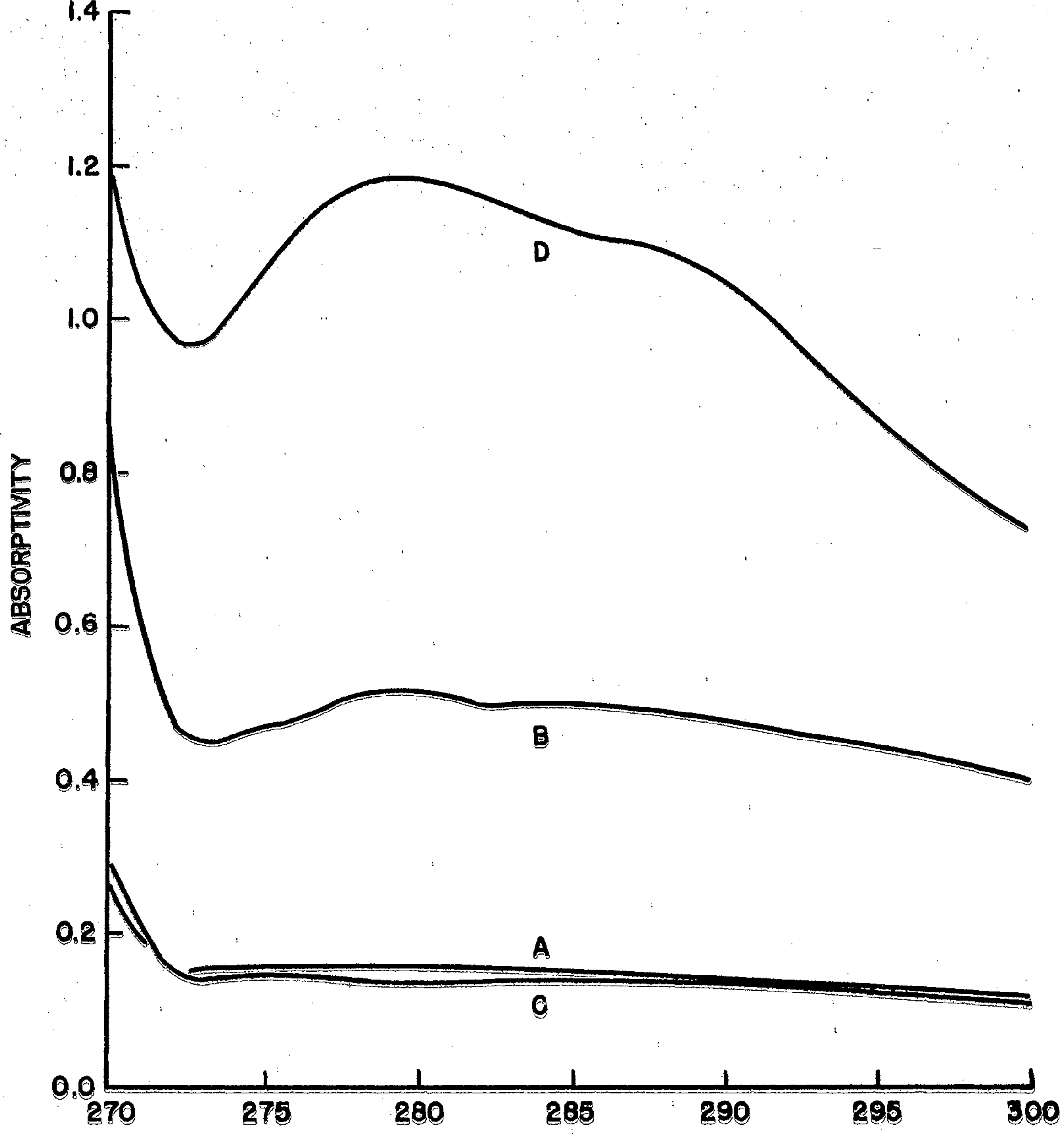
To examine this change further and to get an indication as to whether this absorption followed Beer's Law, a new solution of aluminum bromide 0.0015 M in benzene was prepared. The spectrum after one hour did not show the definite sharp band obtained from the previous solution. The interesting portion of the spectrum is shown in Figure 4. The curves showing peaks were obtained after the solution had been several hours in the cell. Curve A in Figure 4 is the spectrum of the solution one hour after its preparation. There was at this time no visible evidence of hydrolysis if it is assumed that the color of the solution is due to a binary complex and not the presence of traces of water. Curve B in this figure is the spectrum of the same solution 13



0.001 M Al_2Br_6 IN BENZENE

CHANGE IN ULTRAVIOLET CUT-OFF WITH TIME

FIGURE 3

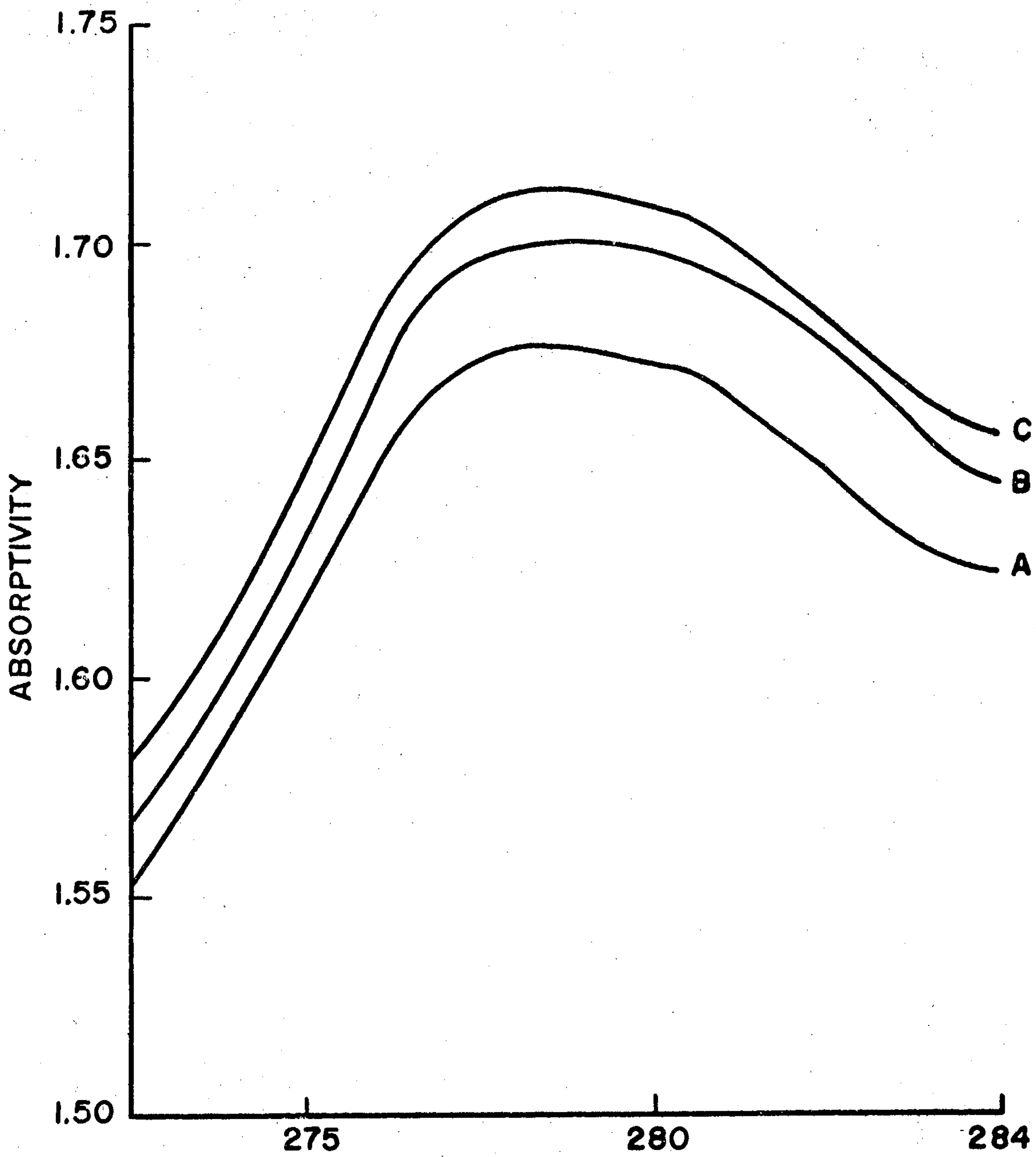


WAVE LENGTH IN MILLIMICRONS

0.0015 $\underline{M}$ Al_2Br_6 IN BENZENE

EFFECT OF DIFFUSION UPON 278 mμ MAXIMUM

FIGURE 4



WAVE LENGTH IN MILLIMICRONS
0.0015 M Al_2Br_6 IN BENZENE
36 HOURS OLD
TEMPERATURE EFFECT ON ABSORPTIVITY

FIGURE 5

hours old, twelve of which were spent in the cell. There was a small amount of flocculent solid on the bottom of the cell when these measurements were made, indicating some hydrolysis. After the solution was 24 hours old, the cell was filled with a fresh portion and its spectrum run. This is shown in curve C of Figure 4. The filled cell was stored in a desiccator overnight. When the spectrum was determined again the following day, the solution was 36 hours old. The spectrum is shown in Figure 4, curve D. The cell was always stoppered with a male joint while it contained a solution or with the flask itself. A flocculent residue on the bottom of the cell when curve D was obtained again indicated hydrolysis of the metal halide. Thus a definite relationship was indicated between hydrolysis and the appearance of the absorption maximum at 278 mμ. The maximum apparently does not obey Beer's Law.

The curves in Figure 5 were obtained from the same solution that gave curve D in Figure 4. They were obtained by re-running that portion of the spectrum as rapidly as possible three times. The difference is thought to be due to temperature changes of the solution while in the cell compartment. The letters indicate the order in which the curves were obtained. No more than three minutes were required to obtain all three curves.

The data in Figure 4 indicate that the absorption maximum at 278 mμ in the aluminum bromide-benzene system is dependent upon the presence of water or oxygen. Since the rate of diffusion through an ungreased but clamped ball joint must be very low, the pressures inside and outside being equal, the concentration of the water (and oxygen) inside must be slight even after 36 hours. The water may conceivably have either or both of two effects upon the system. In one role it might act as a catalyst in the formation of a complex product between the reactants. In the second it would actually participate in the reaction and become permanently involved in the formation of a new compound, losing its identity. If the absorption is truly due to a complex, the problem then becomes one of deciding <u>what</u> complex. The water, functioning as a catalyst, would be expected to produce a pi complex. If it is a third reactant, a complex of the sigma type would be expected wherein water is involved just as hydrogen halides are thought to be. In spite of the fact that the cell was tightly capped as indicated above, there was visible evidence of hydrolysis as stated. The complex is thus thought to be of the sigma rather than the pi type. This interpretation discounts the possibility of an insoluble pi complex in favor of the formation of a slightly soluble complex between the arene and the product of partial hydrolysis of the metal halide.

The findings concerning the aluminum bromide-benzene system appear in excellent agreement with the results of Schall and of Eley and King. The data indicate that the complex absorbing at 278 mμ also reported by the latter two workers above was not a true pi complex. This does not imply that a pi complex does not exist between the components, however. As shown by curves A and C of Figure 4, it does indicate that, if such a complex is formed, the equilibrium very greatly favors the reactants. This is in accord with both theoretical (46, 47, 48, 49, 50) and experimental (12, 22) considerations.

The interpretation above has neglected consideration of the time required for the establishment of equilibrium in the solutions as a factor in producing the observed absorption. Comparison of curves A and C in Figure 4 indicate that time has little effect upon the absorption of the binary system.

Considering the indication that the absorption maximum at 278 mμ in the system now considered is dependent upon the presence of water (or perhaps oxygen), the band in question does not appear spurious as suggested (20, 37) but may actually indicate a complex. While the existence (20) of spurious absorption is not questioned, the value of nonconformity to Beer's Law (37) as a criterion for deciding that a weak band is spurious when it lies on the edge of a second strong band is doubted. Quantitative measurements on the edge of strong bands are subject to some uncertainty, even with "compensation", due to the effects of variations in slit width which are not well known. Beyond this, the existence of some spurious absorption might indeed explain the nonconformity of the total in this particular case.

The Aluminum Bromide-m-Xylene System

It was thought that perhaps the proposed method of study could be applied to complexes of aluminum bromide with the more basic hydrocarbons m-xylene and mesitylene. To begin this work the ultraviolet cut-off of m-xylene was determined in cyclohexane solution. It was found to be at about 280 mμ for concentrations around 0.1 M. A 0.001 M solution of aluminum bromide in m-xylene dried with phosphorus pentoxide was prepared and its spectrum obtained to determine whether the same difficulty would be encountered here as was found in the benzene solutions. An absorption band having a maximum at 308 mμ was observed; this indicated complex formation. The spectrum of the same solution was again determined at the end of 24 hours. No appreciable change in absorption had occurred in spite of the settling of a flocculent orange solid to the flask bottom. The absorption of the complex was far enough removed from the absorption edge of the m-xylene to make the system appear promising.

In the preparation of the above solution the phosphorus pentoxide was removed from the m-xylene by filtration through a filter paper. The m-xylene in the flask before the metal halide ampoule was broken appeared slightly turbid, but the faint cloud vanished upon the breaking of the ampoule. Apparently some of the phosphorus pentoxide had passed through the filter.

Because of the possible presence of a third component in the solution above, it was thought necessary to check the result by obtaining the spectrum of an aluminum bromide solution in m-xylene dried with sodium sand. The spectrum of a 0.01 M solution in m-xylene so dried revealed an absorption maximum at 338 mμ compared to the 308 mμ peak for the previous solution. This was taken as proof of interference by phosphorus pentoxide in the previous solution.

It was next necessary to explore the possibility of working with dilute solutions of aluminum bromide and m-xylene in an inert solvent. Accordingly, a solution was prepared in cyclohexane 0.003 M in m-xylene and 0.007 M in aluminum bromide. The solution was turbid, as were the next two prepared. In the preparation of the last solution, however, the aluminum bromide ampoule was broken before the addition of the m-xylene. The resulting solution was clear, but turbidity developed slowly after the addition of the arene. It was concluded that the turbidity was due to the formation of an insoluble complex. The solutions were allowed to settle overnight and afterward appeared perfectly clear, some oily material having settled out on the flask walls and bottom.

In addition to the oil, a few solid particles that were definitely crystalline could be seen on the flask walls. The oil was greenish-yellow, while the crystals appeared almost, if not entirely, colorless.

Although it appeared certain the study of this system would not be possible by Job's method, the spectra of solutions having aluminum bromide-to-m-xylene concentration ratios of seven-to-three, six-to-four, and five-to-five were obtained, the increment of change being 0.001 M. An absorption maximum was observed at about 365 mμ for these solutions. The concentration of the complex in the cyclohexane phase appeared unchanged with changes in the ratio of concentrations of reactants. Work with this system was abandoned after an additional qualitative test showed the solubility of the complex in carbon disulfide to be uselessly small.

Apparently the complex in the cyclohexane solution was different than the one observed in m-xylene as solvent. A change in solvent was not thought sufficient reason for the rather large difference in the wave lengths at which the maxima occurred, particularly since the change was not from a solvent of high or low polarity to one at the opposite extreme.

The change in the color of one of these solutions upon brief exposure to air was also interesting. The color progressed from a pale yellow to a pink with the production of turbidity. As the turbidity increased, the pink faded. Undoubtedly a different complex was formed as a result of partial hydrolysis of the catalyst.

The Aluminum Bromide-Mesitylene System

Although the same result was expected from the mesitylene aluminum bromide system as from the one above, it was decided to make at least one solution from which the complex absorption maximum could be obtained and which would also indicate its solubility. A solution in heptane was made 0.007 M in aluminum bromide and 0.003 M in mesitylene. As expected, the solution was initially turbid but cleared when allowed to stand for a few hours. After standing, a dull orange oil was seen condensed on the flask walls. The following day it was observed that almost colorless crystalline spires had grown out of this oil. Several star-shaped patches of such crystals also appeared. The cell was filled with the clear solution and its spectrum run against pure heptane. An absorption band was observed having a maximum at about 390 mμ. This indicates a complex with a good deal more stability than the corresponding one from m-xylene and aluminum bromide, as would be expected from a consideration of the relative basicities of the two arenes. No further experiments were performed with mesitylene solutions.

The experiment above and those with m-xylene indicate that these two arenes form solid complexes with aluminum bromide, as suggested by Brown and Frith (8).

The Titanium Tetrachloride-Benzene System

The remaining time was spent in experiments employing titanium tetrachloride as the acceptor molecule. As already stated, these efforts resulted in solutions that were turbid. No measurements could be made.

Suggestions for Future Work

Recent work on the solubility of aluminum chloride in hydrocarbon solvents by Fairbrother, Scott, and Prophet (22) bears on this research. Their determinations were made in both aliphatic and aromatic hydrocarbons. They found that aluminum chloride in benzene and toluene pretreated several times with the metal halide in a vacuum system to remove water gave colorless solutions that became yellow when cooled to -195°C. Solutions in *m*-xylene and mesitylene were yellow at room temperature and darkened on cooling. They attribute the formation of colored solutions to the presence of trace amounts of water in the solvents in the case of benzene and toluene at ordinary temperatures. In line with this, they think that water is necessary for the formation of the so-called "red oils". They represent the complexes so formed as

$$X_nMOH^{-}\ldots{}^{-}HArH.$$

This appears a most reasonable view and may explain the yellow to pink color change noted previously in the discussion of the *m*-xylene-aluminum bromide system. Their experiments appear to be the best in the literature from the standpoint of exclusion of water from the solvents and system. Undoubtedly, complexes in these systems were truly pi complexes. The lack of color in the benzene and toluene solutions does not mean that a complex is not formed between the compounds, but that the equilibrium vastly favors the reactants at ordinary temperatures. This is probably, but not necessarily, the case with aluminum bromide in these solvents also. The aluminum bromide complexes at ordinary temperatures would be more readily observable than those of aluminum chloride with the same solvents because of the somewhat greater acidity of the bromide (33). The far greater solubility of aluminum bromide could also be a large factor here.

The above work (22), along with that previously cited by one of the same authors (21), is thought to be of great importance to future studies of these complexes in that it has demonstrated an efficient drying method for the solvents. This is, without doubt, the most important thing in such a study. The work reported here indicated that once the solvent was adequately dried, it could be used with this simple apparatus with good results. It would be most interesting to examine spectroscopically a cooled solution of aluminum bromide and benzene in cyclohexane dried by the method of Fairbrother and coworkers, as well as a solution of the metal halide in the arene itself. The yellow color would make measurements possible in the visible spectral region, thus simplifying the cell problem for the latter solutions. Such data should do much to establish the relationship between the yellow color observed (22) in cold solutions and the absorption at 278 mµ attributed to a benzene-aluminum bromide complex. Several obvious difficulties stand in the way of this work. The work of Reid (58) might be of some technical value in solving these.

The work by Comyns, Howald, and Willard (13) reporting no change in the spectrum of stannic chloride in toluene upon the addition of hydrogen chloride may indicate that this would be an ideal acceptor to experiment with.

This research has shown that ultraviolet absorption data for systems of this type are difficult to obtain. It is suggested that components be chosen in future problems that are known or can be shown to have absorption in the visible spectrum. Should these complexes prove to be soluble in the chosen solvent, the slope ratio method of

Harvey and Manning (32) for establishing their composition might prove useful as an alternate route. If the complexes are not soluble, the investigator might titrate a known weight of the metal halide with the arene, following the concentration of the free arene spectroscopically. Interpretation of data in this case would be similar to that in the method of Harvey and Manning.

SUMMARY

A simple apparatus was developed for the spectrophotometric study of systems of complexes between aromatic hydrocarbons and the metal halides employed as catalysts in the Friedel-Crafts family of reactions. The approach taken was the determination of compositions of these complexes by Job's method of continuous variations and their instability constants from suitable spectrophotometric data.

The aluminum bromide-benzene system was the first to be studied, since the literature contains information on it that provided a means of checking the techniques employed. No complex that absorbed light between wave lengths of 2500 and 220 mμ could be detected between these components each 0.005 *M* in cyclohexane. No distinct absorption characteristic of a complex could be observed in a solution 0.2 *M* in aluminum bromide dimer and 0.8 *M* in benzene. A 0.001 *M* solution of the metal halide in benzene itself was found to have an absorption maximum at about 278 mμ as reported in the literature. Experiments with a 0.0015 *M* solution of the same compound in benzene that failed to give this absorption maximum indicated the necessity of trace amounts of air or water to the appearance of this band. The system was concluded to be unsuitable for study by the proposed method.

Aluminum bromide and *m*-xylene in dilute solution in cyclohexane were found to form a complex having an absorption maximum at about 365 mμ. This complex separated as a yellow oil with a green tint or a nearly colorless crystalline solid. Because of its slight solubility, this complex could not be studied by the intended method. A dilute solution of aluminum bromide in m-xylene itself had an absorption maximum at 338 mμ, which is a complex different than the one observed in the cyclohexane solution.

Aluminum bromide and mesitylene in dilute solution in heptane were found to form a complex having an absorption maximum at about 390 mμ. This complex was again essentially insoluble and appeared as a dull orange oil, gradually crystallizing.

Because of turbidity that could not be overcome in solutions of titanium tetrachloride in cyclohexane, no data were obtained for systems involving this acceptor.

Turbidity was the chief difficulty encountered throughout the work. It was attributed to inadequately dried solvents. This could probably be eliminated by drying the solvent by vacuum distillation from the halide itself employing a cold trap of liquid nitrogen.

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