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A Spectrophotometric Study of the Interactions of Some Lewis Acids with Bases in Organic Solvents[1]

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RECEIVED JANUARY 26, 1960

The interactions of 4-aminoazobenzene with ferric chloride and with stannic chloride in 1,2-dichloroethane were examined in the 200–700 millimicron region. The method of continuous variations indicated a product corresponding to three moles of acid per two moles of base (A_3B_2) for both of these Lewis acid–base reactions. In benzene, ferric chloride exhibited the same A_3B_2 stoichiometry with 4-aminoazobenzene, whereas the behavior of stannic chloride was anomalous. In 1,2-dichloroethane, ferric chloride and aniline gave a product of the form AB, as did tribenzylamine with stannic chloride and with aluminum bromide. All investigations were carried out under anhydrous conditions.

Introduction

While a great many Lewis acid–base reactions have been studied in the gaseous phase, very little work in this regard has been done in solution because of the experimental difficulties involved. In view of the importance of Lewis acid catalysts in organic solvent media, these studies were undertaken in an attempt to obtain some quantitative information spectrophotometrically. The choice of systems was severely limited either by the reactivity of solvents in the presence of certain Lewis acids, by their lack of transparency in the region of study or by the absence of suitable absorption bands in the ultraviolet and visible spectra of the acids and bases.

This paper deals with the interactions of 4-aminoazobenzene with ferric chloride and with stannic chloride in 1,2-dichloroethane and in benzene, with the interactions of ferric chloride with aniline and of stannic chloride and aluminum bromide with tribenzylamine in 1,2-dichloroethane.

Experimental

Reagents.—1,2-Dichloroethane, commercial grade, Matheson, Coleman and Bell, was treated twice with concentrated sulfuric acid, neutralized with potassium hydroxide and washed several times with distilled water. This mixture was distilled to give the solvent-water azeotrope, which was stored over calcium chloride for 24 hr. Approximately 50% of the total volume was collected as a middle fraction through a one-meter column packed with glass helices. The resulting middle fraction was then refluxed over phosphorus pentoxide for 24 hr. after which it was distilled again, with the middle fraction being collected in a dry flask, protected from atmospheric moisture, and finally transferred to a dry box. The purified material had a boiling point of 83.0° and gave 50% transmission through a one-cm. quartz cell in the region 238–242 millimicrons.

Cyclohexane, Shell Chemical Co. (sp. gr. 20/20, 0.777–0.780) contained a trace of benzene which was removed by passage through a one-meter, 21-mm. i.d. column of 60–200-mesh silica gel. The eluted cyclohexane was refluxed over phosphorus pentoxide for 24 hr. and fractionated through a one-meter column of packed helices. A middle fraction was then collected in a dry flask, protected from atmospheric moisture and transferred to the dry box.

Benzene was purified and dried as described by Zenchelsky and Segatto.[2]

Aniline, Fisher Scientific Co. (Cat. No. A-739), was refluxed over zinc dust and then over potassium hydroxide pellets. A small middle fraction was then collected in a dry flask, protected from atmospheric moisture, transferred to the dry box and used immediately.

Azobenzene (*trans*), tribenzylamine and 4-aminoazobenzene were obtained in the best commercial grades available and recrystallized until their melting points agreed with those contained in the literature. These were then dried *in vacuo*, in the presence of phosphorus pentoxide, for 24 hr. after which they were transferred to dry screw cap vials and stored in the dry box.

Aluminum bromide was prepared from the elements,[3] purified by successive distillations and sublimations in an all-glass system at 10^{-5} mm. and sealed off in fragile glass ampoules.

Stannic chloride, J. T. Baker Analyzed Reagent, was redistilled *in vacuo* in an all-glass system and sealed off in large ampoules with fragile tips.

Ferric chloride, Fisher Scientific Co., anhydrous, reagent grade, was used as obtained, after removal of a surface layer of the yellow hydrate. A portion of the sample was resublimed in an atmosphere of chlorine[4] and compared with the original material. No difference was observed in the results obtained with either sample or in their absorption spectra.

Dry Box.—Trace amounts of moisture capable of producing hydrogen halides by hydrolysis of the Lewis acids were carefully avoided, since concentrations of acid were as low as 10^{-3} to 10^{-5} molar. For this reason a commercial dry box with predrying chamber was employed for preparation of solutions. It was found that with sufficient phosphorus pentoxide present and provided at least 4 hr. elapsed after opening the port between the box and predrying chamber, an ampoule of aluminum bromide could be broken without any yellow coloration or appearance of hydrogen bromide fumes. The box was not sufficiently dry, however, to avoid fuming when titanium tetrachloride ampoules were opened.

Spectrophotometric Measurements.—A Cary, Model 11, spectrophotometer was used. Absorbance measurements in the visible region were made at nominal slit widths of 0.002 to 0.010 mm. Measurements made at 270 millimicrons used a slit opening of 0.015 mm. Solutions were prepared in the dry box at 25 ± 1.5° and spectrophotometric measurements were made at 24 ± 1°. Quartz cells with ground stoppers were stored in the dry box when not used for measurement.

Procedure.—Molar absorptivities were determined for solutions of tribenzylamine ($\epsilon_{259.5} = 937$), 4-aminoazobenzene ($\epsilon_{375} = 27100$), *trans*-azobenzene ($\epsilon_{450} = 534$) and aniline ($\epsilon_{290} = 1880$), in 1,2-dichloroethane. These values then were used to determine the concentrations of the stock solutions of bases prepared in the dry box.

Stannic chloride concentrations were determined by adding a weighed[5] amount of solution to an excess of aqueous sodium hydroxide and performing a Mohr titration after adjusting the acidity. In some cases a Fajans titration was used.

Aluminum bromide concentrations were determined in a manner similar to that for stannic chloride. Since aluminum bromide–dichloroethane solutions are not stable for long periods,[6] cyclohexane was used as solvent in preparing the

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[1] This paper represents a part of the work submitted by Raymond J. Shuba to the Graduate School, Rutgers, the State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1958.

[2] S. T. Zenchelsky and P. R. Segatto, THIS JOURNAL, **80**, 4796 (1958).

[3] L. F. Audrieth, Editor-in-Chief, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1950, p. 33.

[4] *Ibid.*, p. 192.

[5] A suitable weight pipet is described in: R. van Dyke and H. E. Crawford, THIS JOURNAL, **73**, 2018 (1951).

[6] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 596.

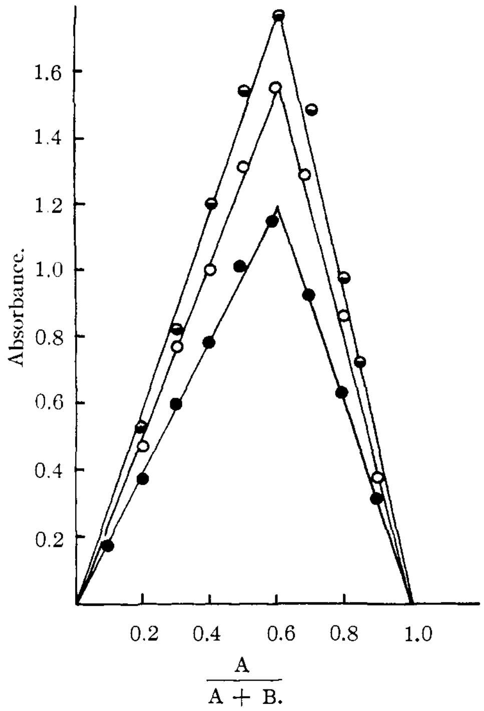

Fig. 1.—Stoichiometry of the interaction between the Lewis acids, A, and 4-aminoazobenzene, B, by the method of continuous variations: ○, ferric chloride (in 1,2-dichloroethane); ●, stannic chloride (in 1,2-dichloroethane); ◓, ferric chloride (in benzene); wave length, 512 mμ.

stock solution. No turbidity was observed, indicating that the solvent was dry.[7]

Ferric chloride is not very soluble in 1,2-dichloroethane hence solution concentrations were determined spectrophotometrically, using thiocyanate.

Results

Figure 1 shows the A_3B_2 stoichiometry observed for the interaction between ferric chloride, A, and 4-aminoazobenzene, B, in 1,2-dichloroethane. The shape of the continuous-variations plot renders unlikely the existence of multiple equilibria. Moreover, Fig. 2 shows an isobestic point at 428 millimicrons, while a second one occurs at 335 millimicrons. Upon increasing the acid-to-base ratio beyond 3 to 2, the absorbance of the complex at 512 millimicrons remained constant. Identical results and spectra were obtained for the interaction between stannic chloride and 4-aminoazobenzene. The continuous-variations plot for this reaction is also shown in Fig. 1.

When higher concentrations of acid and base were used, approximately one molar, a solid adduct precipitated in the case of both acids. Determination of chloride indicated the composition AB_2 in both cases. With stannic chloride, the same stoichiometry was observed in the presence of either excess acid or excess base. The limited solubility of ferric chloride in 1,2-dichloroethane prevented use of excess acid, but the same AB_2 product was obtained from solutions containing either excess base or equimolar amounts of acid and base. These products were deep magenta in color and dissolved slowly in 1,2-dichloroethane

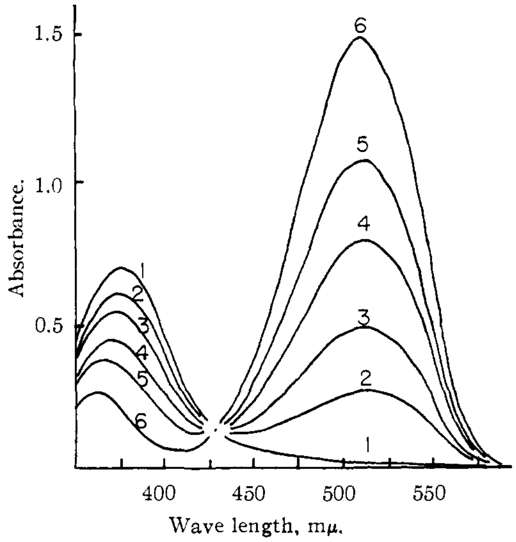

Fig. 2.—Absorption spectra of 2.59 × $10^{-5}M$ 4-aminoazobenzene in the presence of varying concentrations of ferric chloride (in 1,2-dichloroethane). Ferric chloride concentrations are: 1, 0; 2, 7.42 × 10^{-6}; 3, 1.48 × 10^{-5}; 4, 2.23 × 10^{-5}; 5, 2.97 × 10^{-5}; 6, 4.45 × 10^{-5} M.

to give absorption spectra identical with those observed in dilute solution.

Anal. Calcd. for $SnCl_4 2{\cdot}C_{12}H_{11}N_3$: Cl, 21.6. Found: Cl, 22.2. Calcd. for $FeCl_3{\cdot}2C_{12}H_{11}N_3$: Cl, 19.1. Found: Cl, 18.7.

These reactions were also investigated in a less polar solvent, benzene. The results for ferric chloride were identical with those found in 1,2-dichloroethane. Figure 1 shows the A_3B_2 stoichiometry observed. Stannic chloride, on the other hand, exhibited different behavior. Precipitates were observed at concentrations as low as 10^{-5} molar, preventing a quantitative study of the stoichiometry. Absorption spectra of some of these turbid solutions are shown in Fig. 3. These

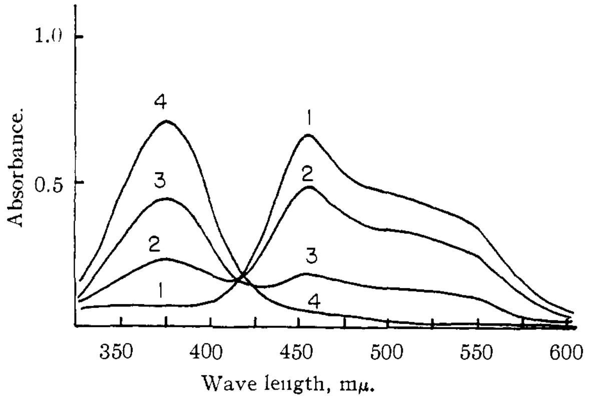

Fig. 3.—Absorption spectra of 2.62 × 10^{-4} M 4-aminoazobenzene in the presence of varying concentrations of stannic chloride (in benzene). Stannic chloride concentrations are: 1, 3.21 × 10^{-5}; 2, 2.14 × 10^{-5}; 3. 1.07 × 10^{-5}; 4, 0.0 M.

show the presence of two, and possibly three, maxima. The one at about 456 millimicrons is close to that of azobenzene, at 450 millimicrons. The shoulder at longer wave lengths suggests the

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(7) F. Fairbrother and K. J. Field, *J. Chem. Soc.*, 2614 (1956).

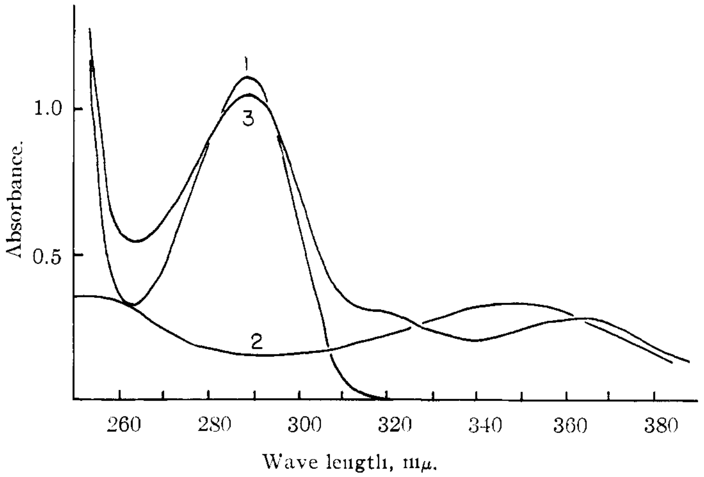

Fig. 4.—Absorption spectra of aniline, ferric chloride and their adduct in 1,2-dichloroethane: 1, 5.74×10^{-4} *M* aniline; 2, 1.06×10^{-4} *M* ferric chloride; 3, 1.06×10^{-4} *M* ferric chloride with 1.06×10^{-4} *M* aniline.

existence of a band near 512 millimicrons as observed for the interaction between ferric chloride and 1,2-dichloroethane in benzene. Although the lower solubility of the stannic chloride adduct can be explained in terms of greater ionic character of the product, the absorbing species also appear to be more complex.

The possibility that the A_3B_2 stoichiometry, observed for both acids in 1,2-dichloroethane, is the result of an equimolar mixture of AB and A_2B is further rendered unlikely by the following considerations. Vosburgh and Cooper[8] have shown that the presence of multiple complexes can be detected by applying the method of continuous variations at several wave lengths. If the observed stoichiometry is wave length dependent, then more than a single equilibrium must be involved. Results obtained in this study at 475, 500 and 525 millimicrons were, however, identical. The possibility of the existence of a non-absorbing species seems remote when the nature of the base is considered.

An attempt to explain the unusual A_3B_2 stoichiometry observed in the preceding study led to an investigation of the behavior of some simpler bases with these two Lewis acids. The reaction product between aniline and stannic chloride was insoluble in 1,2-dichloroethane. The solid adduct was analyzed and found to be AB_2 (*Anal.* Calcd. for $SnCl_4 \cdot C_{12}H_{14}N_2$: Cl, 31.7. Found: Cl, 32.9). In the case of ferric chloride the aniline adduct is soluble in 1,2-dichloroethane, having an absorbance maximum at approximately 363 millimicrons. This is shown in Fig. 4. Since the absorption band of the adduct overlaps the ferric chloride band at 350 millimicrons, the method of continuous variations was not used. However, it was observed that the absorbance of the adduct increased, upon addition of aniline to the acid until they were present in equimolar amounts, and it remained constant upon continued addition of excess base. Thus it was assumed that the complex in solution must be of the form AB. Because of the low solubility of ferric chloride in 1,2-dichloroethane, it was impossible to prepare a solid adduct.

A similar study was made with azobenzene as base. The absorption spectrum of azobenzene shows an intensification of the weak band, at 450 millimicrons, upon addition of either ferric chloride or stannic chloride. Absorbance readings are not constant with time, indicating some slow side reaction. The method of continuous variations plot obtained by taking readings rapidly after mixing the reactants, suggested the complex to be of the type AB.

Another confirmation of the A_3B_2 stoichiometry observed between stannic chloride and 4-aminoazobenzene in 1,2-dichloroethane was obtained in the following manner. The stoichiometry of the reaction between tribenzylamine and stannic chloride in 1,2-dichloroethane was determined by the method of continuous variations. These results are shown in Fig. 5, while the spectra are shown in Fig. 6. The product is of the type AB. On the assumption that tribenzylamine is a much stronger base than 4-aminoazobenzene, known amounts of the former were added to solutions of the stannic chloride-4-aminoazobenzene complex in 1,2-dichloroethane; and the amount of 4-aminoazobenzene liberated was calculated from the increase in absorbance of that base ($\epsilon_{375} = 27.1 \times 10^3$). As expected, each mole of tribenzylamine liberated two-thirds mole of 4-aminoazobenzene. These results are shown in Table I. It also was observed that pyridine behaves like tribenzylamine in liberating 4-aminoazobenzene from its stannic chloride complex. These effects are striking because the color changes are plainly visible.

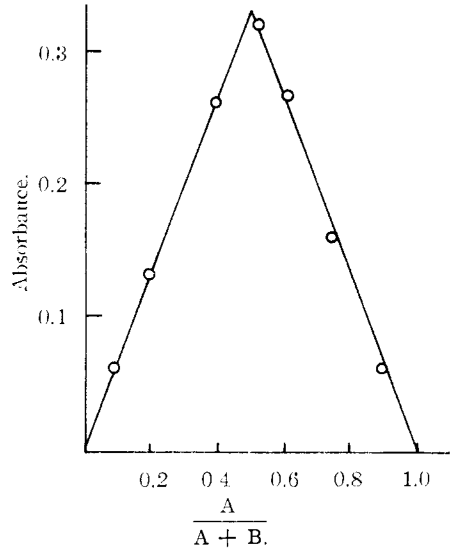

Fig. 5.—Stoichiometry of the interaction between stannic chloride, A, and tribenzylamine, B, in 1,2-dichloroethane by the method of continuous variations. Concentrations of the reactants at the maximum are: stannic chloride, 3.70×10^{-4} *M*; tribenzylamine, 3.55×10^{-4} *M*; wave length, 270 mμ.

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[8] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

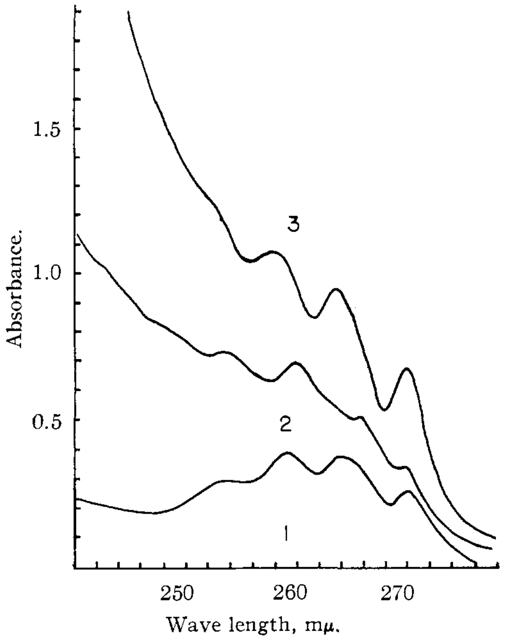

Fig. 6.—Absorption spectra of the adduct between aluminum bromide and tribenzylamine, 1; of tribenzylamine, 2; and of the adduct between stannic chloride and tribenzylamine, 3, in 1,2-dichloroethane. Values of ϵ_{270} are: 1, 670; 2, 430; 3, 900.

It is interesting that the absorption maximum of the ferric chloride-4-aminoazobenzene complex in 1,2-dichloroethane, 512 millimicrons, lies close to that for 4-aminoazobenzene in 50% alcohol solution and 6 M with respect to HCl, 500 millimicrons.[9]

TABLE I

DISPLACEMENT OF 4-AMINOAZOBENZENE BY TRIBENZYLAMINE

Tribenzylamine added × 10³, mmoles	4-Aminoazobenzene liberated × 10³, mmoles Calcd.	Found
4.19	2.79	2.80
8.37	5.58	5.49
11.6	7.71	7.64
16.7	11.1	11.2
20.4	13.6	13.5
25.1	16.7	16.4

The reaction between aluminum bromide and tribenzylamine in 1,2-dichloroethane was also investigated. The absorbance at 270 millimicrons was found to increase with time when aluminum bromide was present in excess of equimolar amounts. A yellow color was formed with even larger excesses of aluminum bromide. Absorbance readings, in the presence of excess aluminum bromide, therefore were extrapolated to the time of mixing. As aluminum bromide was added to the base, the absorbance increased linearly until a molar ratio of unity was reached and remained constant upon further addition. This is shown in Fig. 7. Thus the product indicated is of the form AB. It appears to be the only product formed in solution since Beer's law is obeyed in the range of concentrations from 10^{-3} to 10^{-7} molar.

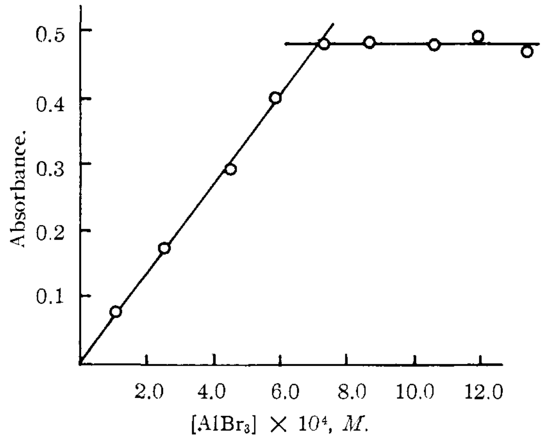

Fig. 7.—Absorbance of 7.20 × 10^{-4} M tribenzylamine in the presence of increasing concentrations of aluminum bromide in 1,2-dichloroethane; wave length, 270 mμ.

Since aluminum bromide and stannic chloride react similarly with tribenzylamine in solution, their solid adducts were prepared from more concentrated solutions. That of stannic chloride had the form AB (*Anal.* Calcd. for $SnCl_4 \cdot C_{21}H_{18}N$: Sn, 21.7; Cl, 25.9. Found: Sn, 21.9; Cl, 25.5). On the other hand, the aluminum bromide adduct was of the form A_2B_3 (*Anal.* Calcd. for $2AlBr_3 \cdot 3C_{21}H_{18}N$: Br, 34.4. Found: Br, 34.6). To eliminate the possibility of aluminum bromide interaction with the solvent 1,2-dichloroethane, the solid adduct was prepared also from cyclohexane solution and was found to be identical with the one from 1,2-dichloroethane solution.

All of the complexes described above were so little dissociated that it was impossible to evaluate their equilibrium constants spectrophotometrically.

Discussion

The composition of the products, A_3B_2, observed for the interaction between stannic chloride and 4-aminoazobenzene as well as between ferric chloride and 4-aminoazobenzene, in 1,2-dichloroethane, is unusual and difficult to explain; but that the mechanism of interaction must be the same for the two acids is suggested by the fact that they exhibit identical stoichiometry, AB_2, in their solid adducts with 4-aminoazobenzene and that in both cases the solids dissolve in 1,2-dichloroethane to give the A_3B_2 species.

It is interesting that Fe(III) exhibits, the less common, pentacoördination in the above solid adduct; whereas, the more usual, tetracoördination appears in the AB complex between ferric chloride and aniline in 1,2-dichloroethane. The reduction of Fe(III) to Fe(II) by the amine, which would give a coördination number of four in the solid adduct, appears highly unlikely, particularly at room temperature. Antler and Laubengayer[10] reported the apparent reduction of some titanium tetrachloride by trimethylamine, and Fowles and McGregor[11] found that ferric chloride is reduced by diamines but in both of these cases elevated

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[9] E. Sawicki, *J. Org. Chem.*, **22**, 623 (1957).

[10] M. Antler and A. W. Laubengayer, THIS JOURNAL, **77**, 5250 (1955).

[11] G. W. A. Fowles and W. R. McGregor, *J. Chem. Soc.*, 136 (1958).

temperatures were employed. Moreover, the halide determination for the solid adduct was sufficiently sensitive to distinguish between the respective complexes involving Fe(III) and Fe(II).

Anal. Calcd. for $FeCl_3 \cdot 2C_{12}H_{11}N_3$: Cl, 19.1. Calcd. for $FeCl_2 \cdot 2C_{12}H_{11}N_3$: Cl, 13.6. Found: Cl, 18.7.

The observations made in this study, together with some others previously reported in the literature, suggest a possible explanation of the A_3B_2 adducts between ferric chloride and 4-aminoazobenzene and between stannic chloride and 4-aminoazobenzene in 1,2-dichloroethane. First, the work of Sawicki,[12] Klotz[13] and Murrell[14] casts considerable doubt on the necessity for the existence of a quinoid-type structure to produce a red shift in the aminoazobenzenes in acid solution. This fact would permit inferences on the behavior of the metal halides to be drawn from that observed for the proton in solutions of the aminoazobenzenes. Further indication of this similarity in behavior is obtained in the comparison of the molar absorptivity of 4-aminoazobenzene in alcoholic hydrogen chloride with that of the 4-aminoazobenzene-stannic chloride or ferric chloride complex, (see section on Results). The difference in wave lengths of maximum absorption, 500 *vs.* 512 millimicrons, must simply reflect the difference in solvents. Secondly, although McGuire, *et al.*,[15] report virtually no change in the absorption spectrum of azobenzene in the presence of alcoholic hydrogen chloride, Miller, *et al.*,[16] did observe a slight increase in absorbance upon acidifying an alcoholic solution of azobenzene but there was no shift in the wave length of maximum absorption. Similarly, addition of either stannic chloride or ferric chloride to azobenzene, in 1,2-dichloroethane, merely intensified the weak band at 450 millimicrons without producing a spectral shift. No solid adduct could be isolated for this interaction.

Consistent with the facts above, it may be assumed that first two moles of 4-aminoazobenzene react with one mole of metal halide to produce a transient intermediate, AB_2, which also corresponds to the composition of the solid adduct. This reaction presumably involves the amino nitrogen of the base rather than the less basic azo nitrogen atoms. The spectral shift observed would result from this step, as it does in the case of proton addition to 4-aminoazobenzene. This reaction can then be followed by addition of one mole of metal halide at each pair of azo nitrogens to produce the A_3B_2 species by analogy with the formation of an AB adduct between the halides and azobenzene in solution. This second step would produce increased absorption without any further spectral shift. The existence of AB_2 in the solid adduct could be explained on the basis of the weakness of the azo-metal bond in the absence of solvent, a fact which might also explain the inability to obtain a solid adduct between azobenzene and stannic chloride or ferric chloride. The verification of this explanation will require an extensive investigation of the absorption spectra of the aminoazobenzenes as well as of their related compounds in the presence of Lewis acids.

The reaction of tribenzylamine with aluminum bromide and with stannic chloride in 1,2-dichloroethane is unusual in that, while both metal halides form an adduct AB in solution, aluminum bromide gives a solid adduct of the composition A_2B_3 rather than AB as is the case for stannic chloride. Kelley and McCusker[17] report similar A_2B_3 solid adducts for the reaction of dioxane with antimony, arsenic and bismuth trihalides. In addition, Sheka[18] reports the formation of AB and A_2B_3 products between pyridine and aluminum bromide in benzene solution.

Recent work has indicated a tendency for metal tetrahalides to form AB, rather than the more common AB_2, adducts with secondary or tertiary amines, which is presumably the result of steric effects. Such adducts, AB, have been reported by Fowles and Pleass[19] for vanadium tetrachloride, by Antler and Laubengayer[10] for titanium tetrachloride and by Fergusson, *et al.*,[20] for stannic chloride.

Acknowledgment.—The authors gratefully acknowledge the support of the Colgate–Palmolive Company by means of a research fellowship to R. J. S.

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(12) E. Sawicki, *J. Org. Chem.*, **22**, 367 (1957).

(13) I. M. Klotz, H. A. Fiess, J. G. Chen Ho and M. Mellody, THIS JOURNAL, **76**, 5136 (1954).

(14) J. N. Murrell, *J. Chem. Soc.*, 296 (1959).

(15) W. S. McGuire, T. F. Izzo and S. Zuffanti, *J. Org. Chem.*, **21**, 632 (1956).

(16) J. A. Miller, R. W. Sapp and E. C. Miller, THIS JOURNAL, **70**, 3458 (1948).

(17) C. J. Kelley and P. A. McCusker, *ibid.*, **65**, 1307 (1943).

(18) I. A. Sheka, *Zhur. Obshchei Khim.*, **26**, 1340 (1956).

(19) G. W. A. Fowles and C. M. Pleass, *J. Chem. Soc.*, 1674 (1957).

(20) J. E. Ferguson, D. K. Grant, R. H. Hickford and C. J. Wilkins, *ibid.*, 99 (1959).