cannot be great enough to account for the large shifts, since it is easy to show that the complete removal of the tin valence electrons would not give shifts of the magnitude observed. The second-order paramagnetic term in Ramsey's shielding expressions[37] must, therefore, be primarily responsible for the observed shifts, but no calculations of this effect in tetrahedrally symmetric molecules have yet been made.

Solvent Effects on Shifts and Indirect Spin–Spin Couplings.—Except for the observations on the HCl solutions of $SnCl_2 \cdot 2H_2O$ our data on solvent effects are very limited, but in the main it demonstrates that care must be taken in using solutions for shift or coupling measurements. Presumably, the unusually large effects observed in the Sn^{119} spectra are the result of the well known tendency of tin compounds to coördinate strongly with many substances. It would seem that n.m.r. spectra should become quite useful in studies of complex

formation by compounds of tin and other elements.

Line Widths and Relaxation Times.—The widths of some of the Sn^{119} lines are not unprecedented. The P^{31} lines in compounds such as PCl_3, $POCl_3$ and $PSCl_3$ are broadened,[38–40] although those in PBr_3, $POBr_3$ and $PSBr_3$ are not.[38,40] The Si^{29} lines in chlorosilanes are difficult to observe[5] and the C^{13} resonances in CCl_4, $CHCl_3$, CH_3CCl_3 and similar compounds are broad and weak,[3] although CBr_4 has a strong resonance and a fairly short spin–lattice relaxation time (T_1). It has now been found that the Sn^{119} resonance in $SnCl_4$ is very broad and that the $SnBr_4$ resonance is slightly broadened and has a T_1 estimated at considerably less than one second. Apparently, some interactions with the halogen nuclei are not completely averaged out by their rapid quadrupole-induced relaxation.

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Molecular Addition Compounds of Tin(IV) Chloride. I. Interaction with Benzonitriles in Benzene Solution

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Infrared spectra of benzene solutions containing tin(IV) chloride and benzonitriles have been utilized in an evaluation of the equilibria leading to addition compound formation. The results indicate that the formation of the 1:1 addition compound is the most important equilibrium in dilute solutions but that some 2:1 addition compound is also formed. The dependence of the values of the equilibrium constants on the nature of the *meta* or *para* substituent in the benzonitrile has been examined. Dielectric constant data for the tin(IV) chloride–benzonitrile system in benzene have been analyzed in the light of the equilibrium constants obtained from the infrared data to obtain dipole moment values for the 1:1 and 2:1 addition compounds. The moment calculated for the 1:1 addition compound is 8.4 ± 0.2D; the moment calculated for the 2:1 compound is about 3.1D. The latter value may, however, be as high as 5D or as low as zero.

The Lewis acid character of tin(IV) chloride, first investigated extensively by Pfeiffer,[1] has been the subject of considerable study. With monofunctional bases which do not undergo a complicating reaction such as dehydrohalogenation[2] the solid compounds obtained are usually of the stoichiometry AB_2, where A represents $SnCl_4$ and B represents the base molecule. In cases where solid compounds are not isolated, the formula of the addition compound has been determined by cryoscopic,[3] calorimetric and thermometric[4] or one of a number of other methods.

Despite the considerable literature dealing with tin(IV) chloride (hereinafter abbreviated TC) addition compounds, very little is known about their structures or behavior in solutions. The Lewis acid character of TC is generally pictured as arising from the use of vacant 5d atomic orbitals on the tin atom. In AB_2 the bonding is assumed to be sp^3d^2, which leads to an octahedral arrangement of hybrid orbitals about the central atom. This

arrangement gives rise to the possibility of *cis–trans* isomerism. This fact was recognized early by Ulich and co-workers,[5] who attempted to determine the geometry of AB_2 species by a combination of freezing point lowering and dielectric constant measurements on benzene solutions of TC with bases such as ethers, ketones and nitriles. Recognizing the possibility of a number of simultaneous equilibria involving the species A, B, AB, $(AB)_2$ and AB_2, these workers attempted to evaluate the various equilibrium constants by using the freezing point lowering data. They concluded that in benzene solutions of TC and benzonitrile at 20° the AB_2 species does not exist, that there is a small amount of AB dimer formed and that the principal complex species is AB. The freezing point lowering data on the basis of which the various K's were evaluated do not, however, possess the necessary sensitivity and freedom from random error which is required for precise determination of equilibria.

More recently, Osipov[6,7] has reported dipole

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(6) (a) O. A. Osipov, *J. Gen. Chem. U.S.S.R.* (*Eng. Transl.*), **26**, 343 (1956); **27**, 1502, 2953 (1957).
(7) Y. B. Kletenik, O. A. Osipov and E. E. Kravtsov, *Zhur. Obschchei Khim.*, **29**, 11 (1959).

moments for AB_2 compounds in benzene, calculated on the assumption that when stoichiometric amounts of acid and base are mixed the AB_2 species is formed quantitatively. This assumption seems to be quite unfounded, and the calculated values of dipole moment are therefore open to serious question.

There is a need for a more detailed and reliable study of the equilibria which obtain in solutions of TC and Lewis bases. The present paper reports the results of a study of benzene solutions of TC with benzonitriles. The important equilibria have been evaluated by means of infrared spectrophotometric methods and the dielectric constant behavior of the TC-benzonitrile system in benzene has been analyzed in the light of these results. Infrared studies of TC-benzonitrile solutions have been reported by Coerver and Curran.[8] Shifts in the infrared frequency of the $C\equiv N$ band which result from addition compound formation were reported. In addition, qualitative indication of dissociation of the complex was given. These authors were unable to obtain positive evidence for the presence of a 1:1 complex.

Experimental

Materials.—Reagent grade benzene was fractionally crystallized twice, then fractionally distilled from phosphorus pentoxide. Storage was over sodium wire; $n^{23}D$ 1.4978, d^{30} 0.86800.

Eastman aniline-free benzonitrile was dried with magnesium sulfate and fractionated at reduced pressure; $n^{25}D$ 1.5260. m- and p-Tolunitriles were Eastman white label materials, dried with magnesium sulfate and fractionally distilled.

The remaining m- and p-substituted benzonitriles, Eastman materials, were purified by repeated sublimations under reduced pressure.

Baker and Adams tin(IV) chloride was refluxed over clean mercury for several hours and twice distilled under nitrogen atmosphere.

Sample Preparation.—All operations involving transfer of reagents were conducted in a dry-box. Solutions were made up by weight. Molar concentrations of tin(IV) chloride in the solutions at 30°, the temperature at which the spectra were obtained, were calculated from the densities of pure tin(IV) chloride and of the solutions of benzonitriles in benzene; additivity of densities was assumed. Since the corrections to the solvent density are small for dilute solutions, no significant error arises from such an assumption.

Spectra.—The spectra were obtained on a Perkin–Elmer Model 112 spectrometer fitted with a lithium fluoride prism. Two fixed-thickness cells, 0.48 and 0.985 mm. with rock salt windows, were employed.

A constant temperature chamber was employed to maintain the solutions at a fixed temperature during the runs. This consisted of a metal box lined with asbestos board and fitted with double windows of silver chloride. The temperature in the box was maintained with a stream of preheated air which was led in through a number of openings. All runs were conducted at 30.0 ± 0.4°.

The spectra were obtained in the range 2220–2290 cm.$^{-1}$, the region in which the $C\equiv N$ vibrational band occurs. This region was scanned for each sample at least twice, and pure solvent background traces were obtained at frequent intervals. A fixed slit width of 0.20 mm. was employed. The chemical stability of the solutions was evidenced by the fact that the spectrum of a particular sample could be reproduced to within experimental error 24 hr. after its initial run.

A series of solutions of each benzonitrile in the absence of TC was examined in order to obtain the Beers law plot for the nitrile band of the compound. The concentrations of nitrile and TC required to obtain evidence of interaction varied with the substituent on the nitrile. For p-nitro

(8) H. J. Coerver and C. Curran, THIS JOURNAL, **80**, 3522 (1958).

the concentrations of both solutes were in the range 0.1–0.3 M, whereas for p-methoxy they ranged from 0.01–0.07 M for the nitrile and 0.02–0.12 M for TC.

Evidence of interaction was seen in the appearance of a second absorption band at slightly higher frequency than the free nitrile absorption.

Dielectric Constant Measurements.—The apparatus employed in the measurements of dielectric constant has been described elsewhere.[9] In the present work the bath temperature was set at 30.0°. A total of fourteen solutions were studied. Three of these contained only TC as solute; the remaining eleven contained both TC and benzonitrile in varying proportions. Weight fractions of benzonitrile ranged from 0.001 to 0.01; for TC from 0.05 to 0.25. Since it is true that TC in benzene solutions is non-polar, or of low polarity, and therefore does not radically change the dielectric constant of the medium, it was felt that high concentrations of this substance could be tolerated without the likelihood of causing a noticeable change in the values of the relevant equilibrium constants.

Analysis of the Spectral Results.—By a comparison of each spectrum with the pure solvent spectrum the values of log (T_0/T) where T is the observed transmittance of the solution and T_0 that of the solvent were computed for 2 cm.$^{-1}$ intervals in the region of interest. These values were then graphed $vs.$ the frequency in cm.$^{-1}$.

Analysis of the spectra was complicated somewhat by the fact that for two of the compounds studied, benzonitrile and p-nitrobenzonitrile, the new band which appears is not symmetrical. Thus, for p-tolunitrile, the spectrum which is obtained when appreciable interaction is evident can be easily resolved into two symmetrical bands separated by about 24 cm.$^{-1}$. In the case of the two compounds mentioned above, however, there is evidently a third, much weaker, band between the two major bands. All of the spectra obtained for these two compounds with TC were analyzed with the assumption that this third band exists.

The new band (or bands) are evidently due to interaction of the benzonitriles with TC. By graphical resolution of the over-all absorption the residual absorption due to the complexed nitrile at the frequency of the free nitrile band could be determined and the net absorbance due to free nitrile calculated. Using the Beers law plot for the particular nitrile, the concentration of the free nitrile in the solution was then determined.

Ulich, Hertel and Nespital concluded on the basis of their freezing point lowering data that the predominant species in solutions prepared by dissolving $SnCl_4(C_6H_5CN)_2$ in benzene is the 1:1 complex. We begin an analysis of the infrared data, therefore, with the assumption that the only equilibria of importance in solutions of benzonitriles and TC are the formation of the 1:1 species, with possibly formation of the 2:1, in accordance with the equilibria

$$A + B \rightleftharpoons AB \qquad K_{11} = \frac{[AB]}{[A]\cdot[B]} \quad (1)$$

$$AB + B \rightleftharpoons AB_2 \qquad K_{12} = \frac{[AB_2]}{[AB][B]} \quad (2)$$

Evidently, unless K_{12} is very much larger than K_{11} the 1:1 species will predominate over the 2:1 in solutions which do not contain a large excess of base. Indeed, when acid is present in excess, the

(9) T. L. Brown, D. Y. Curtin and R. R. Fraser, $ibid.$, **80**, 4339 (1958).

AB_2 species should exist in negligible quantities. It was found, in agreement with this expectation, that in solutions containing excess TC the data could be used to calculate a K_{11} which was constant over a wide range of both acid and base concentrations. On the other hand, values of K_{12} calculated on the assumption that this is the predominant equilibrium were far from constant. The constancy obtained for the values of K_{11} under these conditions also argues that the formation of an $(AB)_2$ dimeric species is not very important.

For solutions containing excess base, it was not possible to calculate a constant value for either K_{11} or the K representing the formation of a 2:1 ($K_{11} \times K_{12}$). Evidently, another equilibrium, presumably that represented by (2), begins to assume significant proportions in these solutions. If it is assumed that only the 1:1 species is present the *apparent* equilibrium constant for the reaction represented by (1), K'_{11}, has the form

$$K'_{11} = \frac{b_0 - b}{b(a_0 - b_0 + b)} \qquad (3)$$

where a_0 and b_0 represent the initial concentrations of acid and base, respectively, and b represents the concentration of base at equilibrium, the experimentally determined quantity. If in addition to the AB species the AB_2 type adduct is also formed, the correct expression for K_{11} is

$$K_{11} = \frac{b_0 - b - 2[AB_2]}{b(a_0 - [AB] - [AB_2])} \qquad (4)$$

where the square brackets indicate concentrations. K_{12} has the form

$$K_{12} = \frac{[AB_2]}{b[AB]} \qquad (5)$$

Let $b_0 - b = p$

$[AB_2] = x = K_{12}b[AB]$

$a_0 - b_0 + b = q = a_0 - p$

Then (4) can be written as

$$K_{11}b = \frac{p - 2x}{q + x} = \frac{p - 2x}{q\left(1 + \frac{x}{q}\right)}$$

for values of $x/q \ll 1$ the expression can be written as

$$K_{11}b = \frac{p - 2x}{q}\left(1 - \frac{x}{q}\right) = \frac{p}{q} - \frac{2x}{q} - \frac{px}{q^2} + \frac{2x^2}{q^2} \qquad (6)$$

Now, x/q is in fact always considerably less than one in the concentration range employed. Neglecting the term in $(x/q)^2$, and rewriting (6) in terms of the apparent constant, K'_{11} and K_{11}

$$b(K'_{11} - K_{11}) = \frac{[AB_2](2a_0 - p)}{(a_0 - p)^2} \qquad (7)$$

$$K'_{11} = K_{11} + K_{12}\left[\frac{[AB](2a_0 - p)}{(a_0 - p)^2}\right] \qquad (8)$$

This expression can be utilized for evaluation of K_{11} and K_{12} by a series of approximations, the first being to let $[AB] = p$. When values of K'_{11} are graphed *vs.* the values for the quantity in brackets, the plot is a straight line, with slope K_{12} and intercept K_{11}. A second approximation is carried out using the value of K_{12} thus obtained to calculate a better value for AB using
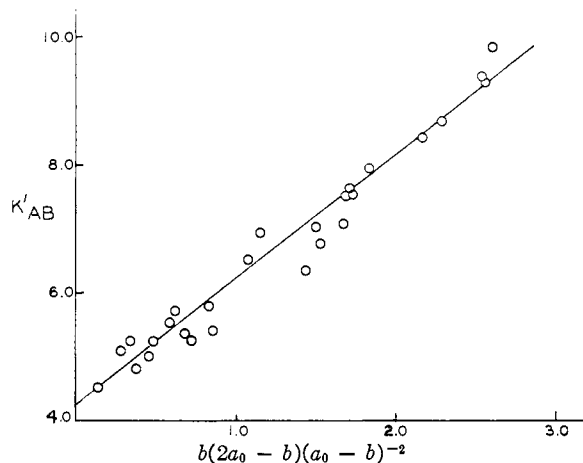
$$AB = p - 2[AB_2]$$

Fig. 1.—Graphical determination of K_{11} (intercept) and K_{12} (slope) for the system benzonitrile–tin(IV) chloride.

and the expression for K_{12}, given by (5)

$$[AB] = \frac{p}{1 + 2K_{12}b}$$

The new value of AB is used in (8) to obtain a new graph; successive approximations are carried out until no further change occurs in the values for K_{11} and K_{12}. It was found in practice that the third approximation furnished the desired degree of accuracy. A typical plot (actually, one of the better ones) for the first approximation is shown in Fig. 1. The results of such a treatment of the data for each of the benzonitriles is given in Table I. The results for the *p*-fluoro and *m*-methyl compounds must be considered to be less reliable than the others because fewer data were obtained for these. It was not found possible to obtain conditions suitable for evaluation of K_{12} for the *p*-nitro compound.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE FORMATION OF AB AND AB_2 MOLECULAR ADDITION COMPOUNDS OF TIN(IV) CHLORIDE WITH BENZONITRILES IN BENZENE AT 30°

Substituent	K_{11}[a]	K_{12}[a]
H	4.17	1.97
p-OCH₃	15.5	3.38
m-CH₃	6.8	1.4
p-F	3.4	2.2
p-Cl	2.9	1.5
p-NO₂	0.8	..

[a] In units of liter mole⁻¹.

The significance of the equilibrium constants will be discussed in a later section. The treatment does appear to be successful in accounting for the important equilibria and in yielding reasonable values of equilibrium constants. The nitrile absorption due to the AB_2 species, in those solutions in which it can be observed as a second new absorption, is at a somewhat lower frequency than that due to the AB species. Estimates of the relative absorbancies of the two complex bands are necessarily rather rough, but for benzonitrile it is clear that the smaller middle band becomes relatively more important as the ratio of base to acid increases. This behavior is consistent with the idea that the smaller band is due to the AB_2

species. Where only one band is observed, it would seem that the band due to the 2:1 complex occurs at the same frequency as that due to the 1:1 species. The frequencies and intensities of the $C\equiv N$ absorption in these systems are discussed in a later paper.

Analysis of the Dielectric Constant Data.—The concentrations of A, B, AB and AB_2 were calculated for each of the solutions employed in the dielectric constant studies, using the values for F_{11} and K_{12} for the benzonitrile-TC system listed in Table I. The dielectric constant of the five-component solution can be written as

$$\epsilon = \epsilon_0 + \alpha_1\omega_1 + \alpha_2\omega_2 + \alpha_3\omega_3 + \alpha_4\omega_4 \qquad (9)$$

where ϵ_0 represents the dielectric constant of pure benzene and ω refers to weight fraction. The subscripts 1, 2, 3 and 4 refer to benzonitrile, TC, AB and AB_2, respectively. A value of 17.1 was used for α_1; this was obtained by correcting the data in the literature to $30°$.[10] A value of 0.320 for α_2 was obtained from the data for the three solutions containing only TC. Substitution of the known quantities in (9) yielded a set of eleven simultaneous equations in α_3 and α_4. These were solved graphically to obtain a value for $\alpha_4 : 2.5 \pm 6.3$. Using this value of α_4, α_3, ω_3 was evaluated for each of the eleven equations and was plotted against the known value of ω_3. The slope of the line represents the value of α_3, 21.4. It should perhaps be mentioned that although the value of α_4 is known only very imprecisely, α_3 can still be determined to good precision. The reason for this is that the 2:1 species is present to such a slight extent that it does not influence the dielectric constant to any great extent. In none of the solutions was the AB_2 concentration more than about 20% of the AB.

The solute molar polarization was obtained by use of the Halverstadt–Kumler equation.[11]

The value for $\beta = \partial v/\partial\omega$ was calculated by assuming that the molar volume of the complex, either AB or AB_2, is just the sum of the molar volumes of the components and assuming that the molar volumes are unchanged in benzene solution, as compared with the pure substances. Any minor deviations from these assumptions would not noticeably affect the calculated dipole moment. The value of molar polarization calculated for the AB and AB_2 species are thus 1500 and 295 cm.[3] The molar refractivities of these two species were taken as the sum of the molar refractivities of the components, which gave 75 and 104 cm.[3], respectively, for AB and AB_2. The dipole moments calculated from these quantities, neglecting atom polarization, are 8.4 D for AB and 3.1 D for AB_2. It is probable that the moment for AB is good to within 0.2 D, while that for AB_2 could be as high as perhaps 5 D or as low as zero.

Discussion

The values for the equilibrium constants in the system benzonitrile-TC, though not in good numerical agreement with the data of Ulich, Hertel and Nespital, do qualitatively substantiate their conclusion that *the formation of the 1:1 complex is the predominating equilibrium in dilute solution.* Contrary to their conclusion, however, it is not found necessary to postulate the existence of a dimeric species $(AB)_x$, and it *is* clear that the 2:1 complex does exist to some extent in the solution. The dipole moment studies with the benzonitrile system also clearly indicate the polar character of the 1:1 complex. Since TC is essentially non-polar in benzene solution, it does not seem likely that the solvent occupies a coördination position in the complex; it must be concluded that the tin atom is penta-covalent. A number of configurations are possible in penta-valency[12]; the most attractive of these is that of symmetry C_{3v}, in which the orbitals employed by the tin atom are $sp^2 + p_z + d_{z^2}$. The bond angles in the complex are then left somewhat variable, depending on the strength of the Lewis acid–base bond, and on steric requirements. The dipole moment is certainly consistent with such a structure, although other possibilities are not excluded. For example, the structure which possesses C_{4v} symmetry remains as a possibility.

The dipole moment value for the AB_2 complex is so uncertain that no conclusions regarding the structure of the complex can be drawn. It does seem that a *cis* octahedral configuration about the tin atom should produce a moment at least as great as that for the 1:1 species, and it does appear fairly certain that the experimentally determined moment is considerably smaller, but beyond this nothing more definite can be said. It is anticipated that future work will provide a more precise value for the moment of the 2:1 compound.

The reaction of benzonitrile with TC is an example of an electrophilic reaction, *i.e.*, one in which the attacking reagent, in this case TC, exerts an electron demand on the substrate molecule. The effect of variation of the ring substituent on the equilibrium constant in this type of reaction can be discussed in terms of the electrophilic substituent constant, σ^+.[13] The values of the slope, ρ, in graphs of $\log K_{11}$ and $\log K_{12}$ *vs.* σ^+ are -0.84 and -0.37, respectively. It is interesting to note that the value of ρ is larger for the 1:1 formation than for the 2:1. This, coupled with the fact that the values for K_{12} are smaller than the corresponding values of K_{11}, makes it seem likely that the heat of reaction in which the 1:1 species is formed is greater than that for the 2:1. The implication is that the 1:1 complex is a weaker Lewis acid toward benzonitrile than TC itself. This point will not be entirely clear, however, until values of the equilibrium constant have been determined at different temperatures.

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