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EQUILIBRIA BETWEEN ORGANOTIN TRICHLORIDES AND NITROGEN DONORS IN ETHER AND THE COMPARISON OF THEIR ACCEPTOR STRENGTHS WITH STANNIC CHLORIDE

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INTRODUCTION

Equilibrium studies have been variously reported for the interactions of stannic halides[1]—mainly the chloride but also the bromide and iodide— with organic bases in non-aqueous solvents. The relative quantitative acceptor strengths of these halides, and also those of other covalent metal halides[2], have been obtained in one series of studies[1a,b] from the equilibrium constants for their interactions, in ether and in *o*-dichlorobenzene solutions, with a number of structurally similar bases, namely anilines.

Equilibrium studies with organotin halides are, however, scarce. Okawara *et al.*[3] investigated the reversible interaction between the ligand, 2,2'-bipyridine, and the acceptors dimethyl- and di-n-butyltin dichlorides (and also stannic chloride) in the solvent acetonitrile. 1 : 1-Chelate complexes were obtained. The effect of dialkyl-substitution was found to reduce the acidity of the tin chloride by a factor of 10^3 (as measured by the equilibrium constants). However, some doubt must be expressed about the accuracy of the very large equilibrium constant obtained for stannic chloride and hence about the comparison of the acidities.

Another equilibrium study was made by Matwiyoff and Drago[4]. 1 : 1-Adducts were formed from trimethyl- and triethyltin chlorides and tetramethylene sulphone. No comparison of their acidities with other Lewis acids was possible.

We report here upon the equilibria between some nitroanilines and diaminonitrobenzenes and phenyl-, methyl- and n-butyltin trichlorides in ether solution at 25°. The effect of the monoorgano-substitution on the acidity of the tin tetrachloride is also reported. The method of study was visible spectroscopy.

EXPERIMENTAL

Materials

Tin chlorides. (*i*) *Phenyltin trichloride* was prepared from tetraphenyltin and stannic chloride by Kocheshkov's method[5]. B.p. 102°/2 mm. (Found: Cl, 35.0. $C_6H_5Cl_3Sn$ calcd.: Cl, 35.2%.) (*ii*) *Methyltin trichloride* was prepared from methyltriphenyltin and stannic chloride[6]. M.p. 44°. (Found: Cl, 44.2. CH_3Cl_3Sn calcd.: Cl, 44.3%.) (*iii*) *n-Butyltin trichloride* was obtained from Fluka Chemical Co. It was redistilled (b.p. 90°/10 mm). (Found: Cl, 37.6. $C_4H_9Cl_3Sn$ calcd.: Cl, 37.7%.)

Solvents. Diethyl ether and *o*-dichlorobenzene were the purest commercial samples available. They were dried over calcium hydride and redistilled.

Ligands. All the nitroanilines were commercial samples, recrystallized from ethanol. The observed m.p.'s were within 1° of the literature values.

The diaminonitrobenzenes were commercial samples, chromatographed on alumina and recrystallized from ethanol. All m.p.'s were within 1° of the literature values.

Experimental method and calculation of the equilibrium constants.

A Unicam S.P. 500 spectrophotometer was used with a thermostatted cell-housing maintained at 25±0.1°. All solutions for optical measurements were prepared (in a dry-box) by dilution of stock solutions. The molarities of the acid stock solutions were obtained by potentiometric titration for chloride ion (after hydrolysis in dilute nitric acid). Stoppered silica cells of 1 cm path length were filled in the dry box.

The absorbances were measured at the maxima of the visible bands of the donors and whenever possible at the maxima of any visible bands of the 1 : 1 adducts as well as at least one other wavelength. A minimum of five solutions were used for the p*K* determination for each system. The spectra were generally stable for several hours and no precipitation was observed.

When complete complex formation was achievable (*i.e.*, with the systems involving the more basic ligands) equilibrium constants were calculated from

$$K = \frac{[\mathrm{B \cdot RSnCl_3}]}{[\mathrm{B}][\mathrm{RSnCl_3}]} = \frac{(D_0 - D)}{(D - D_\infty)[\mathrm{RSnCl_3}]} \tag{1}$$

where D_0, D and D_∞ are respectively the absorbances at a given wavelength in the absence of $\mathrm{RSnCl_3}$, at a given acid concentration and for complete complex formation, with a given stoichiometric donor concentration $[\mathrm{B}]_0$.

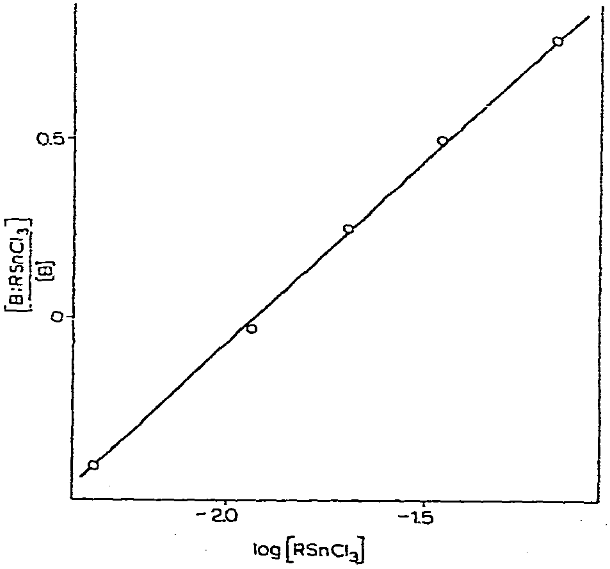

Fig. 1. Plot of log ($[\mathrm{B \cdot RSnCl_3}]/[\mathrm{B}]$) against log $[\mathrm{RSnCl_3}]$ for the methyltin trichloride/1,2-diamino-4-nitrobenzene interaction.

Thus a graph of log $(D_0-D)/(D-D_\infty)$ against log [RSnCl$_3$] should be linear of unit slope and the pK can be obtained from the value of the intercept (Fig. 1). (Generally $[B]_0$ was *ca.* 10^{-4} *M* with the minimum $[RSnCl_3]_0$ *ca.* 10^{-3} *M*. Thus the equilibrium concentration of the acid could be taken as the stoichiometric concentration, $[RSnCl_3]_0$). The values of the slopes obtained from the above plots were always very close to unity (within 4%), indicating that none other than 1 : 1 complexes were present.

For systems involving the less basic donors, complete complexation was not possible even with the most concentrated acid solutions and eqn. (1) was replaced by the following expression.

$$\frac{[RSnCl_3]}{(D_0-D_\infty)}=\frac{[RSnCl_3]}{(D-D_0)}=\frac{1}{K(D_0-D_\infty)}$$

Hence a plot of [RSnCl$_3$] against $[RSnCl_3]/(D-D_0)$ should be rectilinear and *K* (and p*K*) can be found from the values of the slope and intercept (Fig. 2). Good linear plots were always obtained, showing that only 1 : 1 adducts were formed.

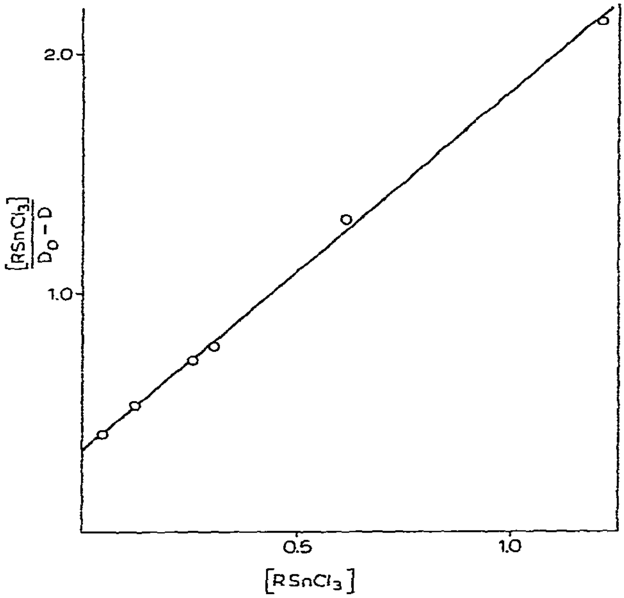

Fig. 2. Plot of $[RSnCl_3]/(D_0-D)$ against [RSnCl$_3$] for the phenyltin trichloride/3-nitroaniline interaction. Data at 370 mμ.

Different samples of RSnCl$_3$ were used to determine each p*K*. The reproducibility was always within ±0.03 units.

RESULTS AND DISCUSSION

I. Nitroanilines as ligands

All the nitroaniline–organotin trichloride interactions gave soluble 1 : 1 complexes in ether. No other stoichiometries were evident. Table 1 provides the p*K* values for these interactions and Table 2 gives a comparison of acidities of stannic chloride and the organotin trichlorides.

TABLE 1

pK VALUES FOR THE INTERACTIONS BETWEEN ORGANOTIN TRICHLORIDES AND ANILINE BASES, B, IN ETHER SOLUTION AT 25.0±0.1°

$K = [B \cdot RSnCl_3]/\{[B][RSnCl_3]\}$; K_a = dissociation constant of BH^+ in water at 25°.

(I) Diaminonitrobenzenes		pK_a	pK^a		
No.	*Benzene derivative*		$MeSnCl_3$	*n*-$BuSnCl_3$	$PhSnCl_3$
1	1,2-Diamino-4-nitro-	2.70^b	−1.95	−1.66	−2.70
2	1,3-Diamino-4-nitro-	1.01^b	−0.75	−0.66	−0.66
3	1,4-Diamino-3-nitro-		−1.90	−1.62	−2.30
	(II) Monoaminonitrobenzenes *Aniline derivative*				
4	4-Methyl-3-nitro-	2.90	−0.35	+0.10	−0.93
5	3-Nitro-	2.50	-0.03^c	$+0.47^c$	−0.62
6	2-Methyl-5-nitro-	2.32	$+0.40^c$		−0.21
7	4-Chloro-3-nitro-	1.86			−0.05
8	3-Methyl-4-nitro-	1.45			$+0.22^c$
9	4-Nitro-	0.99			$+0.44^c$
10	2,5-Dimethyl-4-nitro-	1.52			$+0.33^c$
11	2-Methyl-4-nitro-	0.94			$+0.62^c$

[a] pK values have limits of ±0.03. [b] These are the dissociation constants for the monoprotonated species and were obtained in this study by standard methods. [c] The adducts showed charge-transfer absorption.

TABLE 2

COMPARISON OF THE pK VALUES FOR THE INTERACTIONS BETWEEN SOME NITROANILINES AND ORGANOTIN TRICHLORIDES AND TIN TETRACHLORIDE IN NON-AQUEOUS SOLVENTS

Lewis acid (aniline)	*pK values (in Et_2O at 25°)*				
	$MeSnCl_3$	*n*-$BuSnCl_3$	$PhSnCl_3$	$SnCl_4{}^a$	
4-Methyl-3-nitro-	−0.35	+0.10	−0.93	−2.70	-3.71^b
3-Nitro-	−0.03	+0.47	−0.62	−2.38	-3.68^b

[a] Ref. 1d. [b] In *o*-dichlorobenzene at 20°.

Effect of the alkyl-substitution on the acidity. Okawara[3] showed that dialkyl-substitution greatly reduced the acidity of stannic chloride. Our results clearly indicate that a considerable effect is also caused by the replacement of only one halogen with either a phenyl, a methyl or a n-butyl group in the tetrachloride. (The substitution of another organic group has a further large reducing effect on the acidity as shown by both diphenyl- and di-n-butyltin dichlorides not detectably affecting any of the bases used in this study—including the more basic diaminonitrobenzenes.) Previously this reduction in acidity has been shown only qualitatively *i.e.* by the greater number of ligands giving isolatable complexes with stannic chloride[7] and also by the tetrachloride being a better catalyst in Friedel–Crafts reactions[8]. We can now derive the quantitative relative strengths of the three organotin trichlorides and stannic chloride towards aniline bases in ether to be*:

$SnCl_4$ (670) : $PhSnCl_3$ (12) : $MeSnCl_3$ (3) : n-$BuSnCl_3$ (1)

The decreasing order clearly follows the increasing order of electron release of the substituent. This, of course, makes the electron density at the central tin atom higher and hence a poorer acceptor is obtained.

Some doubts concerning the accuracy of Okawara's comparison are raised on two counts.

(1) The equilibrium constant obtained for the stannic chloride—a,a'-bipyridine interaction was very high ($\sim 5 \times 10^6$). Thus in Okawara's spectroscopic method a ligand concentration of 10^{-5} M was used, with a range of stannic chloride concentrations from 10^{-6} to 10^{-2} M. At the lower molarities of the halide, water must surely have been present in at least a comparable concentration and significant hydrolysis could be a possibility.

(2) The stannic chloride interaction differed from those of the other two chlorides in giving a 2:1 complex, as well as the 1:1 adduct, at the higher chloride concentrations.

In the present study, and in our earlier studies[1a,b,d], the chloride concentrations were at least 10^{-3} M and all the interactions produced 1:1 adducts only. For these reasons, the comparisons resulting from this study are considered to be valid.

However, this quantitative comparison in ether, although important, might not have very much general significance in other media. The same applies to Okawara's study in acetonitrile, since both solvents are strongly co-ordinating ligands and stannic chloride complexes with both have been obtained[7]. The effect of the ether co-ordination on the acidity of stannic chloride is clearly visible from the corresponding pK values in ether and *o*-dichlorobenzene, shown in Table 2. (*o*-Dichlorobenzene is considered a non-co-ordinating solvent.) Unfortunately, adducts of organotin trichlorides with nitroanilines are insoluble in *o*-dichlorobenzene even at concentrations of 10^{-4} M and so a direct comparison of acidity with stannic chloride cannot be made in this solvent. It was, however, possible to use mixed ether/*o*-dichlorobenzene solvent systems for one study with 4-methyl-3-nitroaniline and phenyltin trichloride. Two mixed solvents were used—namely 20:80 and 40:40 (v/v) *o*-dichlorobenzene (ODB)/ether—and the pK values obtained are given below.

Solvent	Et_2O	ODB/Et_2O 20:80	ODB/Et_2O 40:60
pK	−0.93	−0.95	−0.96

The results show that changing the solvent as above has a barely significant effect on the acidity of the trichloride and suggests that in pure *o*-dichlorobenzene the pK values of the trihalides generally probably only differ by 0.10 units at the most from their values in ether. The very small ΔpK for $PhSnCl_3$ is in keeping with its poor acceptor strength since the stronger an acceptor, the larger will be the value of ΔpK between the two solvents[1d].

Thus the effect of the mono-organo-substitution is calculated to reduce the

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* Okawara found the relative orders towards the chelating ligand, 2,2'-bipyridine, to be in acetonitrile:

$SnCl_4$ (3.3×10^3) : Me_2SnCl_2 (1.5) : n-Bu_2SnCl_2 (1)

acidity of stannic chloride in a non-co-ordinating solvent, like *o*-dichlorobenzene, by the factors:

Ph: 5×10^2; Me: 1.6×10^3; n-Bu: 4×10^3

Spectra of the adducts. Further evidence was obtained to support the view[1a] that the weaker interactions produce adducts having charge-transfer absorption while the stronger interactions give adducts with anilinium ion-type spectra. Only the two weakest acids, $MeSnCl_3$ and $n\text{-}BuSnCl_3$, gave adducts having charge-transfer absorption with 3-nitroaniline. The maxima of these absorptions were at 405 mμ and had extinction coefficients about half that of the parent base. Moreover bases nos. 8, 9 and 11 in Table 1, all give complexes with $PhSnCl_3$ but not with $SnCl_4$, having charge-transfer absorption with maxima in the region 395–405 mμ and with extinction coefficients of comparable magnitude to those of the free bases.

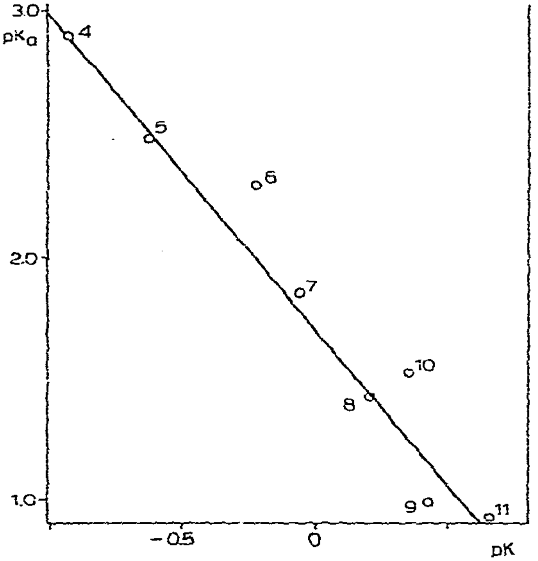


Fig. 3. Plot of pK_a against pK for phenyltin trichloride. (The aniline donors are numbered as in Table 1.)

Brønsted and Lewis basicities of the anilines. Comparison of the Brønsted and Lewis basicities (towards $PhSnCl_3$) is shown in Fig. 3 which contains a plot of pK against pK_a. It is apparent that similar factors influence both the Brønsted and Lewis basicities. The two most ill-fitting points arise from bases, nos. 6 and 10, which have methyl groups *ortho* to the amino group. (A third base, no. 11, has also an *ortho* methyl group, but this gives a point which does not fall so far off the line.) Steric effects could be present in these two cases. No ligands were used which had *ortho* groups other than methyl- but N,N-dimethyl-3-nitroaniline clearly showed a large steric effect. Its pK_a (2.66) suggests that it should complex at least as readily as 3-nitroaniline[4] but with phenyltin trichloride it showed only an extremely small interaction even in the most concentrated acid solutions.

II. Diaminonitrobenzenes as ligands

Spectral effects. The visible absorption bands of nitroanilines arise from intramolecular charge-transfer[10] and in ether solution it is generally found that 2-nitroanilines absorb in the region 390–400 mμ, 3-nitroanilines between 365–370 mμ and 4-nitroanilines between 350–360 mμ. The spectrum of each of the three diaminonitrobenzenes shows only one visible absorption band and this visible band does not occur in a region such that it may simply be attributed to a charge-transfer transition, in the excited state, to the nitro group from one or other of the two amino groups present in the base (Table 3). Moreover, instead of two charge-transfer bands arising from the two donor sites, there is only one such band which must arise from donation from some donor centre resultant from the two amino groups.

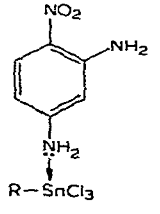
TABLE 3

SPECTRAL DATA FOR THE DIAMINONITROBENZENES IN ETHER SOLUTION

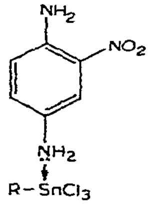
$\lambda_{max}(B)$ and $\lambda_{max}(A)$ are the wavelengths of the maximum visible absorption of the base and the adduct species in mμ.

Benzene derivative	$\lambda_{max}(B)$	$\lambda_{max}(A)$
1,2-Diamino-4-nitro-	380	
1,3-Diamino-4-nitro-	376	398
1,4-Diamino-3-nitro-	466	396

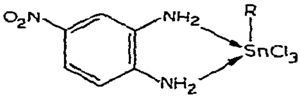
The spectra of the adducts derived from the bases 1,3-diamino-4-nitro- and 1,4-diamino-3-nitrobenzenes show bands at 398 mμ and 396 mμ respectively, which are within the region in which 2-nitro-anilines normally absorb (both the bases, of course, contain amino groups in positions *ortho* to the nitro group). As the stoichiometries of all the adducts are 1 : 1, it follows that the amino groups in the *para* and *meta* positions, respectively, relative to the nitro groups in the two bases, are those involved in the co-ordination and the two *ortho* amino groups remain free [see (I) and (II)].



(I)



(II)



(III)

R = Ph
Me
n-Bu

No reductions in the intensity of the adducts' visible bands were caused by the most concentrated solutions of $RSnCl_3$. Figs. 4 and 5 show typical spectra for these diaminonitrobenzene/$RSnCl_3$ interactions.

The adducts of the third base, 1,2-diamino-4-nitrobenzene, showed no visible absorption and this indicates that both amino groups are used in the co-ordination. As the stoichiometries were 1 : 1 and as the two amino groups are *ortho* to each other, it follows that a chelate complex is formed to give a six-co-ordinate tin species, (III).

Discussions concerning the co-ordination of 1 : 1 tin adducts in ether solution have been made elsewhere[1b].

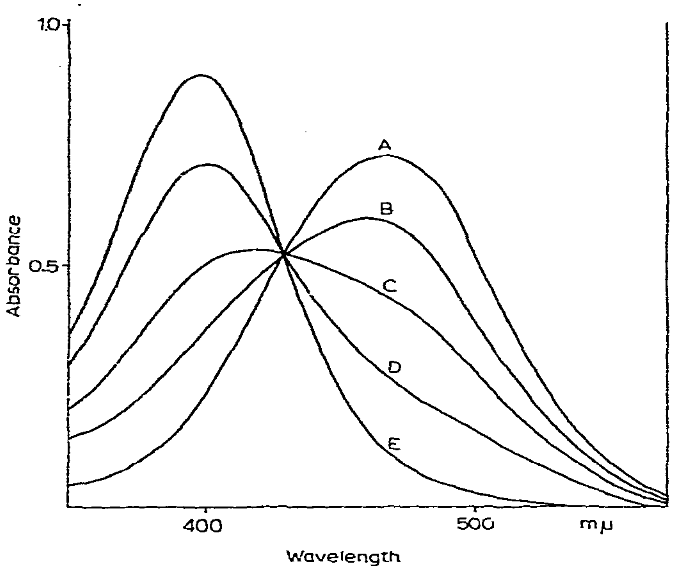


Fig. 4. The visible spectra of the n-butyltin trichloride/1,4-diamino-3-nitrobenzene interaction. [n-BuSnCl$_3$]: A, 0; B, 8.0×10^{-3}; C, 19.1×10^{-3}; D, 66.9×10^{-3}; E, 1190×10^{-3} mole/litre; [B] $\simeq 3 \times 10^{-4}$ mole/litre.

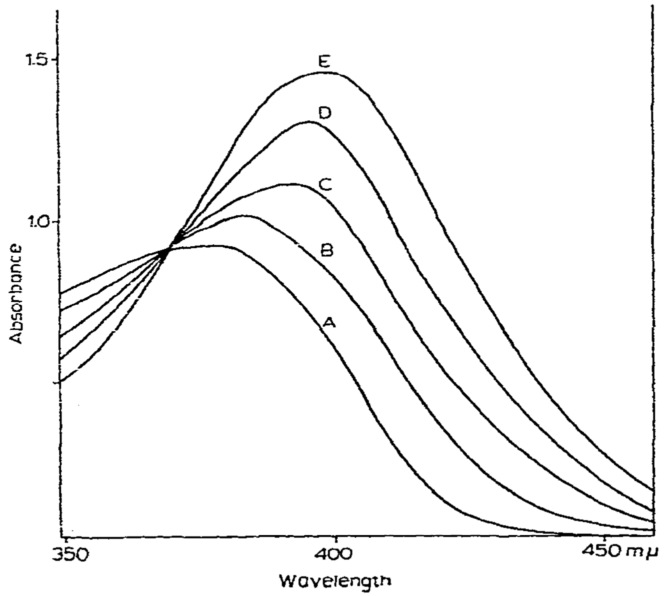


Fig. 5. The visible spectra of the methyltin trichloride/1,3-diamino-4-nitrobenzene interaction. [MeSnCl$_3$]: A, 0; B, 4.7×10^{-2}; C, 11.7×10^{-2}; D, 23.3×10^{-2}; E, 45.9×10^{-2} mole/litre; [B] $\simeq 3 \times 10^{-4}$ mole/litre.

Protonation of 1,2-diamino-4-nitrobenzene by Brønsted acids occurs in two stages. The monoprotonated species clearly shows the spectrum of a 4-nitroaniline derivative, indicating that the amino group, *meta* to the nitro group, is the more basic of the two such groups. Diprotonation, as with the other two diamines, yields a colourless adduct. (Mono-protonation of these other diamines produce analogous spectra to those of the organotin trichloride adducts.)

The pK values. In view of their pK_a values, and the data for the monoamines, two at least of these donors are anomalously basic towards the Lewis acids (Table 1). Anomalous basicity is often encountered for chelating ligands but another effect for all three bases may arise from the fact that pK_a values are obtained in water while the pK values are measured in ether. Water, but not ether, is able to hydrogen bond to amino groups and in so doing at least partially to engage the amino lone pair of electrons, making these less available for distribution to other parts of the molecule which carries the amino group. The diamines, but not the monoamines, possess an amino group—that *not* undergoing protonation—which can experience this effect, an effect which would be absent if the pK_a value could be determined in ether. In this way the diamines may appear less basic in water than in ether and their anomalous behaviour compared with the monoamines become understandable.

Because of their great basicity in ether, stannic chloride is too powerful an acceptor to allow fruitful study with these donors and a comparison of the acidities of the three organotin trihalides alone had therefore to suffice. Some differences in the quantitative relative strengths of acids are expected when using very different references bases and some slight, but not serious differences are, in fact, found for bases 1, 3 and 4. It is interesting that almost the same relative acidities are therefore observed towards two of the diamines—including the chelating base—as towards the simple monoamines, 4-methyl-3-nitroaniline. The behaviour of base 2, towards which the acidity range is compressed, appears exceptional.

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SUMMARY

Equilibrium constants for the interactions in ether solution of phenyltin trichloride, n-butyltin trichloride and methyltin trichloride with aromatic nitro-monoamines and -diamines have been obtained in a spectroscopic study. 1:1 Complexes were obtained in all cases. The effect the organic substitution has on the acidity of tin tetrachloride in ether (and also *o*-dichlorobenzene) is also reported.

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