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Nuclear magnetic resonance studies and structural investigations of the chemistry of organotin compounds

Part I. ^{119}Sn NMR studies of the pyrazine adducts of some organotin compounds

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Abstract

A procedure is described for the analysis of the concentration dependence of NMR chemical shift data on the chemical equilibria present in solution. This procedure has been used to study the equilibrium between $SnMe_3Cl$ and 4-methylpyridine in benzene, and the values obtained for the thermodynamic parameters are in good agreement with those previously determined by a calorimetric method. The equilibria of the adduct formation reactions of $SnPh_2Cl_2$, $SnPh_2Br_2$ and $SnPh_2I_2$ with pyrazine in chloroform and acetonitrile have also been investigated. In chloroform solution, both 1 : 1 and 1 : 2 (M : L) adducts are formed, whereas only 1 : 1 adducts are formed in acetonitrile under the experimental conditions used. For all three organotin compounds the interactions are relatively weak. The Lewis acidity of the $SnPh_2X_2$ organotin species decreases in the order Cl > Br > I.

Introduction

The structural chemistry of pyrazine complexes is of considerable interest since this ligand has been shown to perform several structural roles [1]. When pyrazine (L) reacts with a Lewis acid (M), three possible stoicheiometries can result: (i) ML, (ii) M_2L and (iii) ML_2. A number of spectroscopic and synthetic investigations of inorganic and organotin(IV) pyrazine complexes were reported [2–7] prior to the first crystallographic communication of an organotin(IV) pyrazine complex [8]. Tin(IV) chloride and tin(IV) bromide are somewhat unusual in their ability to form both 1 : 1 and 1 : 2 (M : L) complexes [5]; all other products were formulated as ML, including the adduct having the composition $SnPh_2Cl_2 \cdot$ pyrazine. However, X-ray crystallographic investigations of the latter [8] revealed an interesting structure in which there were alternating layers of 1 : 1 and 2 : 1 (M : L) complexes. Later the

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crystal structures of $SnMe_2Cl_2$ and $SnMe_2Br_2$ adducts with pyrazine were reported [1,9]. The former has a metal to pyrazine ratio of 2, whereas the latter is polymeric with 1 : 1 stoicheiometry. The crystal structures also revealed unusually long Sn–N bond lengths in the $SnPh_2Cl_2$ and $SnMe_2Cl_2$ adducts, but quite normal Sn–N bond lengths were observed for the $SnMe_2Br_2$ adduct.

In view of the anomalous Sn–N bond lengths encountered in the above structures and the unpredictability of the Sn : pyrazine ratios which have been obtained, further investigation of a wider range of Sn^{IV} Lewis acids with pyrazine and related ligands seemed warranted.

An integral part of such an investigation is an examination of the solution chemistry of these adducts. It is well established that the triorganotin halides form only 1 : 1 complexes in both solution and in the solid state [10]. On the other hand, the diorganotin dihalides are known to form both 1 : 1 and 1 : 2 adducts (M : L) with a variety of bases. However, recent studies [11] suggest that in solution, the 1 : 1 stoicheiometry dominates. With the advent of pulsed Fourier Transform NMR techniques [12], the strong dependence of δ ^{119}Sn on the nature of the coordination about tin [13,14] (there is a large shift of the ^{119}Sn resonances to lower frequencies on going from tetrahedral to trigonal bipyramidal to octahedral geometries) render ^{119}Sn NMR an extremely useful tool in the investigation of weak donor–acceptor interactions in solution.

This work describes a study of the interactions of pyrazine with a number of diphenyltin dihalides in both chloroform and acetonitrile based on direct observation of the the ^{119}Sn nucleus. In all the systems studied, the organotin(IV) Lewis acid was found to exist in rapid (on the NMR time-scale) equilibrium with pyrazine. Equilibrium constants and chemical shifts have been determined from the concentration dependence of δ ^{119}Sn using a non-linear least-squares computer program. Thermodynamic parameters have been calculated from the temperature dependence of the equilibrium constants.

Experimental

Materials

$SnMe_3Cl$ (Aldrich Chemical Co.) was purified by sublimation prior to use. $SnPh_2Cl_2$, prepared as previously described [15], was purified by repeated crystallisation from petroleum spirit (40 : 60). $SnPh_2Br_2$ was prepared and purified by similar procedures. $SnPh_2I_2$ was prepared by refluxing diphenyltin dichloride with potassium iodide in dry acetone, and was purified by recrystallisation from petroleum spirit (40 : 60).

Benzene was dried and distilled over calcium hydride and stored over sodium wire. Acetonitrile was dried and distilled over calcium hydride immediately prior to use. Chloroform was dried and distilled over phosphorus pentoxide. Petroleum spirit (40 : 60) was dried over calcium chloride, then distilled and stored over sodium wire.

Instrumentation and techniques

^{119}Sn NMR spectra were recorded on a Jeol JNM GX 270 FT NMR spectrometer operating at 100.55 MHz (frequency width 80.6 MHz, pulse width 5 μs, 90°, pulse delay 0.3 s, points 32 K). The inverse gated proton decoupling technique

without nuclear Overhauser effect was employed. All shifts were measured relative to internal $SnMe_4$ (0.05 mol dm^{-3}). Non-deuterated solvents were used with an external D_2O lock. At least 1024 scans were accumulated for each spectrum. Solutions for NMR analysis were prepared by use of volumetric glassware, and to avoid concentration effects on the ^{119}Sn chemical shifts [16], the total substrate concentration was maintained at $\leqslant 0.1$ mol dm^{-3}. Successive additions of pyrazine were made to 2 cm^3 of the tin substrate in a 10 mm NMR tube and over the concentration and temperature ranges employed, in no case did precipitation occur. The volumes were corrected for the addition of added pyrazine. NMR spectra were recorded after each addition.

The temperature of the NMR probe was calibrated by using methanolic proton shifts and all samples were allowed to equilibrate in the spectrometer for a minimum of 20 minutes before spectra were recorded.

Calculation of equilibrium constants

Since all the tin species were in rapid equilibrium under the experimental conditions used, only a single ^{119}Sn NMR resonance was observed. The chemical shift of this resonance, δ_{calc}, is given by eq. 1 and is the weighted average of the chemical shifts of the various tin-containing species present, M_mL_n, where M represents the alkyltin halide, L represents the Lewis base and i and j represent the maximum values of m and n respectively.

$$\delta_{calc} = \sum_{\substack{m=1 \\ n=0}}^{\substack{m=i \\ n=j}} \delta_{mn} m[M_mL_n]/[M]_{total} \tag{1}$$

Since

$$[M_mL_n] = \beta_{mn}[M]^m[L]^n \tag{2}$$

eq. 1 can be written as eq. 3

$$\delta_{calc} = \sum_{\substack{m=1 \\ n=0}}^{\substack{m=i \\ n=j}} \delta_{mn}\beta_{mn} m[M]^m[L]^n/[M]_{total} \tag{3}$$

Thus the problem resolves itself into finding the optimum values for the various δ_{mn} and β_{mn} values that best fit the experimental data.

A non-linear least squares program EQNMR [17] was used to calculate these parameters. Graphical output showing the experimental chemical shifts (15–40 data points) plotted against the total ligand concentration together with the fitted curve obtained by using the "best-fit" values of the various parameters was possible. Recent versions of the program also give a plot of the magnified residuals. Various models could be readily tested, e.g. models having ML, ML_2 and M_2L or ML and ML_2 only. In most instances, visual inspection of the graphical output was sufficient to determine which model gave the "best-fit". However, this comparison could also be carried out quantitatively using the function shown in eq. 4 where W_i is the weight attributed to observation i.

$$R = 100\left(\frac{\Sigma W_i(\delta_{obs} - \delta_{calc})^2}{\Sigma W_i \delta_{obs}}\right)^{1/2} \quad (4)$$

In the present investigation, unit weights were used at all times. The quantity R is essentially a normalised standard deviation, and unlike the sums of the residuals retains its significance for data having widely different chemical shifts. In the case of non-linear curve fitting where there are constraints, the use of a parameter such as R is more meaningful than using the diagonal elements of the inverted matrix to calculate uncertainties.

The program is quite insensitive to relatively "poor" initial estimates of the parameters to be fitted, and once the correct model was selected, convergence was rapid.

A table of the concentrations of all "complexed" and "free" species can also be obtained and another option in the program allows these to be output in graphical form.

$\Delta H°$ and $\Delta S°$ values were calculated from plots of ln K against $1/T$ using eq. 5.

$$\ln K = -\Delta H°/RT + \Delta S°/R \quad (5)$$

Results and discussion

In all of the systems studied, the organotin(IV) Lewis acid and its adducts were found to be present in rapid (on the NMR time-scale) equilibrium, and consequently a single averaged ^{119}Sn resonance was observed. Although the observed resonance broadened on cooling, it remained a singlet even when solutions were cooled to $-80°$C. Similar fast exchange processes have been observed for the interactions of PCl_5 with pyrazine by use of ^{1}H NMR spectroscopy [18], and for the interactions of SnR_2X_2 (X = Cl, Br) with tributylphosphine oxide and other bases by use of ^{31}P and ^{119}Sn NMR spectroscopy [19,20].

In view of the fact that a variety of adducts, e.g. ML, ML_2 and M_2L [M = $SnPh_2X_2$], could be formed when solutions containing $SnPh_2X_2$ were titrated with pyrazine, each of the systems investigated was subjected to a thorough investigation in order to determine the exact stoicheiometry of the complexes present under the titration conditions. This was a relatively simple task, since a variety of models could be readily tested by use of the program EQNMR [17]. Each of the systems investigated was subjected to an analysis using at least three different models:

(i) Model A assumed that only ML was formed;

(ii) Model B assumed that both ML and ML_2 coexisted;

(iii) Model C assumed that ML and M_2L were formed.

Owing to the fact that an accurate value for ^{119}Sn chemical shift of the $SnPh_2X_2$ species could be readily obtained in the absence of added ligand, its value could be fixed during the refinement process. However, because of the low values of the equilibrium constants it was not possible to determine the ^{119}Sn chemical shifts independently for the various adducts formed. The "goodness" of fit was examined both visually and statistically. If the inclusion of additional species resulted in no significant improvement in R then it was assumed that these additional species were not present, or at least were present in exceedingly small concentrations ($\leqslant 3\%$ of

total metal concentration). Once a system was refined, the "guessed" starting values of the parameters were varied in order to ensure that a true minimum in the squares of the residuals had been achieved. An advantage of the program EQNMR is that when the experimental data are of good quality, the final fitted parameters are not dependent on the initial (guessed) values of the parameters, as they appear to do when an earlier fitting procedure is used [21]. In an additional test of the validity of the model used, the ^{119}Sn shift of the $SnPh_2X_2$ substrate under study was treated as a variable, and in all instances, the fitted shifts were in excellent agreement with the directly determined experimental values (see Table 2).

In order to validate the overall experimental procedures, the equilibrium constant and thermodynamic parameters for the reaction between $SnMe_3Cl$ and 4-methylpyridine in benzene, which had been previously investigated by Graddon [22] by a calorimetric method, were redetermined. The previous work had indicated that $SnMe_3Cl$ forms only a 1 : 1 adduct with 4-methylpyridine in benzene, and the data were processed on the basis of this assumption. The results obtained in the present investigation together with those reported by Graddon are shown in Table 1 and it is readily apparent that the agreement between the two sets of results is very satisfactory. Finally, all models were tested by using "ideal" synthesised data, and in all cases, the program EQNMR reproduced the data exactly.

Reactions of $SnPh_2X_2$ with pyrazine in chloroform

It was apparent from the outset that the interactions between all three substrates and pyrazine in this solvent were relatively weak, so that relatively high concentrations of pyrazine had to be used in order to ensure that appreciable concentrations of the adducts were formed. In most instances, the upper limit of the pyrazine concentration was dictated by solubility considerations.

The data for $SnPh_2Cl_2$ could be refined by use of either model A or model B (Table 2). Examination of the parameter R shows that the fit obtained with Model B is marginally better than that obtained with Model A. Additionally, the shift obtained for the ML species with Model A appears to be too negative compared to the values previously obtained for similar five-coordinate species. This view is reinforced by comparison with δ_{ML} for the five-coordinate adduct in acetonitrile in which only the 1 : 1 adduct is formed. Some solvation by acetonitrile would also be present in this latter complex. On balance, model B must be favoured for this system. Figure 1(a) shows a plot of the experimental and calculated ^{119}Sn chemical shifts against total pyrazine concentration while Fig. 2 shows a plot of the distribution of the species present as a function of the total base concentration.

The data for $SnPh_2Br_2$ could also be refined by using either model A or B. However, model B is favoured by both the value of R and the unreasonably negative

Table 1

Thermodynamic parameters for formation of the 1/1 adduct between $SnMe_3Cl$ and 4-methylpyridine in benzene at 303 K

K/ mol^{-1} dm^3	$\Delta H°$/ kJ mol^{-1}	ΔG/ kJ mol^{-1}	$\Delta S°$/ J K^{-1} mol^{-1}	Ref.
2.8	−33.6	−2.6	−102	Graddon [23]
3.2	−30.1(0.7)	−2.8	−90.0(2.2)	this work

Table 2

Parameters for the formation of adducts of $SnPh_2X_2$

X	Model	Temp./ K	Solvent	$10^2 K_1$/ $mol^{-1} dm^3$	$10^2 K_2$/ $mol^{-1} dm^3$	δM_{obs}	δM_{calc}	δML *	δML_2 *	R	No.	Data
a. With pyrazine												
Cl	A	294	CH_3CN	142	–	−128	−130	−246	–	1.33	23	[a]
Cl	A	303	CH_3CN	125	–	−121	−122	−229	–	2.10	20	[b]
Cl	A	308	CH_3CN	119	–	−117	−118	−220	–	1.48	20	[b]
Cl	A	313	CH_3CN	109	–	−113	−114	−215	–	1.21	20	[b]
Cl	A	294	$CHCl_3$	62.8	–	−28.8	−27.8	−385	–	3.75	23	[c]
Cl	B	294	$CHCl_3$	114	27.8	−28.8	−27.8	−232	−381	3.70	23	[c]
Cl	A	303	$CHCl_3$	38.3	–	−28.4	−28.4	−373	–	3.18	21	[d]
Cl	B	303	$CHCl_3$	87.6	16.5	−28.4	−28.1	−189	−411	2.87	21	[d]
Cl	A	313	$CHCl_3$	27.6	–	−28.5	−28.5	−365	–	2.78	21	[d]
Cl	B	313	$CHCl_3$	67.5	10.8	−28.5	−28.2	−175	−448	2.27	21	[d]
Br	A	294	CH_3CN	102	–	130	−131	−249	–	1.74	22	[e]
Br	A	294	$CHCL_3$	13.2	–	−72.5	−71.4	−474	–	4.80	24	[f]
Br	B	294	$CHCl_3$	84.0	14.3	−72.5	−72.1	−134	−417	4.20	24	[f]
I	A	294	CH_3CN	28.0	–	−248	−247	−323	–	0.85	32	[g]
I	A	294	$CHCl_3$	9.56	–	−240	−239	−775	–	2.88	27	[h]
I	B	294	$CHCl_3$	7.37	25.5	−240	−240	−277	−304	1.05	27	[h]
b. With acetonitrile in chloroform												
Cl	A	294	$CHCl_3$	1.92	–	−28.8	−25.8	−683	–	6.49	15	[i]
Cl	B	294	$CHCl_3$	10.9	11.2	−28.8	−28.2	−111	−221	2.68	15	[i]

* All shifts relative to $SnMe_4$. [a] Maximum pyrazine concentration 0.95 mol dm^{-3}. [b] Maximum pyrazine concentration 0.71 mol dm^{-3}. [c] Maximum pyrazine concentration 2.75 mol dm^{-3}. [d] Maximum pyrazine concentration 2.14 mol dm^{-3}. [e] Maximum pyrazine concentration 0.91 mol dm^{-3}. [f] Maximum pyrazine concentration 3.7 mol dm^{-3}. [g] Maximum pyrazine concentration 3.2 mol dm^{-3}. [h] Maximum pyrazine concentration 6.3 mol dm^{-3}. [i] Maximum acetonitrile concentration 6.02 mol dm^{-3}.

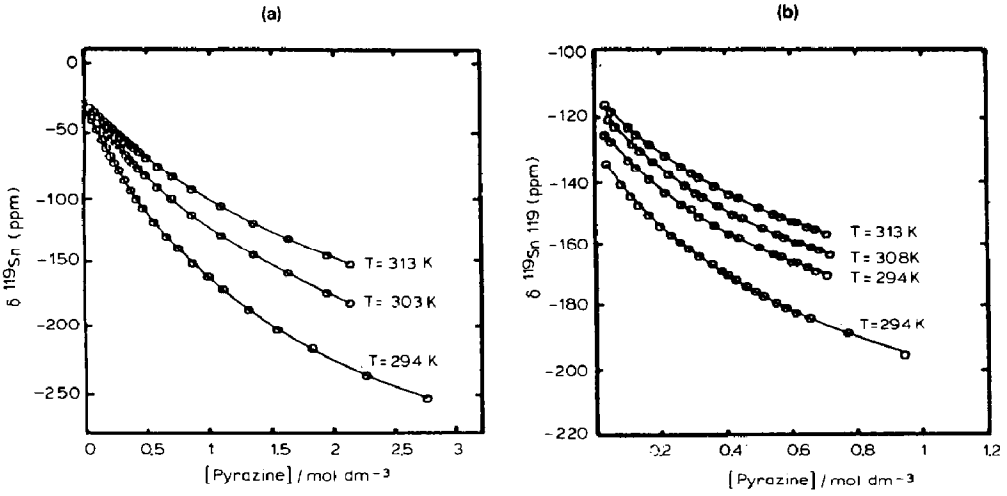

Fig. 1. Concentration and temperature dependence of δ ^{119}Sn in the $SnPh_2Cl_2$–pyrazine system showing experimental (○) and calculated (solid line) data for concurrent formation of 1:1 and 1:2 (M:L) complexes in chloroform (a) and 1:1 complex formation in acetonitrile (b). In (a) the $SnPh_2Cl_2$ concentration varies in the range 0.0979 to 0.0837 mol dm^{-3} while in (b) it varies in the range 0.1010 to 0.0682 mol dm^{-3}.

value obtained for δ_{ML} in model A. As in the case of $SnPh_2Cl_2$, there is no evidence for the presence of an M_2L species.

The interaction between $SnPh_2I_2$ and pyrazine is very weak, and although solubility considerations enabled the use of rather high concentrations of pyrazine,

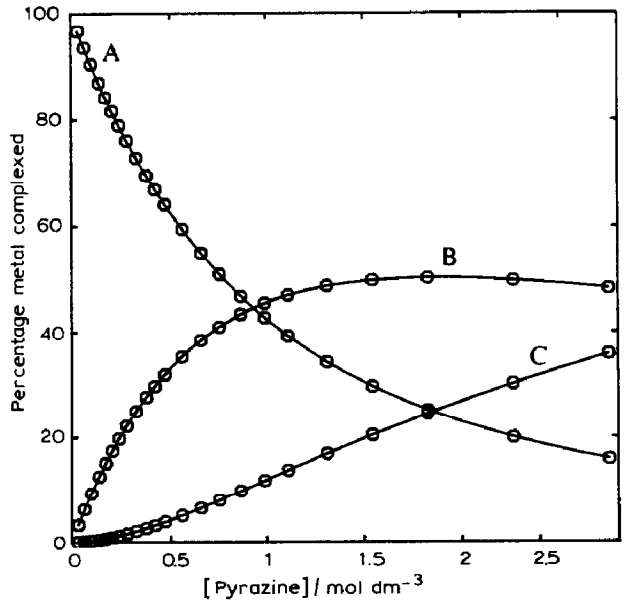

Fig. 2. Distribution plot for the $SnPh_2Cl_2$–pyrazine system (Model B) in chloroform at 294 K; (A) $SnPh_2Cl_2$; (B) $SnPh_2Cl_2$·pyrazine; (C) $SnPh_2Cl_2$·(pyrazine)$_2$. Open circles show the concentrations at which experimental measurements were carried out.

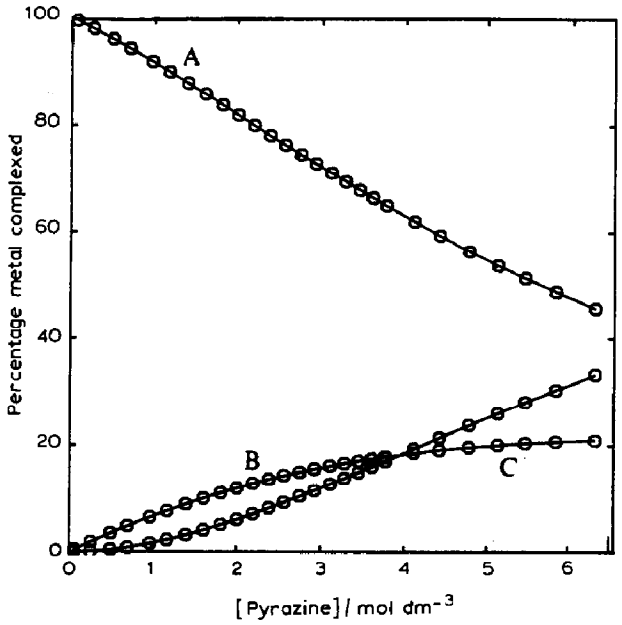

Fig. 3. Species distribution plot for the $SnPh_2I_2$–pyrazine system (Model B) in chloroform at 294 K; (A) $SnPh_2I_2$; (B) $SnPh_2I_2$·pyrazine; (C) $SnPh_2I_2$·(pyrazine)$_2$. Open circles show the concentrations at which experimental measurements were carried out.

it was apparent from the measured values of the chemical shifts that the the degree of complex formation was quite small. Nevertheless, the data could be refined, and it is apparent from Table 2 that they are consistent with a model involving the simultaneous formation of 1 : 1 and 1 : 2 (M : L) adducts (model B). Figure 3 shows a species distribution plot obtained by use of the values from Table 2. It is apparent that even at the highest concentration of pyrazine used, only about 30% of the organotin species is complexed.

These results show that in chloroform solutions, $SnPh_2X_2$ (X = Cl, Br, I) Lewis acids form adducts of both 1 : 1 and 1 : 2 stoicheiometries with pyrazine. Furthermore, it is apparent from Fig. 2 and 3 that the 1 : 1 adducts are the dominant species present under the conditions used. The chemical shifts calculated for the adducts are typical of those normally found for five- and six-coordinate diorganotin species [12–14,23].

The values of the equilibrium constants indicate that the adducts formed by $SnPh_2X_2$ (X = Cl, Br, I) with pyrazine have relatively low stabilities. The equilibrium constants are considerably lower than those previously reported for the analogous 1 : 1 and 1 : 2 (M : L) complexes of SnR_2Cl_2 (R = Ph, Me, n-Bu) with pyridine and substituted pyridines [24]. For the 1 : 1 adducts, the stability order is Cl > Br > I. This is to be expected on the basis of the reducing Lewis acidity on going from the chloride to the bromide to the iodide substrate.

In chloroform, $K_1 > K_2$ for both the $SnPh_2Cl_2$ and $SnPh_2Br_2$–pyrazine systems, but for the $SnPh_2I_2$–pyrazine system it is found that $K_2 > K_1$. Thus, the ratio K_1/K_2 decreases in the order Cl, Br, I. The present result for the iodide parallels previous results with SnI_4 and diorganotin diiodide systems. For example, tin(IV) iodide forms both ML and ML_2 complexes with dimethylsulphoxide and dimethyl-

formamide, and for the stepwise formation constants of these adducts, $K_2 > K_1$ [25]. Furthermore, Graddon has recently reported [26] the equilibrium constants for formation of adducts of diorganotin diiodides with pyridine and 4-methylpyridine, and in these systems K_2 is also larger than K_1 (for pyridine $K_1 = 0.6$, $K_2 = 6$; for 4-methylpyridine $K_1 = 2.8$, $K_2 = 10$). The extremely low stability of the 1 : 1 adducts of diorganotin diiodides is thought to be entropic in origin, with the large iodine restricting the fluxional behaviour of the five-coordinate 1 : 1 adduct.

Reactions of $SnPh_2X_2$ with pyrazine in acetonitrile

For all three systems in this solvent, the data are consistent with the presence of a 1 : 1 adduct as the major species (Model A). There is no evidence for the presence of any M_2L or ML_2 tin species under the conditions used.. The value of R is encouragingly small for all three substrates. Overall, the values of the chemical shifts calculated for the 1 : 1 adducts are somewhat more negative that those calculated for the analogous 1 : 1 adducts in chloroform. This is consistent with a situation in which there is weak coordinative interaction between the metal centre in the 1 : 1 adduct and acetonitrile solvent. Since this effectively raises the coordination number of tin, the ^{119}Sn resonance should be shifted slightly upfield from the shift usually observed for five-coordinate adducts. Similar upfield shifts have been observed for $SnBu_2(OMe)_2$ in going from non-coordinating solvents to the coordinating hexamethylphosphortriamide [27]. That solute–solvent interactions play an important role in solutions containing organometallic compounds where the metal can behave as a Lewis acid has been pointed out recently by Fujiwara et al. using ^1H T_1 measurements [28].

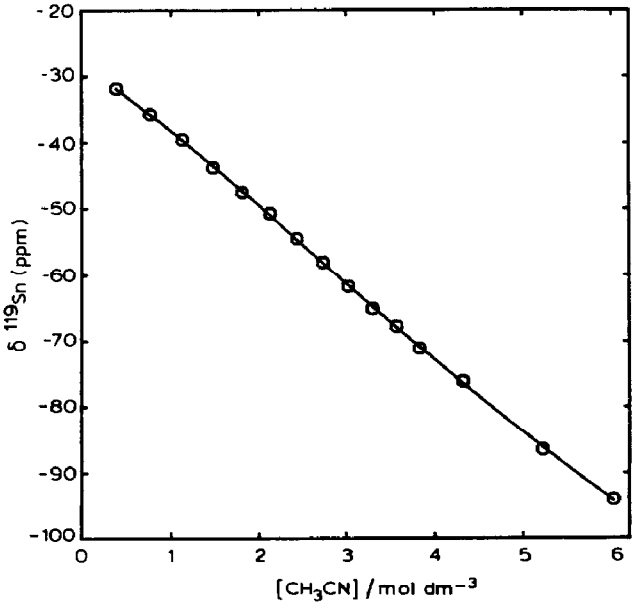

Fig. 4. Plot of δ ^{119}Sn against total acetonitrile concentration for the $SnPh_2Cl_2$–acetonitrile system in chloroform at 294 K. Open circles represent experimental points while the solid line represents the values calculated using the fitted parameters obtained using Model B.

Acetonitrile is a coordinating solvent and in solution there is adduct formation with the substrate diorganotin dihalides. Evidence for this stems from several sources. Firstly, the observed resonances of the $SnPh_2X_2$ species themselves (Table 2) are found to be at a much lower frequency (more shielded) in acetonitrile and are more typical of five-coordinate type shifts than the four-coordinate type found in non-coordinating solvents. Secondly, the temperature dependence of the ^{119}Sn chemical shifts in the $SnPh_2X_2$ substrates is found to be much greater in acetonitrile than in chloroform. Figures 1(a) and 1(b) illustrate the difference in the temperature dependence of the ^{119}Sn chemical shift in $SnPh_2Cl_2$ in chloroform and acetonitrile, respectively. This greater temperature dependence at zero concentrations of added ligand in acetonitrile is indicative of a metal–solvent interaction. Finally, the interaction of acetonitrile with $SnPh_2Cl_2$ was investigated by titrating acetonitrile into a solution of the Lewis acid in chloroform. The dependence of the ^{119}Sn chemical shift on the acetonitrile concentration is shown in Fig. 4 and the data were found to best fit a model containing adducts of both 1:1 and 1:2 (M:L) stoicheiometries with the unusual situation of $K_2 > K_1$. ($K_1 = 0.109$; $K_2 = 0.112$; $\delta_{ML} = -111$; $\delta_{ML2} = -220$; $R = 2.7$.) It is evident from Fig. 4 that these data reproduce the experimental data very well indeed.

The formation constants of the 1:1 adducts in acetonitrile were found to be larger than those for the analogous species in chloroform; the stability order remains the same however, Cl > Br > I. Okawara et al. [29] have studied the complex formation equilibria between 2,2-bipyridine and tin Lewis acids in solution. They found that the formation constants increased with increasing polarity of the solvent. This is rationalised on the basis that the tin–halogen bond is affected by coordination about tin and that a dipolar situation exists viz $N^{\delta+}$–Sn–$Cl^{\delta-}$, the stability of which would depend on the polarity of the solvent. Extended Hückel calculations (to be reported) are supportive of such a dipolar situation. Whilst such a phenomenon may be a contributing factor in the systems under investigation here, it is by no means the only factor involved. Solvent phenomena may determine, to a large extent, the magnitude of the observed entropy term for such reactions and consideration of such phenomena would suggest that adduct formation in acetonitrile might be more favoured since greater solvation of reactants by this solvent would lead to greater release of solvent molecules on complex formation (eq. 5) and hence a more positive and more favourable entropy term.

$$MS + LS = MLS + S \qquad (5)$$

Thermodynamic considerations

Solvation phenomena such as those mentioned above manifest themselves in the thermodynamic parameters for the formation of the 1:1 pyrazine adduct of $SnPh_2Cl_2$ (Table 3). While the enthalpies of formation of the 1:1 pyrazine adducts of $SnPh_2Cl_2$ with pyrazine are negative in both chloroform and acetonitrile, $\Delta H_1°$ is more negative in the former solvent. This is consistent with the displacement of coordinated solvent from $SnPh_2Cl_2$ in acetonitrile in the course of adduct formation. The cleavage of the tin–solvent bond in the course of solvent displacement lowers the exothermicity of the reaction.

The values of $\Delta S°$ observed for 1:1 adduct formation are small and negative, being less negative in acetonitrile than in chloroform. The negative values may be

Table 3

Thermodynamic parameters for formation of the 1:1 adducts of $SnPh_2Cl_2$ with pyrazine at 294 K

Solvent	ΔH_1°/ kJ mol^{-1}	ΔS_1°/ J K^{-1} mol^{-1}	K
$CHCl_3$	−19.2(0.7)	−64.7(2.3)	1.09
CH_3CN	−10.4(0.7)	−32.3(2.2)	1.42

due for the main part to decreases in the translational and rotational freedom of pyrazine.

Using the terminology of Fujiwara et al. [30], the entropy change on complex formation for the reaction in eq. 6 can be equated

$$A + B = AB \tag{6}$$

to the difference in the third-law entropies of its components (eq. 7) were ΔS°_{AB} (calculated) is considered to correspond to the gas phase value of ΔS°.

$$\Delta S^\circ_{AB}\ (\text{calculated}) = \Delta S^\circ_{AB} - (\Delta S^\circ_A + \Delta S^\circ_B) \tag{7}$$

Assuming that the vibrational and electronic contributions to the entropy are similar on going from reactants to product and considering only the translational and vibrational contributions [30], the value of ΔS°_{AB} (calculated) for the $SnPh_2Cl_2$–pyrazine system is found to be −239 J K^{-1} mol^{-1}. The discrepancy between the observed and calculated values may be explained on the basis of solvation phenomena. The formation of new chemical bonds and their contribution to the vibrational entropy is very small as is the restriction on internal motion on complex formation [30]. In contrast to this however, solvation by chloroform cannot be considered negligible. The proton in chloroform has weak acidic character and can form weak hydrogen bonds with pyrazine. Furthermore, chloroform is a relatively polar solvent and hence can solvate by means of electrostatic attraction. Kuroi et al. [31] have studied the interaction between pyrazine and halomethanes and have found evidence for 1:1 complex formation between pyrazine and chloroform (K_1 = 1.04 mol^{-1} dm^3 at 293 K). Such complex formation is considered to be due to hydrogen bonding, charge transfer, or to a combination of both. Thus, complex formation in chloroform may best be considered as taking place according to eq. 5 and hence the observed entropy would be expected to deviate markedly from the calculated value.

In acetonitrile, solvation of both the pyrazine and the tin moiety will occur to a much greater extent than in chloroform. Evidence for this stems from the fact that the entropy change observed on formation of the 1:1 pyrazine adduct is considerably less negative in acetonitrile than in chloroform, consistent with the release of additional solvent molecules on complex formation in acetonitrile. More precisely, Fujiwara et al. [32] have shown that for the reaction A + B = AB where A, B, and AB are weakly solvated and where the numbers of solvation are a, b, and c, respectively, the number of solvent molecules released on complex formation i.e. $a + b - c$) is given by eq. 8 where S°_L is the entropy of the solvent. For reaction of $SnPh_2Cl_2$ with pyrazine in chloroform and acetonitrile these

$$a + b + c = (\Delta S^\circ_{soln} - \Delta S^\circ_{calcd})/S^\circ_L \tag{8}$$

calculations yield values for $(A + b - c)$ of 0.59 and 0.85, respectively. This is entirely consistent with greater solvent release in acetonitrile.

Temperature dependence of δ ^{119}Sn

Worthy of mention is the temperature dependence of the ^{119}Sn chemical shifts of the complexed species investigated in the present work. The temperature dependence of the ^{119}Sn chemical shift of the 1 : 2 pyrazine adduct of $SnPh_2Cl_2$ in acetonitrile is linear and there is a shift to lower field with increasing temperature (Table 2). The temperature dependence of 2.97 ppm K^{-1} is quite large. In chloroform solutions an unusual situation arises. The temperature dependencies of the chemical shifts are again linear; however, while δ ^{119}Sn for the 1 : 1 adduct, $SnPh_2Cl_2 \cdot pyz$, shifts to lower field on increasing temperature (1.68 ppm K^{-1}), it shifts to higher field (-3.4 ppm K^{-1}) in the case of the 1 : 2 adduct, $SnPh_2Cl_2 \cdot 2pyz$.

The effect of temperature on the ^{119}Sn nuclear shielding is little understood. However, Mitchel [34] has observed shifts to higher field with increasing temperature for both $SnPr^i_2Br_2$ and $SnPr^iBr_3$ in the absence of complexation or autoassociation phenomena. Furthermore, the unassociated methyltin complexes $SnMe_2(OBu^t)_2$, $SnMe(OBu^t)_3$ and $SnMeI_3$ all having highly shielded tin nuclei exhibit variable shifts to lower fields with increasing temperature, 0.06, 0.11 and 0.26 ppm K^{-1} respectively [35]. A detailed analysis of the variation of the temperature dependence of δ ^{119}Sn with concentration for the systems studied here together and an account of the unique profiles produced by such an analysis, will be presented in a subsequent publication.

Solution versus solid state studies

It is evident from this investigation that the interactions between pyrazine and the diphenyltin dihalides in solution differ somewhat from those found in the solid state. X-ray crystallographic investigations [8] indicate that diphenyltin dichloride forms both a 1 : 1 polymer and a 2 : 1 (M : L) dimer, both of which exist in the same crystal lattice. In the 1 : 1 polymeric species, tin is six-coordinate and the solid state ^{119}Sn NMR chemical shift is only -153.2 ppm. This contrasts markedly with the six-coordinate 1 : 2 (M : L) species formed in chloroform, the calculated chemical shift of which is -381 ppm (Table 2). There is no evidence for the existence of a polymeric species in either chloroform or acetonitrile. Tin is five-coordinate in the 2 : 1 (M : L) dimeric species and δ ^{119}Sn (solid state) is -129.6 ppm. There is no evidence for the existence of this 2 : 1 dimer in solution. In chloroform, the only five-coordinate species formed in the 1 : 1 monomeric adduct with a calculated chemical shift of -232 ppm (Table 2) and in acetonitrile, there is evidence of only the 1 : 1 adduct.

We have carried out a detailed structural investigation of the pyrazine adducts of diorganotin dihalides in the solid state, the results of which will be published shortly. Diphenyltin dibromide forms a 2 : 1 (M : L) dimer, yet the present study indicates the existence of both 1 : 1 and 1 : 2 complexes in chloroform and a 1 : 1 complex in acetonitrile. Diphenyltin diiodide also forms a 2 : 1 (M : L) dimer in the solid state, yet its solution chemistry is similar to that of the dichloride and the dibromide. Clearly, the species formed in solution are very different to those observed in the solid state, a situation that is by no means unprecedented [33].

Conclusions

This investigation demonstrates that with the program EQNMR even very weak interactions between organotin species and Lewis bases can be investigated in solution by use of data from nuclear magnetic resonance shift studies. The program is capable of evaluating both the equilibrium constants and the chemical shifts in a wide range of equilibria. It goes without saying, however, that the uncertainty of the determined parameters will generally increase as the strength of the interactions between the Lewis acid and the Lewis base decreases. When the interactions are very weak, even at the relatively high ligand concentrations used in the present studies, the fraction of the Lewis acid converted into the adduct will be considerably < 1. In this situation, the limiting value of the chemical shift for the highest adduct formed cannot be independently determined, and there is considerable extrapolation involved in calculating this parameter. When a number of adducts are formed simultaneously in solution, it is rarely possible to determine experimentally the shifts of the individual species present.

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