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

II. * ^{119}Sn NMR investigations of the pyrazine adducts of dialkyltin(IV) dihalides

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Abstract

The interactions of SnR_2X_2 (R = Me, Et, ^{n}Pr, ^{n}Bu; X = Cl, Br, NCS) with pyrazine (L) have been investigated in both chloroform and acetonitrile. Equilibrium constants have been determined by using ^{119}Sn chemical shifts and the computer program EONMR. In chloroform, $Sn^nBu_2Cl_2$ and $Sn^nBu_2Br_2$ form complexes of composition ML and ML_2, with ML the dominant species. In acetonitrile all of the tin(IV) complexes form only the 1:1 adducts (ML). Thermodynamic parameters have been determined for these systems in both solvents.

Key words: Tin; Diazine; Pyrazine; Nuclear magnetic resonance

1. Introduction

The interactions of organotin(IV) halides and their complexes with biological systems have been reviewed [2]. Diorganotin dihalides and their complexes are becoming increasingly important in the area of antitumour activity and cancer chemotherapy. In particular, both dibutyltin(IV) dichloride and dioctyltin(IV) dichloride exhibit cytotoxic activity towards T-lymphocytes and have potential as anti-T-cell tumour agents [3]. Dialkyltin(IV) dihalides have also been shown to be active against P388 lymphocytic leukaemia [4,5]. An important class of compounds in this area are diorganotin(IV) dichloride complexes with N-donor ligands that have *trans* organo-groups and *cis* halogens [6].

In view of the biological importance of organotin species and the extensive occurrence of pyrazines in nature [7], particularly in purine and pyrimidine bases, determination and interpretation of data on the interactions of organotin species with the simple *bis* monodentate pyrazine and related diazine ligands can provide an important reference point for research on complexes of organotins with nucleotides or nucleosides. Such studies thus represent an important starting point for seeking understanding of the antitumour activity of diorganotin(IV) dihalides and their nitrogen donor adducts. Furthermore, these systems serve as important models for understanding the general toxicology of organotin compounds.

We recently reported [1] a method for the elucidation of the stoichiometries and stabilities of complexes formed when a Lewis acid (M) reacts with a base (L) to form M_mL_n species in solution. In particular, this interactive procedure for the analysis of the concentration dependence of NMR chemical shift data on the chemical equilibria present in solution has been applied to the study of the interactions between pyrazine and the Lewis acids $SnPh_2X_2$ (X = Cl, Br, I) in both chloroform and acetonitrile. In chloroform solution, both complexes of composition ML and ML_2 were found to co-exist whereas in acetonitrile, only the ML complex was formed. The value of K_1 for formation of

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the ML complexes was found to decrease in the order (X =) Cl > Br > I. As part of our continuing investigations of such systems, we now report the results of our studies on the interactions between the dialkyltin(IV) dihalides, SnR_2X_2 (R = Me, Et, ^{n}Pr and ^{n}Bu; X = Cl, Br) and pyrazine in both chloroform and acetonitrile. Equilibrium constants and thermodynamic parameters for these systems have been determined.

2. Experimental details

2.1. Materials

$SnMe_2Cl_2$ (Aldrich Chemical Co.) was purified by sublimation prior to use. $Sn^nPr_2Cl_2$ was prepared by interaction of Sn^nPr_4 and $SnCl_4$ and purified by recrystallization from petroleum spirit (b.p. 40–60°C). $SnEt_2Cl_2$ was prepared similarly from $SnEt_4$. $Sn^nBu_2Cl_2$ (Aldrich Chemical Co.) and $Sn^nBu_2Br_2$ (Aldrich Chemical Co.) were purified by distillation *in vacuo*.

Acetonitrile was dried and distilled over calcium hydride. Chloroform was dried and distilled over phosphorus pentoxide. Petroleum spirit (b.p. 40–60°C) was dried over calcium chloride, and after distillation was stored over sodium wire.

2.2. Instrumentation and techniques

The ^{119}Sn NMR spectra were recorded on a Jeol JNM GX 270 FT NMR spectrometer operating at 100.55 MHz (frequency width 80.6 KHz, 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 determined relative to internal $SnMe_4$, (0.05 mol dm^{-3}). Undeuterated 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 [8] the total substrate concentration was maintained at ≤ 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. No precipitation was observed over the concentration and temperature ranges employed. Following each addition of pyrazine, 20 min more was allowed for the solution to reach the probe temperature and the spectrum then recorded. The probe temperature was calibrated by use of a methanol thermometer.

Equilibrium constants were calculated using the program EQNMR [9] as previously described [1]. The merit function R used to decide the "goodness of fit" is given by eqn. (1).

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

3. Results

As with the diphenyltin(IV) dihalides previously reported [1] the dialkyltin dihalide Lewis acids and their adducts were found to be in rapid equilibrium with

TABLE 1. Parameters for formation of adducts of SnR_2X_2 with pyrazine

SnR_2X_2 [a]	Solvent	T (K)	$10^2 K_1$ (mol^{-1} dm^3)	$10^2 K_2$ (mol^{-1} dm^3)	δ_M (ppm)		δ_{ML} (ppm)	δ_{ML_2} (ppm)	R	No. Data
					Expt.	Calc.				
$SnMe_2Cl_2$ [a]	CH_3CN	294	91.0	38	37	−80	–	0.537	31	
$SnMe_2Cl_2$ [a]	CH_3CN	303	73.4	–	44	44	−75	0.548	22	
$SnMe_2Cl_2$ [a]	CH_3CN	313	65.1	–	47	46	−74	–	0.352	22
$SnEt_2Cl_2$ [a]	CH_3CN	294	78.5	–	34	34	−69	–	3.74	18
$SnEt_2Cl_2$ [a]	CH_3CN	303	58.6	–	37	37	−67	–	1.90	18
$SnEt_2Cl_2$ [a]	CH_3CN	313	49.4	–	43	43	−59	–	1.05	18
$Sn^nPr_2Cl_2$ [a]	CH_3CN	294	55.4	–	41	40	−66	–	1.61	21
$Sn^nPr_2Cl_2$ [a]	CH_3CN	303	43.5	–	45	45	−62	–	0.783	21
$Sn^nPr_2Cl_2$ [a]	CH_3CN	313	33.7	–	51	50	−58	–	0.682	21
$Sn^nBu_2Cl_2$ [b]	$CHCl_3$	294	40.0	1.48	125	125	−82	−405	0.535	21
$Sn^nBu_2Cl_2$ [a]	$CHCl_3$	303	24.3	–	126	126	−121	–	0.402	21
$Sn^nBu_2Cl_2$ [b]	$CHCl_3$	303	27.4	1.80	126	126	−95	−169	0.403	20
$Sn^nBu_2Cl_2$ [b]	$CHCl_3$	313	17.0	–	126	126	−131	–	0.182	20
$Sn^nBu_2Cl_2$ [b]	$CHCl_3$	313	20.2	2.02	126	126	−91	−175	0.181	20
$Sn^nBu_2Br_2$ [a]	$CHCl_3$	294	3.97	–	90	91	−488	–	0.654	26
$Sn^nBu_2Br_2$ [b]	$CHCl_3$	294	15.1	12.7	90	90	−46	−138	0.467	26
$Sn^nBu_2Br_2$ [a]	CH_3CN	294	33.5	–	44	43	−66	–	0.402	29
$Sn^nPr_2Br_2$ [a]	CH_3CN	294	35.8	–	41	42	−64	–	0.550	22
$Sn^nBu_2(NCS)_2$ [a]	CH_3CN	294	89.8	–	−261	−260	−314	–	0.204	20

[a] Model A; [b] Model B.

pyrazine, and only a single averaged ^{119}Sn resonance was observed in each case. Although cooling of solutions containing the Lewis acids and pyrazine to −80°C resulted in broadening of the observed resonance, separate resonances for the individual species present were not observed for any of the systems.

Pyrazine can behave as a unidentate ligand, and in so doing can form adducts having the stoichiometries ML or ML_2, where M represents the diorganotin(IV) Lewis acid. The stepwise stability constants for the formation of these complexes are given by eqns. (2) and (3). Alternatively, it can behave as a bis-monodentate ligand

$$M + L \overset{K_1}{\rightleftharpoons} ML \quad (2)$$

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2 \quad (3)$$

and form dimeric adducts M_2L. In view of this, all the systems were thoroughly investigated in order to determine the stoichiometries of the species formed in solution. This was done by using the program EQNMR as previously reported [1]. Each of the systems studied was subjected to analysis by use of at least three different models. Model A assumed only the presence of ML, model B that of both ML and ML_2, and Model C that of ML and M_2L species.

3.1. Reactions in chloroform

The interactions between the Lewis acids $Sn^nBu_2X_2$ (X = Cl, Br) and pyrazine in chloroform were very weak, and so, high concentrations of ligand were required in order to bring about appreciable adduct formation. Data for the $Sn^nBu_2Cl_2$–pyrazine system could be refined using both models A and B (Table 1). During the fitting procedure, all the equilibrium constants and the chemical shifts were treated as variables. The calculated value of δ_M was in good agreement with the directly measured value (Table 1). Examination of the R values (eqn. (1)) shows that the fit obtained for model B is marginally better than that obtained for model A. Figure 1 illustrates the fits obtained for model B at various temperatures. Thus, the $Sn^nBu_2Cl_2$–pyrazine system in chloroform is best described by a model in which both ML and ML_2 species are formed, with $K_1 > K_2$. Figure 2 shows a species distribution plot as a function of the free ligand concentration, and clearly illustrates the fact that the 1:1 adduct is the dominant species present. At 294 K, at a pyrazine concentration of 4.66 mol dm^{-3}, only 4.2% of the tin is present as the ML_2 complex, and this is further reduced at higher temperatures. This is because eventhough the K_2 values increase somewhat with temperature, the overall stability constant for formation of ML_2 (K_1K_2) decreases with increasing temperature. Arising from this, the difference between the K_1 values produced by models A and B at a given temperature decreases with increasing temperature, and the reliability of the calculated values of δ_{ML_2} also decreases greatly with increase in temperature. Indeed the chemical shift of −405 ppm calculated for ML_2 at 294 K is typical for that of a six-coordinate dioganotin(IV) dihalide complex.

The equilibrium constants for successive formation of the ML and ML_2 species (Table 1) are much smaller

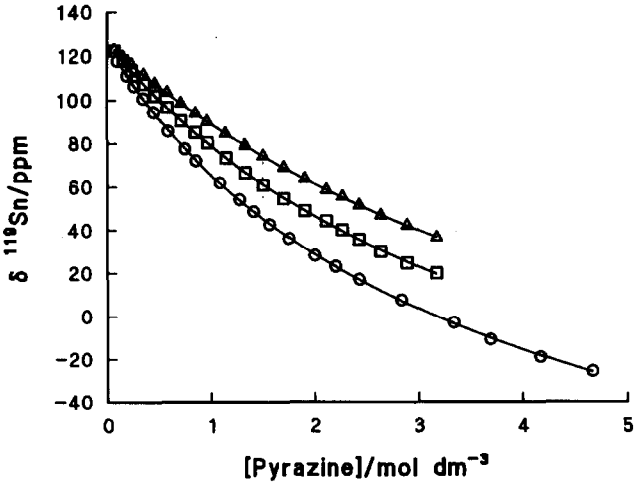

Fig. 1. Plot of δ ^{119}Sn against pyrazine for reaction of Sn^nBuCl_2 with pyrazine in chloroform at temperatures: ○, 294; □, 303; △, 313 K. x-axis, [pyrazine] (mol dm^{-3}); y-axis, δ ^{119}Sn/ppm.

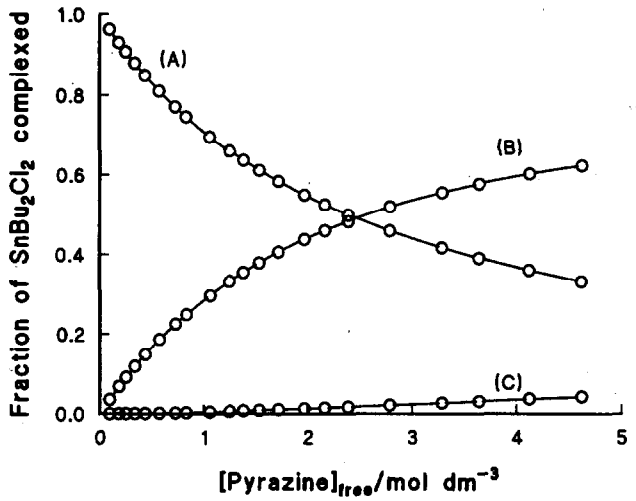

Fig. 2. Species distribution plot for reaction of Sn^nBuCl_2 with pyrazine in chloroform at 294 K. (A) $Sn^nBu_2Cl_2$; (B) $Sn^nBu_2Cl_2(pyz)$; (C) $Sn^nBu_2Cl_2(pyz)_2$. x-axis, free pyrazine concentration (mol dm^{-3}); y-axis, fraction of free and complexed $Sn^nBu_2Cl_2$.

that those reported for the ML and ML_2 species formed by $SnPh_2Cl_2$ in chloroform with the same ligand [1]. This is to be expected on the basis of the lower Lewis acidity of $Sn^nBu_2Cl_2$.

The interaction of pyrazine with $Sn^nBu_2Br_2$ in chloroform is much weaker than that with $Sn^nBu_2Cl_2$. This is apparent also from the chemical shifts. The chemical shift on complex formation is a measure of the strength of the acid–base interaction. At 294°C the value of $(\delta_M-\delta_{ML})$ for the Sn^nBuCl_2–pyrazine interaction is 206 ppm, while that for $Sn^nBu_2Br_2$ under the same conditions is only 136 ppm. Despite the weakness of the interaction between pyrazine and $Sn^nBu_2Br_2$ and the relatively small degree of complex formation, the data could be fitted to model B. The value obtained for K_1 (Table 1) is smaller than the corresponding value for $Sn^nBu_2Cl_2$, in keeping with the lower Lewis acidity of $Sn^nBu_2Br_2$. As in the case of $Sn^nBu_2Cl_2$, K_1 is larger than K_2. However, the ratio K_1/K_2 is smaller. In these respects the results parallel those for $SnPh_2X_2$ (X = Cl or Br) in chloroform [1], and indeed for successive formation of 1:1 and 1:2 complexes with $SnPh_2I_2$, K_2 is actually larger than K_1. Similar observations have been made by Graddon [10] for the interactions of pyridine with diphenyltin(IV) dihalides in benzene solutions. It appears that the stability of the 1:2 complex relative to that of the 1:1 species rises in the sequence (X =) Cl < Br < I.

3.2. Reactions in acetonitrile

In contrast to the data for the chloroform systems, the data for systems studied in acetonitrile were always consistent with the exclusive formation of 1:1 adducts (model A). Equilibrium constants together with calculated shifts for the 1:1 adducts are listed in Table 1. The concentration and temperature dependence of δ ^{119}Sn for the SnR_2X_2 (R = Me, Et, ^{n}Pr, ^{n}Bu) systems are shown in Fig. 3.

The formation constants (Table 1) for 1:1 adduct formation of $Sn^nBu_2X_2$ (X = Cl, Br) with pyrazine in acetonitrile are larger than those in chloroform, and the calculated shifts (δ_{ML}) are considerably more negative. This is probably due to coordination of the 1:1 pyrazine adduct by acetonitrile.

As in chloroform, the order of stability of the 1:1 adducts as X is varied is Cl > Br. In acetonitrile, $Sn^nBu_2(NCS)_2$ forms a more stable 1:1 complex with pyrazine than either the chloride or bromide. This is in accord with the findings of Graddon et al. [11] with respect to formation of 1:1 adducts of $Sn^nBu_2X_2$ (X = Cl, NCS) with pyridine in benzene, and is attributable to the rod-like nature of the NCS ligand and consequent lower steric interference. As the alkyl groups on tin are varied, the stability decreases in the order Me > Et > ^{n}Pr > ^{n}Bu, in keeping with the order of Lewis acidity of the dialkyltin(IV) dihalides.

Thermodynamic parameters were determined from

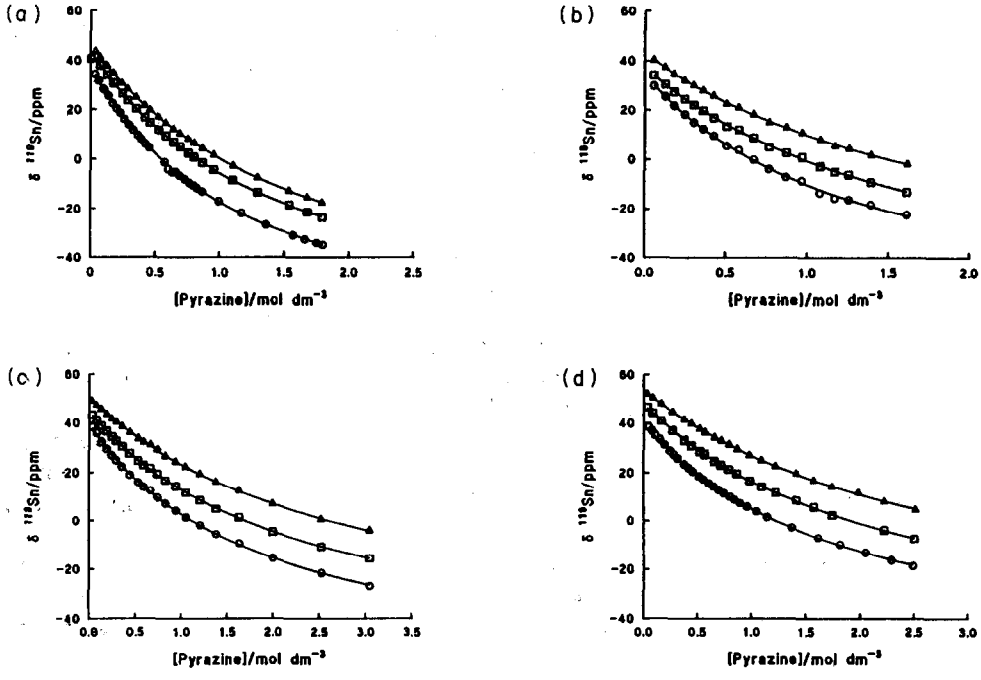

Fig. 3. Plots of δ ^{119}Sn against [pyrazine] for reaction of SnR_2Cl_2 with pyrazine in acetonitrile at temperatures: ○, 294; □, 303; △, 313 K. (a) $SnMe_2Cl_2$; (b) $SnEt_2Cl_2$; (c) $Sn^nPr_2Cl_2$; (d) $Sn^nBu_2Cl_2$. *x*-axis: [pyrazine] (mol dm^{-3}); *y*-axis: δ ^{119}Sn (ppm).

van't Hoff plots for the temperature dependence of the equilibrium constants, and are listed in Table 2.

4. Discussion

In general, the dialkyltin(IV) dihalides tend to form complexes of ML and ML_2 stoichiometries with monodentate ligands in solution and complexes only ML with bidentate ligands such as 2,2'-bipyridine and 1,10-phenanthroline [10]. For complexation with monodentate ligands, there is evidence to suggest that the complexes ML are favoured in solution [12], and in some cases in which stable complexes ML_2 have been isolated in the solid state the solution studies have given evidence only for complexes of 1:1 stoichiometry [1]. In the present study, the data for interactions in chloroform solution were consistent with the successive formation of ML and ML_2 species, but the complex ML was the dominant species. In acetonitrile solution, only complexes of 1:1 stoichiometry are formed. However, comparison of the calculated chemical shifts for the 1:1 complexes in acetonitrile with those calculated for the analogous species in chloroform suggest that tin is six coordinate, with an acetonitrile molecule completing the coordination sphere.

The magnitude of the equilibrium constants for adduct formation in both acetonitrile and chloroform indicates that pyrazine is a much weaker donor than pyridine or the monomethyl-substituted pyridines [10,11,13]. Pyrazine ($pK = 0.65$) would be expected to give rise to a less stable dialkyltin(IV) dihalide complexes than ($pK = 5.24$) or picoline in view of the lower electron density at nitrogen resulting from the presence of a second nitrogen in the ring, and consequent withdrawal of electron density into the ring. Thus the magnitude of the equilibrium constants found in the present study can be rationalized on this basis.

None of the systems in the current investigation provided evidence for the formation of complexes M_2L, although such complexes with pyrazine acting in a bis monodentate fashion are known to in the solid state [1,14]. This difference between the solid state and solution chemistry of these systems is not unprecedented [15,16]. Furthermore, 2,2'-bipyridine usually behaves as a bidentate chelating ligand, giving rise to 1:1 complexes of diorganotin(IV) dihalides and pseudohalides. However, Okawara *et al.* [17] have presented evidence for the formation of an adduct M_2L of 2,2'-bipyridine with tin(IV) tetrachloride in acetonitrile solution where the 2,2'-bipyridine acts in bis-monodentate fashion. Di- and tri-organotin(IV) isothiocyanates also form 2:1 adducts with 2,2'-bipyridine in solution but, by contrast, the analogous organotin(IV) chlorides form only 1:1 adducts [18,19]. In view of this latter observation, and also the fact that pyrazine is a considerably weaker Lewis base than 2,2'-bipyridine, it is not surprising that 1:1 adduct formation between diorganotin(IV) dihalides and pyrazine predominates in solution. On the other hand, it is perhaps a little surprising that $Sn^nBu_2(NCS)_2$ forms only a 1:1 complex with pyrazine in acetonitrile solution. The formation constant for $Sn^nBu_2(NCS)_2 \cdot pyz$ ($K_1 = 0.90$) in acetonitrile is larger than that for the analogous $Sn^nBu_2Cl_2$ complex in the same solvent ($K_1 = 0.56$), and this is consistent with earlier data for tin(IV) systems [11,18,20,21]

The Lewis acidity of SnR_2X_2 with respect to the organo group is in the order Me > Et > ^{n}Pr > ^{n}Bu and the degree of solvation should be in the same order. That this is the case has been clearly demonstrated by Okawara *et al.* [22] who measured the heats of solvation of SnR_2X_2 species (R = Me, Et, ^{n}Bu) in acetonitrile. Some authors suggest, however, that increased solvation reduces metal–ligand association in solution [23]. On this basis, the trends in formation constants should be the reverse of those found in this investigation (Table 1). That this is not the case may be attributable to a combination of factors, the most impor-

TABLE 2. Thermodynamic parameters for reaction of SnR_2Cl_2 with pyrazine in acetonitrile and chloroform

R	Solvent	ΔH^- (kJ mol^{-1})	ΔS^- (J K^{-1} mol^{-1})	K_{298} (mol^{-1} dm^3)
Me [a]	CH_3CN	−13.5(±2.4)	−46.7(±7.8)	0.831
Et [a]	CH_3CN	−18.6(±3.1)	−65.5(±10.1)	0.693
npr [a]	CH_3CN	−20.0(±0.1)	−73.0(±0.2)	0.497
flBu [a]	CH_3CN	−19.4(±1.3)	−71.0(±4.4)	0.498
nBu [a]	$CHCl_3$	−27.7(±1.9)	−101.9(±6.4)	0.339
$SnPh_2Cl_2$ [b]	CH_3CN	−10.4(±0.7)	−32.3(±2.2)	1.34
$SnPh_2Cl_2$ [b]	$CHCl_3$	−19.2(±0.7)	−64.7(±2.3)	1.01

[a] This work; [b] Data from Ref. 1.

tant being the increased polarity on going from chloroform to acetonitrile and the more favourable entropy term in acetonitrile associated with increased solvation [1].

Entropies for formation of 1:1 adducts in chloroform are more negative than those for formation of the same adducts in acetonitrile, in keeping with greater solvation of the Lewis acid substrate in the latter solvent. For example, the entropy of formation of the 1:1 adduct of $SnBu_2Cl_2$ in chloroform is -95 J K^{-1} mol^{-1}, while that in acetonitrile is only -71 J K^{-1} mol^{-1}. For the $SnPh_2Cl_2$–pyrazine systems, the change in the entropy of formation of the 1:1 adduct on going from chloroform to acetonitrile is of similar size [1].

The enthalpy term arises mainly from cleavage of the Sn–solvent bonds and formation of the Sn–N (pyrazine) bond. The value becomes more negative in the order ^{n}Bu > ^{n}Pr > Et > Me. A very good correlation is found between the entropy and the enthalpy, eqn. (4) (correlation coefficient = 0.9965),

$$\Delta S^e = [3.98(\pm 0.24) \times 10^{-3}]\Delta H^e + 7.09(\pm 4.2) \quad (4)$$

Groups of reactions having a common $\Delta H^\ominus/\Delta S^\ominus$ ratio have been treated theoretically by extrathermodynamics methods [24]. Such a group of reactions is known as an isoequilibrium set and the ratio $\Delta H^\ominus/\Delta S^\ominus$ as the isoequilibrium temperature. It can be demonstrated that the condition for the existence of such a set of reactions is that they share a common reaction mechanism. In the case of a set of simple addition reactions (eqn. (5)), this means that the nature of the solvation of all the species in each reaction set and the modes of approach and attachment of the molecules A and B to each other must be similar, as must any restriction on the degrees of freedom of A and B in the complex AB.

$$A + B \rightleftharpoons AB \quad (5)$$

Any departure from these conditions is likely to be revealed in a change in the $\Delta H^\ominus/\Delta S^\ominus$ ratio, or in deviations of points from the straight line plot of $\Delta H^\ominus$ against $\Delta S^\ominus$.

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