Investigation of the Hydrolysis of $[Sn(CH_3)_3(H_2O)_2]^+$ in Aqueous Solution by Tin-119 Nuclear Magnetic Resonance Spectroscopy

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The hydrolysis of $[Sn(CH_3)_3(H_2O)_2]^+$ has been investigated using ^{119}Sn NMR spectroscopy in aqueous solution at 25 °C and ionic strength 0.5 mol dm^{-3}. The ionic strength was adjusted using KCl, KNO_3 or $NaClO_4$. The chemical-shift data were processed using the computer program EQNMR to yield the stability constants and the chemical shifts of the various species present in solution. The results are compared with literature data obtained using other techniques.

It has been recognised for some considerable time that in common with many other elements, organotin halide species form stable cations in aqueous solution.[1,2] In particular, the $[Sn(CH_3)_3(H_2O)_2]^+$ and $[Sn(CH_3)_2(H_2O)_4]^{2+}$ cations are well known and the complexing ability of the former with a series of biologically important ligands has been reported.[3,4] It is also recognised that in common with many other metal ions, these cations can undergo extensive pH-dependent hydrolysis. These hydrolysis reactions have been the subject of previous studies[5,6] and a recent publication[7] has reported a detailed potentiometric and calorimetric investigation of hydroxo complex formation by $[Sn(CH_3)_2(H_2O)_4]^{2+}$ and $[Sn(C_2H_5)_2(H_2O)_4]^{2+}$ in aqueous solution.

Although ^{119}Sn NMR spectroscopy has proved to be extremely useful for determining the stoichiometries and stabilities of tin(IV) complexes in solution, few studies have been carried out in aqueous solution. This technique is appropriate for such studies, as in addition to the stability constants, the chemical shifts of the various species present in solution can usually be obtained and these can give useful information regarding the nature of the bonding in the various tin species present.

We have used ^{119}Sn NMR spectroscopy to investigate the hydrolysis of the $[Sn(CH_3)_3(H_2O)_2]^+$ cation in aqueous solution in a variety of ionic media. The chemical shifts of the various species present have also been determined. These are the first quantitative NMR spectroscopic investigations of the hydrolysis of organotin species in aqueous solution.

Experimental

Trimethyltin hydroxide, prepared by a reported procedure,[8] was purified by sublimation. Trimethyltin chloride (Aldrich) was also purified by sublimation. All the trialkyltin solutions contained a total tin(IV) concentration of 0.1 mol dm^{-3}.

Two procedures were used to determine the equilibrium constant(s) of $[Sn(CH_3)_3(H_2O)_2]^+$. In the first, 0.1 mol dm^{-3} solutions of $[Sn(CH_3)_3(H_2O)_2]NO_3$ and $[Sn(CH_3)_3(H_2O)_2]ClO_4$ were prepared by reacting equimolar quantities of $[Sn(CH_3)_3(H_2O)_2]Cl$ with $AgNO_3$ and $AgClO_4$ respectively in aqueous solution. This led to the formation of a white precipitate of AgCl which was removed by centrifugation. Following this, the ionic strength was adjusted by the addition of KNO_3 or $NaClO_4$. A 0.1 mol dm^{-3} solution of $[Sn(CH_3)_3(H_2O)_2]Cl$ in 0.4 mol dm^{-3} KCl was also prepared. The hydrogen-ion concentrations of these solutions were adjusted by addition of the appropriate mineral acid or sodium hydroxide as required. After the solutions reached thermal equilibrium in the NMR spectrometer, the NMR spectra were recorded. In the second series of experiments, trimethyltin hydroxide was dissolved in aqueous solution at the appropriate ionic strength. The hydrogen-ion concentrations of these solutions were then adjusted as described above following which the NMR spectra were recorded.

pH Readings were recorded on a PT16 digital pH meter equipped with an Amagruss microelectrode. The filling solution in the reference compartment was 3 mol dm^{-3} NaCl. The electrode was calibrated to read hydrogen-ion concentration directly by titrating solutions containing 0.001–0.005 mol dm^{-3} of a strong acid in which the ionic strength was adjusted to 0.5 mol dm^{-3} with the appropriate salt. The endpoints of these titrations were estimated with the computer program Gran1.[9] This program also calculates the correction factor which must be applied to the pH-meter reading in order to obtain $\log[H^+]$.

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 32K). The inverse-gated proton-decoupling technique without nuclear Overhauser effect was employed. All shifts were measured relative to internal $Sn(CH_3)_4$ (0.05 mol dm^{-3}). At least 1024 scans were accumulated for each spectrum. Solutions for the NMR spectral analysis were prepared by use of volumetric glassware and to avoid a concentration effect on the ^{119}Sn NMR chemical shifts, the total tin concentration was <0.1 mol dm^{-3}. All spectra were recorded at 25 °C.

Calculation of Equilibrium Constants.—When all the tin species were in rapid equilibrium, only a single ^{119}Sn resonance was observed. The chemical shift of this resonance, δ_{calc}, is the weighted average of the chemical shifts of the various tin-containing species present, M_mL_n, where M represents $[Sn(CH_3)_3(H_2O)_2]^+$, L the hydroxide ion and i and j the maximum values of m and n respectively [equation (1)]. Since

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

$[M_mL_n] = \beta_{mn}[M]^m[L]^n$ equation (1) can be written as equation (2).

$$\delta_{calc} = \sum_{\substack{m=1\\n=0}}^{\substack{m=i\\n=j}} \delta_{mn}\beta_{mn} m[M]^m[L]^n/[M]_{total} \quad (2)$$

Table 1 Equilibrium constants for the hydrolysis of $[Sn(CH_3)_3(H_2O)_2]^+$ forming the monohydroxo species $[Sn(CH_3)_3(H_2O)(OH)]$

Ionic strength (medium)/mol dm^{-3}	log β	δ_M	$\delta_{M(OH)}$	R
0.5 ($NaClO_4$)	−6.34 (0.08)	41.4 (0.8)	78.4 (1.5)	3.36
0.5 (KNO_3)	−6.35 (0.08)	42.5 (0.8)	78.1 (1.3)	1.70
0.5 (KNO_3)[a]	−6.43 (0.08)	40.7 (0.8)	76.3 (1.3)	1.80
0.5 (KCl)	−6.38 (0.03)	39.9 (0.4)	75.7 (0.6)	1.44
0.5 (KCl)[b]	−6.37 (0.03)	41.2 (0.4)	75.5 (0.6)	1.36
0.5 (KCl)[c]	−6.37 (0.06)	41.1 (0.5)	75.4 (1.2)	1.67
0.5 (KCl)[d]	−6.37 (0.03)	41.0 (0.3)	75.4 (0.6)	1.01
3.0 ($NaClO_4$)	−6.60[e]			
Dilute solution	−6.16[f]			
2.0 (KCl)	−6.40[f]			

[a] $[Sn(CH_3)_3(H_2O)(OH)]$ (0.1) in KNO_3 (0.4 mol dm^{-3}). [b] $[Sn(CH_3)_3(H_2O)(OH)]$ (0.1) in KCl (0.4 mol dm^{-3}). [c] $[Sn(CH_3)_3(H_2O)(OH)]$ (0.1) in KCl titrated with acid (0.4 mol dm^{-3}). [d] $[Sn(CH_3)_3(H_2O)(OH)]$ (0.1) in KCl titrated with base (0.4 mol dm^{-3}). [e] Ref. 5. [f] Ref. 6.

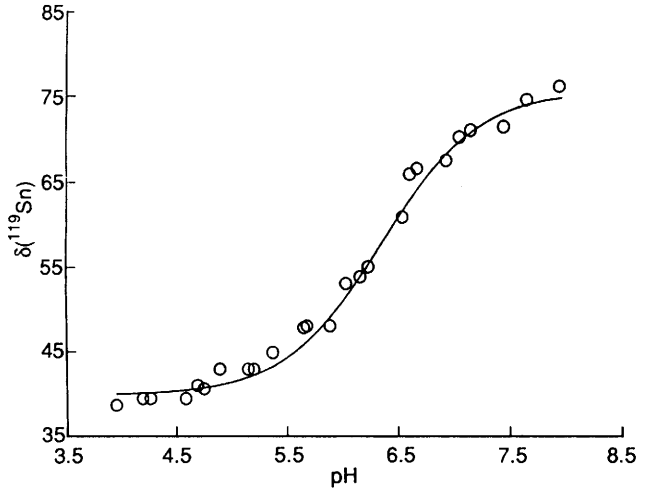

Fig. 1 Plot of $\delta(^{119}Sn)$ against pH for the hydrolysis of $[Sn(CH_3)_3(H_2O)_2]^+$ in aqueous solution at 25 °C and I = 0.5 mol dm^{-3} KCl

Thus the optimum values for the various δ_{mn} and β_{mn} which best fit the experimental chemical-shift data, need to be determined.

The non-linear least-squares program EQNMR[10] was used to calculate these parameters. The program contains three main sections. Section one reads the input data. This consists of (*i*) the concentrations of the various reagents together with the measured chemical shifts, (*ii*) details of the model in the form of the stoichiometric coefficients of the complex species present and (*iii*) initial estimates for the various parameters (stability constants and chemical shifts) to be fitted together with values for any parameters which are to be held constant. Section two contains the non-linear least-squares subroutines which carry out the refinement of the various parameters using the Levenberg–Marquardt method.[11,12] Section three contains the output routines. Output consists of printed tables of the input data, best-fit values of the calculated chemical shifts and formation constants together with estimates of their errors. A table of the concentrations of all species present at each experimental point in the titration is also produced. Graphical output is also provided in the form of three plots. The first of these displays the variation in the concentrations of the various species present as the titration proceeds. The second shows plots of the experimental and measured chemical shifts against the concentration of the titrant and the third the residuals (in magnified form) against the titrant concentration.

EQNMR can deal with chemical-shift data from a wide variety of reactions where the equilibria can be expressed in terms of formation constants. These include acid-dissociation constants, metal-ion hydrolysis and complex formation reactions. Starting values for the equilibrium constants can be input as either K or log K values.

With the aid of EQNMR various models can be readily evaluated. In most instances visual inspection of the graphical output is sufficient to determine the 'best-fit' model. Any systematic deviations between the experimental chemical shifts and those calculated using the 'best-fit' parameters are highlighted by the residuals plot. In addition, quantitative comparison of the fits can be carried out using the function in equation (3) where w_i is the weight attributed to observation i. Where the chemical shifts are of similar magnitude, this function usually enables a choice to be made between potential models. In the present work unit weights were used at all times.

$$R = 100\left[\frac{\Sigma W_i(\delta_{obs} - \delta_{calc})^2}{\Sigma W_i(\delta_{calc})^2}\right]^{\frac{1}{2}} \quad (3)$$

Results

The hydrolysis of metal ions to form mono- and poly-nuclear hydroxo species can be represented by equation (4).

$$xM^{n+} + yH_2O \rightleftharpoons [M_x(OH)_y]^{(xn-y)+} + yH^+ \quad (4)$$

NMR spectra of aqueous solutions of $[Sn(CH_3)_3(H_2O)_2]^+$ in which the ionic strength was adjusted to 0.5 mol dm^{-3} with KCl were recorded in the pH range 3.8–8.0. A single ^{119}Sn resonance was observed indicating that the tin species present were in rapid equilibrium. The NMR data are consistent with the presence of a single hydroxo species, $[Sn(CH_3)_3(H_2O)(OH)]$. Fitting the accumulated data from a number of separate experiments to a model containing only this species gave the results shown in Table 1. Fig. 1 shows the fit obtained in 0.5 mol dm^{-3} KCl using the accumulated data. It is evident that the agreement between the experimental chemical shifts and those calculated using the 'fitted' values of the parameters is excellent. The overall chemical shift difference between the free organotin cation and the monohydroxo species is approximately 36 ppm. This is much smaller than the chemical shifts normally encountered in the complexing of organotin species.[13]

Similar results were obtained for solutions in which the ionic strength was controlled with KNO_3 or $NaClO_4$ and these are also shown in Table 1.

A separate series of experiments was carried out in 0.5 mol dm^{-3} KCl using $[Sn(CH_3)_3(H_2O)(OH)]$ prepared as described in the Experimental section as the source of tin(IV). The pH of a solution containing a total tin concentration of 0.1 mol dm^{-3} was adjusted to pH 8.0 when only a single ^{119}Sn resonance was observed. This solution was then titrated down to pH 3.8 using HCl. Tin-119 NMR spectra were recorded at appropriate intervals. Following this the same solution was then titrated with sodium hydroxide up to pH 8.0. Table 1 shows that the value obtained for the stability constant was the same in both cases. This demonstrates the reversibility of the hydrolysis reaction over the pH range studied.

Discussion

This is the first quantitative ^{119}Sn NMR spectroscopic investigation of the hydrolysis of alkyltin species in aqueous solution. It illustrates both the advantages and shortcomings of the technique compared to the potentiometric and calorimetric methods. Due to the relative insensitivity of the ^{119}Sn nucleus (4.4×10^{-3} relative to the proton at natural abundance)[14] considerably higher total tin concentrations must be used if spectra accumulation times are not to be unduly long. In addition, the species present must be in rapid equilibrium on

the NMR time scale so that narrow single resonances are obtained for ^{119}Sn.

The stability constants obtained for the hydrolysis of $[Sn(CH_3)_3(H_2O)_2]^+$ are somewhat lower than the values reported by Tobias *et al.*[5] but are in good agreement with the value obtained by Asso and Carpeni[6] in 2 mol dm^{-3} KCl (Table 1). The fact that similar results were obtained in all three media using different sources of tin(IV) support the results presented here. The electrode used to measure the hydrogen-ion concentration was individually calibrated for each of the media used. Rather surprising is the relatively minor effect of the chloride ion. It might be expected that the presence of a relatively large chloride concentration would lead to extensive complex formation with $[Sn(CH_3)_3(H_2O)_2]^+$. Similar fears were alluded to by Arena *et al.*[7] in the case of the dimethyltin(IV) and diethyltin(IV) cations.

The ^{119}Sn NMR chemical shift on going from the trimethyltin cation to the monohydroxo species is approximately 36 ppm. Separate experiments have shown that the chemical shift on going from $[Sn(CH_3)_2(H_2O)_4]^{2+}$ to $[Sn(CH_3)_2(H_2O)_3(OH)]^+$ is considerably greater and is of the order of 130 ppm.[15] Chemical shifts can be described quantitatively in terms of the Ramsey equation[16,17] [equation (5)] where σ_T is

$$\sigma_T = \sigma_d + \sigma_p + \sigma_o \quad (5)$$

the total shielding, σ_d is the shielding due to electrons in the ground state, σ_p is the deshielding due to mixing of the ground and excited states and σ_o represents the total shielding contribution from remote atoms. In the case of chemical shifts in heavy nuclei, σ_d and σ_o are usually regarded as negligible compared to σ_p.[18] The parameter σ_p is a function of the energy difference between the ground and excited states and of the symmetry of the cloud charge about the nucleus. Factors which cause asymmetry of the p or d electron distribution produce downfield shifts.

In the present investigation $[Sn(CH_3)_3(H_2O)_2]^+$ exhibits a downfield shift when a co-ordinated water molecule is replaced by a hydroxide ion. The Sn–O bond lengths in co-ordinated OH^- and H_2O are approximately 194[19] and 230 pm[20] respectively. In previous studies,[13,15] when the co-ordination number of tin(IV) was increased or when a weakly bonded ligand was replaced by a strongly co-ordinated ligand, relatively large upfield shifts were observed in all instances. Thus an upfield shift might reasonably be expected when a co-ordinated water molecule is replaced by a hydroxide ion. However, it appears that such a replacement causes a large change in the charge distribution and that this is reflected in the downfield shift.

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