Influence of Temperature on the Thallium-205 Chemical Shift of Dimethylthallium(III) Derivatives

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Thallium-205 chemical shifts for $Tl(CH_3)_2X$ ($X = NO_3$, BF_4, or O_2CCH_3) in several solvents have been determined as a function of temperature, solute concentration and, in some cases, added anion concentration. The observed temperature-dependent chemical shift range is generally larger than those resulting from changes in solute or anion concentration. The origin of the temperature-dependent chemical shift is discussed in terms of the nature of the species present in solution.

RECENTLY, thallium-205 n.m.r. spectroscopy has found increasing application to the study of organothallium(III) species in solution.[1-10] A large part of this work has centred upon the readily available dimethylthallium(III) derivatives, $Tl(CH_3)_2X$ (X = anion). In solution, the species present (monomer, dimer, ion pair *etc.*) depend on the nature of X and the properties of the solvent.[10,11] We have previously shown [1] that the ^{205}Tl chemical shift [δ(Tl)] for $Tl(CH_3)_2X$ is markedly sensitive to changes of anion, solvent, and solute concentration. These results have since been confirmed and measurements extended to include binary solvent mixtures.[3,5] Earlier experiments [1] indicated that the thallium chemical shift in dimethylthallium(III) derivatives exhibited a significant temperature dependence. The objectives of the present study are to quantify this dependence for some representative systems and to ascertain how far these variations can be ascribed to thermally induced changes in the chemical nature of species present in solution.

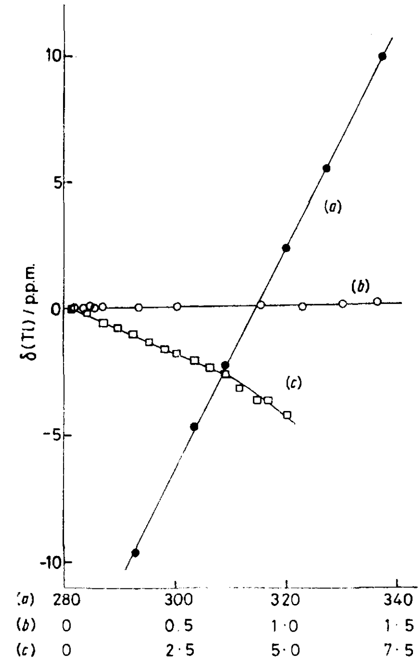

FIGURE 1 $Tl(CH_3)_2(NO_3)$ in H_2O. Dependence of δ(Tl) on (*a*) temperature [mol% $Tl(CH_3)_2(NO_3) = 0.18$], (*b*) mol% $Tl(CH_3)_2(NO_3)$ (at 41 ± 1 °C), and (*c*) mol% NO_3 [at 41 ± 1 °C, mol% $Tl(CH_3)_2(NO_3) = 0.18$]

RESULTS

The variation of thallium-205 chemical shift with temperature and concentration [mol% solute = 100 moles solute/(moles solute + moles solvent)] for $Tl(CH_3)_2X$ in H_2O ($X = NO_3$ or BF_4), dimethyl sulphoxide (dmso) ($X = NO_3$), and CH_3OH ($X = BF_4$ or O_2CCH_3) is shown in Figures 1—4. The dependence of δ(Tl) on the concentration of added potassium salt, KX [mol% X = 100 moles X/(moles X + moles solvent)], for constant $Tl(CH_3)_2X$ concentration, is also shown in Figures 1—3 for $X = NO_3$ in H_2O and dmso, and $X = O_2CCH_3$ in CH_3OH, respectively. The curves for mol% $Tl(CH_3)_2X$ against δ(Tl) have been extrapolated to give the infinite dilution shifts shown in the Table. The errors shown are subjective estimates of the uncertainty in the extrapolation. These errors are large for plots which show considerable curvature at low concentrations and in these cases are generally much larger than experimental error (±0.3 p.p.m.).

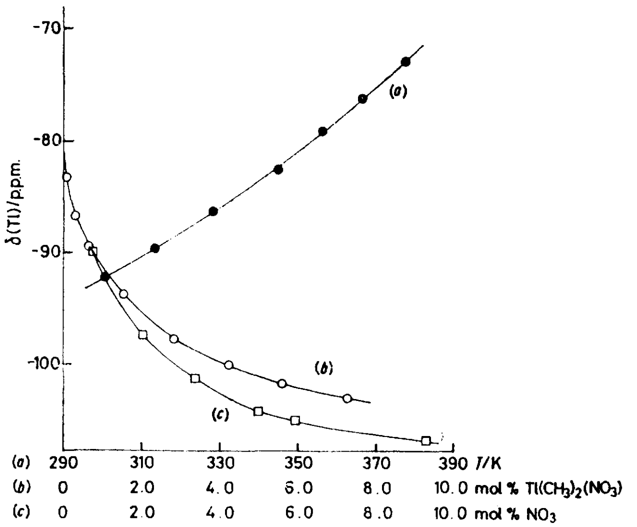

FIGURE 2 $Tl(CH_3)_2(NO_3)$ in dmso. Dependence of δ(Tl) on (*a*) temperature [mol% $Tl(CH_3)_2(NO_3) = 0.70$], (*b*) mol% $Tl(CH_3)_2(NO_3)$ (at 41 ± 1 °C), and (*c*) mol% NO_3 [at 42 ± 1 °C, mol% $Tl(CH_3)_2(NO_3) = 0.75$]

The chemical shift scale (up-frequency denoted positive) is arbitrarily referenced to the infinite dilution shift of

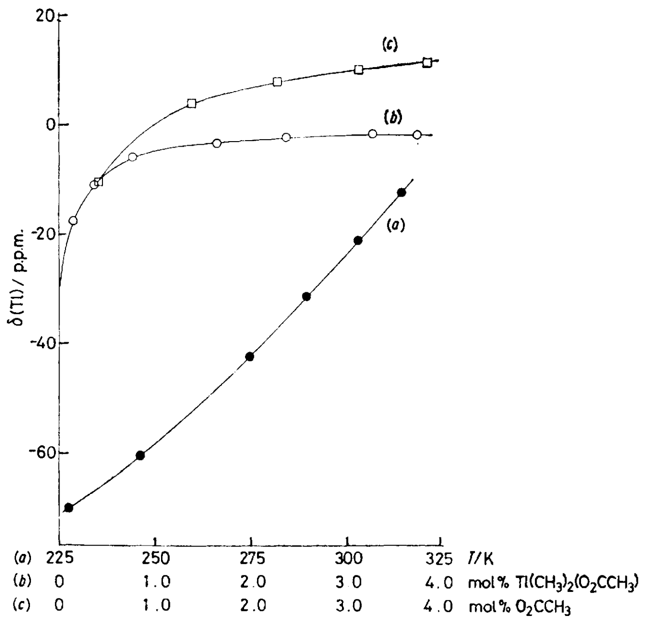

FIGURE 3 $Tl(CH_3)_2(O_2CCH_3)$ in MeOH. Dependence of δ(Tl) on (*a*) temperature [mol% $Tl(CH_3)_2(O_2CCH_3)$ = 0.40], (*b*) mol% $Tl(CH_3)_2(O_2CCH_3)$ (at 41 ± 1 °C), and (*c*) mol% O_2CCH_3 [at 41 ± 1 °C; mol% $Tl(CH_3)_2(O_2CCH_3)$ = 0.42]

$Tl(CH_3)_2(NO_3)$ in H_2O at 41 °C for which Ξ(Tl) = 57 887 038 Hz [where Ξ(Tl) is the frequency of the ^{205}Tl signal for a field in which $SiMe_4$ gives a proton resonance at 100 MHz]. For this system Ξ(Tl) varies linearly, but only slightly, with

$$\Xi(\mathrm{Tl}) = 57\,887\,038 + 8.9\ [\mathrm{mol\%\ Tl(CH_3)_2(NO_3)}] \quad (1)$$

concentration at 41 °C [equation (1)] in agreement with results previously obtained[3] at 23 °C. The temperature dependence of Ξ(Tl) for a 0.18 mol% solution is also linear [equation (2)]. The small concentration dependence of

$$\Xi(\mathrm{Tl}) = 57\,879\,011 + 25.5\,T \quad (2)$$

Ξ(Tl) and use of equation (2) allows fairly accurate prediction of Ξ(Tl) at other temperatures without the need to take into account the solute concentration. For example, Ξ(Tl) at infinite dilution and 23 °C is 57 886 562 Hz.[3] Using equation (2) a value of 57 886 572 Hz is predicted. An aqueous solution of $Tl(CH_3)_2(NO_3)$ (which is readily accessible and easily handled) is, therefore, a particularly useful reference system for situations where it is impossible to report shift values directly in terms of Ξ(Tl).[9] Comparison of Ξ(Tl) at infinite dilution for $Tl(CH_3)_2(NO_3)$ in dmso with previous work[3] is a little less satisfactory, presumably reflecting the difficulty in extrapolating the highly curved plot [$\Xi(Tl)_\infty$: 57 882 350 ± 120 Hz at 41 °C (this work); 57 882 528 at 23 °C[3]].

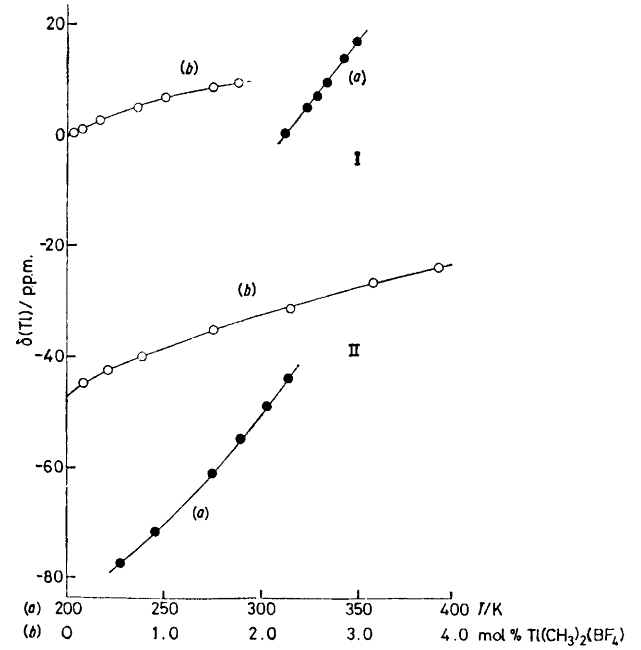

FIGURE 4 $Tl(CH_3)_2(BF_4)$ in H_2O (I), MeOH (II). Dependence of δ(Tl) on (*a*) temperature [I: mol% $Tl(CH_3)_2(BF_4)$ = 0.18, II: mol% $Tl(CH_3)_2(BF_4)$ = 0.40], and (*b*) mol% $Tl(CH_3)_2(BF_4)$ (at 41 ± 1 °C)

The temperature coefficients of δ(Tl) are given in the Table. These values were obtained by linear regression analysis although the plots for non-aqueous solutions actually show slight curvature. We have also found that the temperature dependence of δ(Tl) for dmso solutions of several longer-chain dialkylthallium(III) derivatives, $Tl[CH_3(CH_2)_n]_2(NO_3)$, are closely linear and show up-frequency shifts with increasing temperature. Temperature coefficients are 0.17, 0·52, 0.36, and 0.36 p.p.m. K^{-1} respectively for *n* = 1, 2, 3, and 5.

^{205}Tl infinite dilution chemical shifts and temperature coefficients of chemical shift for $Tl(CH_3)_2X$

X	Solvent	$\delta(Tl)_\infty$ [a]	$d\delta(Tl)/dT$ [b]
NO_3	H_2O	0 ± 0.3	0.44 ± 0.01
NO_3	dmso	−81.0 ± 2.0	0.25 ± 0.01 [c]
O_2CCH_3	CH_3OH	−31.8 ± 12.0	0.67 ± 0.02 [c]
BF_4	H_2O	−0.4 ± 3.0	0.46 ± 0.01
BF_4	CH_3OH	−47.3 ± 2.0	0.39 ± 0.01 [c]

[a] Infinite dilution shift, in p.p.m. Temperature = 41 ± 1 °C. [b] In p.p.m. K^{-1}. Error is standard deviation obtained from linear regression analysis. [c] This is an average value obtained by linear regression analysis of the slightly curved plot.

DISCUSSION

The dimethylthallium(III) derivatives, $Tl(CH_3)_2X$ (X = NO_3, O_2CCH_3, or BF_4), are representative of a large number of potentially ionic organothallium(III) compounds with the formulation TlR_2X. In solution, the degree of ion-pair formation [equation (3)] is expected to depend upon the nature of X, the solvent,

$$\mathrm{Tl(CH_3)_2^+ + X^- \rightleftharpoons Tl(CH_3)_2X} \quad (3)$$

and the solute concentration. The thallium-205 n.m.r. spectrum of such a system shows a single resonance position arising from rapid exchange between thallium-containing species. It is usual[12] to assume that the chemical shift of this signal is an average of the shifts for the individual species weighted according to their relative abundances. δ(Tl) therefore provides a probe of the ion-pair equilibrium.

For a particular choice of anion, solvent, and temperature, δ(Tl) will generally vary with solute concentration. Varying the temperature at constant solute concentration is also expected to change δ(Tl) according to the temperature dependence of the ion-pair formation constant. We find that in four of the five systems studied here the magnitude and, in some cases, the direction of the shift changes induced by temperature variations cannot be accounted for in terms of cation–anion interactions.

δ(Tl) for $Tl(CH_3)_2(NO_3)$ in H_2O varies linearly and only slightly with solute concentration. This might be interpreted in one of three ways. (i) δ(Tl) is unresponsive to changes in the ion-pair equilibrium. This possibility seems unlikely in view of the large concentration-dependent shift ranges (*ca.* 10—100 p.p.m.) generally observed for other $Tl(CH_3)_2X$ systems with a variety of anions and solvents.[1,3,13] (ii) The ion-pair formation constant is large and δ(Tl) is close to the limiting value for $Tl(CH_3)_2(NO_3)$ ion pairs even at low concentrations. This possibility is unattractive when compared with the description of $Tl(CH_3)_2(NO_3)$ in H_2O obtained by other methods, see below. Also, Hinton and Briggs [3] showed that very little shift change occurs at concentrations down to 0.000 53 mol dm^{-3} (0.03 mol dm^{-3} was the lowest concentration used in this work) where the likelihood of dissociation would be considerably increased. (iii) The ion-pair formation constant is small and $Tl(CH_3)_2(NO_3)$ is essentially dissociated over the concentration range studied. This interpretation is consistent with previous results from conductivity measurements [14] and Raman spectroscopy.[15] Further support for the existence of solvated $Tl(CH_3)_2^+$ ions in aqueous $Tl(CH_3)_2(NO_3)$ is the close agreement of δ(Tl) at infinite dilution with that for $Tl(CH_3)_2(BF_4)$ in H_2O at the same temperature. Similar agreement has been found [13] for aqueous solutions of $Tl(CH_3)_2F$ and $Tl(CH_3)_2(O_2CCH_3)$. Although ion-pair formation is evident in aqueous $Tl(CH_3)_2(BF_4)$ (Figure 4), δ(Tl) at infinite dilution should reflect only cation–solvent interactions. Thus a common cationic species is indicated.

In an attempt to estimate the changes in δ(Tl) for $Tl(CH_3)_2(NO_3)$ that would result from ion-pair formation, the shift was measured as a function of added $K[NO_3]$ (Figure 1). Interestingly, the nuclear shielding increased. This is in contrast to the decrease observed on adding solute, although the difference is slight over the common concentration range [$<$ *ca.* 1.5 p.p.m. up to 1.5 mol% $Tl(CH_3)_2(NO_3)$]. Above this range, the dependence of δ(Tl) on mol% $Tl(CH_3)_2(NO_3)$ might also curve sharply to lower frequency, but it seems more likely that the discrepancy is caused either by ion-pair formation under the non-ideal conditions prevailing at the high solute concentrations used in this study, and/or the formation of higher ion aggregates. The variation in δ(Tl) over the temperature range 20—64 °C is much larger than that resulting from this enforced ion-aggregate formation (Figure 1) and above 41 °C (the temperature at which the concentration-dependent studies were carried out) the shift is to low field of that attributable to ion pairing. This implies the presence of a temperature dependence of δ(Tl) for the aquated $Tl(CH_3)_2^+$ ion which is largely independent of cation–anion interactions. This is supported by the observed temperature dependence of $\Xi(Tl)_\infty$ for aqueous solutions of $Tl(CH_3)_2(NO_3)$; 57 886 562 Hz at 23 °C [3] and 57 887 038 Hz at 41 °C.

The curvature of the concentration and added anion dependencies of δ(Tl) for $Tl(CH_3)_2(NO_3)$ in dmso and $Tl(CH_3)_2(O_2CCH_3)$ in MeOH (Figures 2 and 3) are consistent [16,17] with the presence of ion-pair equilibria in these systems. In both cases the ranges of δ(Tl) arising from temperature dependence fall substantially outside the ranges attributable to ion-pair formation. A similar situation exists for $Tl(CH_3)_2(BF_4)$ in CH_3OH (Figure 4). The non-linear concentration dependence of δ(Tl) for $Tl(CH_3)_2(BF_4)$ in H_2O indicates the presence of an ion-pair equilibrium, but in this case the changes in δ(Tl) obtained on varying the temperature are within a range which might be accounted for by temperature dependence of the ion-pair formation constant. In contrast to the solutions in dmso and MeOH, which show slight curvature in the plots of δ(Tl) against temperature, the results for $Tl(CH_3)_2X$ ($X = NO_3$ or BF_4) in H_2O are linear.

The temperature dependence of the thallium-205 chemical shift described here appears to be unusual for metal nuclei of the non-transition elements in that the phenomenon cannot be readily ascribed to changes in the types of species present in solution. Temperature-dependent chemical shifts have been observed for the heavier nuclei of both transition (^{55}Mn; [18] ^{59}Co; [19,20] ^{63}Cu; [21] ^{103}Rh; [22-24] ^{183}W; [25,26] ^{195}Pt [27-29]) and non-transition (^{67}Zn; [30] ^{77}Se; [31] ^{111}Cd; [32] ^{113}Cd; [33] ^{119}Sn; [34-38] ^{133}Cs; [12,39] ^{199}Hg; [40-42] ^{207}Pb [43,44]) elements in diverse types of compound. Temperature-independent shifts have been reported for ^{67}Zn in aqueous $Zn[ClO_4]_2$[30] and ^{119}Sn in various tin(IV) complexes.[45] Temperature coefficients of shift generally range from *ca.* 0.1 to 3.0 p.p.m. K^{-1} and *ca.* 0.1 to 1.0 p.p.m. K^{-1} for transition and non-transition metals respectively. The form of the dependence for transition metals is either linear or approximately linear (^{59}Co; [19,20] ^{183}W; [26] ^{195}Pt [27,28]) and shielding generally decreases with increasing temperature.

The temperature dependence of ^{59}Co shielding has been explained [20,46] in terms of variations in the paramagnetic contribution to the shielding, σ_p, caused by changes in the electonic excitation energy. Thermally induced changes in the occupancy of ground-state vibrational levels alter the effective excitation energy between the ground state and those excited states which can mix with the ground state under the influence of the magnetic field. These ideas have been developed [19] into a theory for the explicit temperature dependence of chemical shift which explains the features of temperature-dependent ^{59}Co [19] and ^{195}Pt [27] shielding in symmetrical cobalt(III), platinum(II), and platinum(IV) complexes. Similar considerations are believed to account for chemical shift temperature dependency in other platinum(II) complexes,[29] some rhodium(III),[24] and some tungsten(II) complexes.[25] The theory is particularly appropriate to transition metals with unfilled *d* orbitals, where the excitation energy is relatively small (*ca.* 10 *Dq*) and hence more sensitive to changes in the population of vibrational levels. It has been noted[21] that the low (0.06 p.p.m. K^{-1}) temperature coefficient of shielding for ^{63}Cu in a complex of Cu^{I}, a d^{10} ion, is consistent with this view. The coefficient for ^{55}Mn in MnO_4^- (Mn^{VII}, d^0) is likewise small,[18] but interestingly the coefficients for the heavier ^{183}W nucleus in WO_4^{2-} and WCl_6 (W^{VI}, d^0) are much larger (0.16 and 0.34 p.p.m. K^{-1} respectively).[26]

The temperature dependence of chemical shifts for non-transition elements has, in many cases,[35-39] been ascribed to thermally induced changes in the types of species present in solution. In the remaining cases the relative importance of such effects has not been determined. This is also true for previously observed temperature-dependent ^{205}Tl chemical shifts {[$Tl(CH_3)_2X]_2$,[9] Tl^+ ionophore complexes,[47-49] Tl^+–H_2O, Tl^+–hexamethylphosphoramide[47]}.

Hafner and Nachtrieb[50] found linear decreases in ^{205}Tl shielding of up to 1.4 p.p.m. K^{-1} for molten thallium(I) salts. Using an ionic model, they ascribe these changes to temperature-dependent vibrational overlap of cation–anion wave functions. We are led to the conclusion that the temperature-dependent ^{205}Tl shifts observed here for dimethylthallium(III) derivatives largely originate from vibrational effects within the $Tl(CH_3)_2^+$ cations and/or from vibrational effects involving the interaction of such species with co-ordinated solvent molecules. Experiments, analogous to those reported here, for thallium(I) salts, TlX, may be helpful in distinguishing the contribution of cation vibrations to the temperature dependence.

EXPERIMENTAL

Sample Preparation.—Dimethylthallium(III) compounds were prepared and purified according to published procedures.[51] Longer-chain dialkylthallium(III) derivatives, TlR_2Br (R = C_2H_5, n-C_3H_7, n-C_4H_9, or n-C_6H_{13}) were prepared according to the method of McKillop *et al.*[52] and converted to the more soluble nitrate derivatives by metathesis with thallium(I) nitrate in water (R = C_2H_5 or n-C_3H_7) or pyridine. Recrystallisation was achieved from water (R = C_2H_5 or n-C_3H_7) or pyridine–water (1 : 4 v/v). Satisfactory microanalyses (C,H,N) were obtained for all dialkylthallium(III) compounds. Potassium salts were analytical grade and were used without further purification. Dimethyl sulphoxide was dried under reduced pressure by refluxing over CaH_2 for several hours followed by distillation. Methanol was dried by refluxing over molecular sieves (4 A) followed by distillation.

Prior to use, non-aqueous solvents were stored over molecular sieves in an atmosphere of dry nitrogen. All operations involving the transfer of non-aqueous solvents were carried out under an atmosphere of dry nitrogen and all associated weighings were carried out on capped n.m.r. tubes. After weighing, capped tubes were sealed with ' parafilm '. Samples for n.m.r. measurements were prepared by adding the appropriate volume of solvent to a weighed amount of solute contained in an n.m.r. tube. The weight of solvent was then determined by reweighing the tube.

Instrumentation.—Thallium-205 n.m.r. spectra were obtained in pulsed Fourier-transform mode at 34.7 MHz on a modified Varian HA-60IL spectrometer fitted with a Varian XL probe. Spectra were obtained on a DEC PDP-11 computer, an Amplifier Research 10LA 10-W broad-band amplifier, and a Polaron 150-W tuned amplifier. The radiofrequency gate, pulse timers, direct current amplifier, and low pass filters were constructed in the laboratory. The field was locked using time-shared modulation with a repetition rate of 1 kHz. The first upfield sideband of a proton solvent resonance was phase detected in dispersion mode using the standard Varian internal reference n.m.r. stabilised controller, type V4354A. All $Tl(CH_3)_2X$ spectra showed a symmetrical seven-line pattern arising from spin–spin coupling to the six equivalent methyl protons, although under the usual operating conditions the weak outermost lines were not detected. Spectra of longer-chain dialkylthallium(III) derivatives were obtained using broad-band proton decoupling. In these cases the field was locked to the ^{19}F resonance of either hexafluorobenzene or trifluoro-*m*-cresol contained in a 5-mm insert within the 12-mm n.m.r. tubes. Variable-temperature spectra were obtained using the standard Varian variable-temperature accessory. Temperatures were measured using a thermocouple contained in a 12-mm n.m.r. tube filled with paraffin oil. This tube was inserted into the probe prior to spectral acquisition and the temperature determined. After replacement with the sample a period of *ca.* 15 min was allowed for the sample to attain the probe temperature. This was confirmed by successively recording spectra until a constant resonance frequency had been obtained. It was considered unnecessary to correct the thallium-205 resonance frequencies for temperature-induced changes in the ^{1}H or ^{19}F lock frequencies. Studies of the temperature dependence of ^{1}H[53] and ^{19}F[27] resonances have shown these effects to be small.

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