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Preliminary communication

THALLIUM-205, CARBON-13 AND PROTON NMR PARAMETERS FOR SOME MONOMETHYLTHALLIUM(III) DERIVATIVES

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Summary

Thallium-205, carbon-13 and proton NMR spectra have been determined for some monomethylthallium(III) derivatives CH_3TlX_2 (X = anion) permitting comparison of NMR parameters in the series CH_3TlX_2, $(CH_3)_2TlX$, $(CH_3)_3Tl$.

As part of an investigation of the factors influencing the NMR parameters of organothallium(III) compounds [1], we have determined the ^{205}Tl, ^{13}C and ^{1}H NMR spectra of some monomethylthallium(III) derivatives CH_3TlX_2 (X = anion). The ^{13}C and ^{205}Tl NMR data appear to be the first available for monoalkylthallium compounds, and consequently permit comparison of NMR parameters in the series CH_3TlX_2, $(CH_3)_2TlX$, $(CH_3)_3Tl$. The results are summarized in Table 1 together with data for $(CH_3)_3Tl$ [2] and representative $(CH_3)_2TlX$ species.

Both $^{1}J(^{205}Tl—^{13}C)$ and $^{2}J(^{205}Tl—^{1}H)$ decrease with increasing methyl substitution. The decrease in $^{2}J(^{205}Tl—^{1}H)$ has previously been noted [3, 4] and a similar situation is found for analogous tin [5, 6], lead [7] and mercury [8] systems. However, the $^{1}J(^{205}Tl—^{13}C)$ and $^{2}J(^{205}Tl—^{1}H)$ coupling constants are large when compared with corresponding constants for tin, lead and mercury compounds. This is apparent for the tin and lead compounds both when the coupling constants are expressed in Hertz and as reduced coupling constants (in N m^{-3} A^{-2}). Conversion of the values for mercury compounds, however, yields couplings comparable to those for thallium. The large changes observed for the thallium system on successive methyl substitution (see Table 2) show clearly that $^{2}J(^{205}Tl—^{1}H)$ and, in particular, the one-bond coupling $^{1}J(^{205}Tl—^{13}C)$ are very sensitive probes for the environment of thallium in organothallium compounds.

TABLE 1

^{205}Tl, ^{13}C AND ^{1}H NMR PARAMETERS FOR METHYLTHALLIUM(III) DERIVATIVES

Compound		Solvent[a]	Conc.[b]	Ξ(Tl)[c]	δ(Tl)[d]	$\delta(^{13}C(CH_3))$[e]	$\delta(^{1}H(CH_3))$[e]	$\lvert ^1J(^{205}Tl-^{13}C)\rvert$[f]	$\lvert ^2J(^{205}Tl-^{1}H)\rvert$[g]
$CH_3Tl(OCOCH_3)_2$	(I)	CH_3OH	1.0	57864691	−272	17.7	1.72	5976	939
	(II)	$CHCl_3$	0.8	57861186	−333	18.7	1.86	5631	911
		CH_3CN	h				1.71[i]		911[i,j]
		CH_2Cl_2	h				1.90[i]		890[i,j]
		acetone	h				1.77[i]		914[i,j]
		pyridine	0.1				1.83		890
		DMSO	0.2				1.32		928
$CH_3Tl(CN)OCOCH_3$	(III)	DMSO	0.4			15.6	1.22	5914	827
$(CH_3)_2TlOCOCH_3$	(IV)	H_2O	0.4	57886824	110	26.7[k]	1.63	2513	407
		$CHCl_3$	h				1.11[i]		377[i,j]
		DMSO	0.2				0.77		437
		pyridine	0.3				1.21		417
		CH_3OH	0.3				1.03		421
$(CH_3)_2TlNO_3$[l]	(V)	pyridine	0.2	57880456	0	22.2	1.50	3080	436
	(VI)	DMSO	0.2	57881787	23	25.9	0.70	2903	449
$(CH_3)_2TlOC_6H_5$[l]	(VII)	pyridine	0.9	57891336	188	22.4	1.28	2807	409
	(VIII)	CH_2Cl_2	0.2	57899766	334	23.1	1.16	2475	372
$(CH_3)_3Tl$[m]	(IX)	$(CH_3)_2O$		57943640	1091		0.40	1930	269

[a] Deuterated solvents were used for ^{13}C and ^{1}H measurements. [b] In mol dm^{-3}. [c] Frequency in Hz (±30) of ^{205}Tl signal for a field in which TMS gives a proton resonance at 100 MHz. [d] In ppm (±1); δ(Tl) = 0 ppm has been assigned arbitrarily. [e] In ppm from internal TMS (downfield positive). Errors for δ(C) and δ(H) are ±0.2 and ±0.02 ppm respectively. [f] In Hz (±3). [g] In Hz (±1); determined from ^{1}H NMR spectra. [h] Saturated solution. [i] Errors; ±0.07 ppm, ±4 Hz. [j] Signals broadened such that separate coupling to ^{205}Tl and ^{203}Tl was unresolved. [k] Relative to internal TSP. [l] Data from ref. 1. [m] Data from ref. 2.

TABLE 2

SUMMARY OF CHANGES IN $^1J(M-^{13}C)$ AND $^2J(M-^1H)$ WITH SUCCESSIVE METHYL SUBSTITUTION IN SOME METHYL—METAL SYSTEMS

System[a]	n	$\Delta\,\lvert ^1J(M-^{13}C)\rvert$[b]		$\Delta\,\lvert ^2J(M-^1H)\rvert$[b]	
		Hz	10^{20} N m^{-3} A^{-2}	Hz	10^{20} N m^{-3} A^{-2}
$(CH_3)_nTlX_{3-n}$[c]	1 2	3463	198.8	532	7.7
	2 3	583	33.4	138	2.0
$(CH_3)_nSnX_{4-n}$	[d]	68 [14]	6.0	57 [6]	1.3
$(CH_3)_nPbX_{4-n}$	[d]	—	—	15 [7]	0.6
$(CH_3)_nHgX_{2-n}$	[d]	1249 [8]	231.6	159 [8]	7.4

[a] X = anionic species. [b] Change in coupling constant with successive methyl substitution. M = ^{205}Tl, ^{119}Sn, ^{207}Pb and ^{199}Hg. [c] Data for samples I, IV and IX, Table 1. [d] Largest changes observed due to successive methyl substitution.

A plot of $^1J(^{205}Tl-^{13}C)$ against $^2J(^{205}Tl-^1H)$ (Fig. 1) shows a linear relationship and the close approach of the line to the origin suggests that common factors dominate the coupling to both carbon and hydrogen [9]. However, while the linear relationship holds for the gross changes dependent upon the

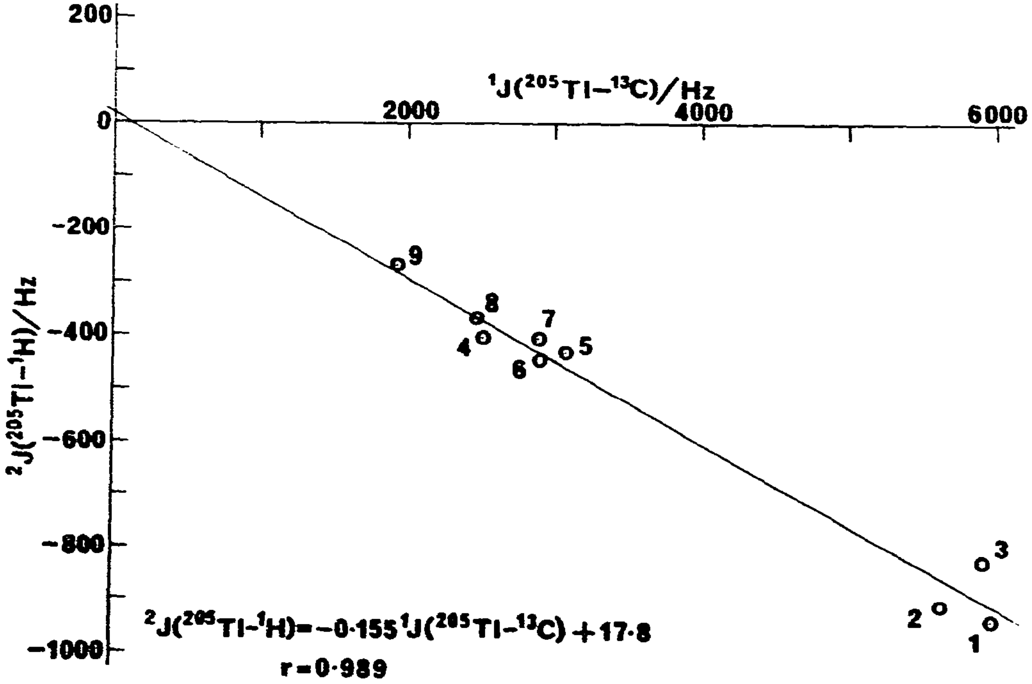

Fig. 1. Relationship between $^2J(^{205}Tl-^1H)$ and $^1J(^{205}Tl-^{13}C)$ for methylthallium(III) derivatives. The signs of $^2J(^{205}Tl-^1H)$ and $^1J(^{205}Tl-^{13}C)$ for $(CH_3)_3Tl$ and $(CH_3)_2TlX$ derivatives (relative to $^1J(^{13}C-^1H) > 0$) are based on results in ref. 2 and a similar assignment is assumed for the analogous couplings in CH_3TlX_2 compounds.

TABLE 3

COMPARISON OF CALCULATED AND OBSERVED RATIOS OF $|^{1}J(^{205}Tl-^{13}C)|$ AND $|^{2}J(^{205}Tl-^{1}H)|$ FOR METHYLTHALLIUM SPECIES

Species	Z_O	$(Z_{eff})^3$	$\alpha^2(Tl)$	Ratio						
				$(Z_{eff})^3$	$\alpha^2(Tl)$	$(Z_{eff})^3 \times \alpha^2(Tl)$	a	b	$|^{1}J(^{205}Tl-^{13}C)|^{c}$	$|^{2}J(^{205}Tl-^{1}H)|^{c}$
$(CH_3)_4Tl^-$	4.7	7310	0.25	0.9	0.8	0.7	—	—	—	0.8[d]
$(CH_3)_3Tl$	5.0	8151	0.33	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$(CH_3)_2Tl^+$	5.4	9021	0.50	1.1	1.5	1.7	1.8	2.2	1.3	1.5
CH_3Tl^{2+}	5.7	9921	1.00	1.2	3.0	3.7	4.3	5.7	3.1	3.5

[a] Values calculated by Maher and Evans [3]. [b] Values calculated by Hatton [15] using thallium optical hyperfine structure constants as estimates of $|\psi_{6s(Tl)}(0)|^2$. [c] Data from I, IV and IX. [d] Data from ref. [12].

extent of methyl substitution, there appears to be no detailed correlation between $^1J(^{205}\text{Tl}—^{13}\text{C})$ and $^2J(^{205}\text{Tl}—^1\text{H})$ for a particular type of methylthallium derivative. The variations in $^1J(^{205}\text{Tl}—^{13}\text{C})$ and $^2J(^{205}\text{Tl}—^1\text{H})$ (< 25%) for $(CH_3)_2TlX$ are attributable to variations in concentration, anion and, most importantly, solvent [1]. The results for monomethylthallium(III) derivatives indicate that anion and solvent are likewise important in determining $^1J(^{205}\text{Tl}—^{13}\text{C})$ and $^2J(^{205}\text{Tl}—^1\text{H})$.

The increase in $^2J(^{205}\text{Tl}—^1\text{H})$ between R_3Tl and R_2TlX ($R = CH_3, C_2H_5$; X = anion) has been interpreted on the assumption that the Fermi contact mechanism is the dominant contribution to the coupling [3]. The approximate expression for the contact contribution to the coupling constant [10, 11] is

$$J(\text{M—X}) \propto |\psi_{ns(\text{M})}(0)|^2 \cdot |\psi_{ns(\text{X})}(0)|^2 \cdot (\Delta E)^{-1} \cdot \alpha^2(\text{M}) \cdot \alpha^2(\text{X})$$

where $|\psi_{ns}(0)|^2$ is the valence *s*-electron density at the nucleus, α^2 represents the *s*-character of the hybrid orbital involved in M—X bonding and ΔE is an average excitation energy. The terms $|\psi_{1s(\text{H})}(0)|^2$, $(\Delta E)^{-1}$ and $\alpha^2(\text{H})$ are assumed constant for given R. Equating $\alpha^2(\text{Tl})$ with the square of the coefficient of the thallium 6*s* orbital in the thallium hybrid orbitals and using the proportionality of $|\psi_{6s(\text{Tl})}(0)|^2$ and $(Z_{\text{eff}})^3$ (where Z_{eff} is the effective nuclear charge on the thallium atom and is approximated by $(Z_0Z)^{½}$; Z_0 = Slater screened nuclear charge and Z = nuclear charge), Maher and Evans [3] predicted values of $^2J(^{205}\text{Tl}—^1\text{H})$ for R_3Tl, R_2Tl^+, RTl^{2+} in the ratios 1:1.8:4.3. Weibel and Oliver [12], however, rationalised $^2J(^{205}\text{Tl}—^1\text{H})$ in methylthallium species solely in terms of changes in *s*-character. These and other relevant ratios are compared in Table 3 with the $^1J(^{205}\text{Tl}—^{13}\text{C})$ and $^2J(^{205}\text{Tl}—^1\text{H})$ data reported in this work and the $^2J(^{205}\text{Tl}—^1\text{H})$ data of reference 12. We have recalculated the ratios using the method of Maher and Evans [3] and find their reported values in error (see Table 3). The recalculated values clearly give better agreement with the experimental data. However, it should be pointed out that comparable agreement is obtained by taking ratios of *s*-characters, a result which is not unexpected on account of the smaller changes in $(Z_{\text{eff}})^3$.

Maher and Evans [3] rightly advise caution in placing significance on the closeness of the calculated and experimental values in view of the approximations involved, especially that the thallium 6*s* orbital participates only in thallium—carbon bonding and that the several different exchange integrals involved in coupling between non-directly bonded atoms have been neglected. The former objection is supported by the observed solvent and anion dependence of $^2J(^{205}\text{Tl}—^1\text{H})$, (Table 1, [1]), although it could reasonably be argued that use of thallium 6*s* orbitals in interactions with solvent or anionic species would reduce the predicted $^2J(^{205}\text{Tl}—^1\text{H})$ ratios R_2Tl^+/R_3Tl and RTl^{2+}/R_3Tl to values nearer than those experimentally observed. The latter objection to this approach is removed when directly bonded thallium—carbon coupling is considered. The correlation between $^1J(^{205}\text{Tl}—^{13}\text{C})$ and $^2J(^{205}\text{Tl}—^1\text{H})$ in the series $(CH_3)_3Tl$, $(CH_3)_2TlX$, CH_3TlX_2 shown in Fig. 1 and the observed ratios of $^1J(^{205}\text{Tl}—^{13}\text{C})$ for $(CH_3)_3Tl$, $(CH_3)_2TlOAc$ and $CH_3Tl(OAc)_2$ (1:1.3:3.1) give considerable support to the assumption of dominance of the Fermi contact mechanism and the importance of $\alpha^2(\text{Tl})$ in determining the general magnitude of these couplings. The conclusion that $^1J(^{205}\text{Tl}—^{13}\text{C})$ is dominated by the contact term is in accord with theoretical considerations which show that the orbital contribution is zero in the absence of multiple bonding between thallium and carbon [10] and the spin-dipolar contribution to $^1J(^{205}\text{Tl}-^{13}\text{C})$ in an isolated thallium—carbon bond is 20 Hz [13].

The other NMR parameter clearly sensitive to the extent of methyl substitution is the thallium-205 chemical shift. The total shift range is 1424 ppm with increasing methyl substitution deshielding the thallium nucleus. The very limited data presently available for organothallium compounds does not yet allow elucidation of the factors influencing δ (Tl). Investigations designed to extend the thallium-205 chemical shift results and to provide further data with which to evaluate the conclusions concerning coupling to thallium are being continued by study of longer-chain alkylthallium(III) derivatives.

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