Journal of Organometallic Chemistry, 118 (1976) 129—134

THE INFLUENCE OF ANION, SOLVENT AND CONCENTRATION ON THE THALLIUM-205, CARBON-13 AND PROTON NMR PARAMETERS OF THE DIMETHYLTHALLIUM(III) ION

P.J. BURKE, R.W. MATTHEWS *,
Department of Chemistry, The Polytechnic of North London, Holloway Road, London, N7 8DB (Great Britain)
and D.G. GILLIES *
Department of Chemistry, Royal Holloway College, University of London, Englefield Green, Surrey (Great Britain)
(Received March 30th, 1976)

Summary

Thallium-205, carbon-13 and proton NMR spectra have been determined for the dimethylthallium(III) derivatives $(CH_3)_2TlX$ (X = NO_3, I, OC_6H_5) as a function of solvent and concentration. The NMR parameters most sensitive to changes in the environment of the thallium nucleus are the ^{205}Tl chemical shift and $^1J(^{205}Tl—^{13}C)$. The thallium-205 chemical shift varies within a 300 ppm range as anion, solvent and concentration are changed, demonstrating the potential of this parameter as a probe for the environment of thallium. The nature of the solvent is the strongest influence on $^1J(^{205}Tl—^{13}C)$, the greatest change being observed for $(CH_3)_2TlNO_3$ between water and pyridine. The solvent dependence of $^1J(^{205}Tl—^{13}C)$ and $^2J(^{205}Tl—^1H)$ is discussed in terms of the approximate expression for the Fermi contact mechanism for spin—spin coupling.

Introduction

Studies of thallium-205 NMR parameters of thallium compounds in solution are rather few in number. The available results, however, indicate the considerable potential of the technique as a probe for the environment of thallium. In particular, ion-pairing [1,2], complex formation [3] and oligomeric behaviour [4,5] have been detected. For organothallium compounds, ^{13}C and ^{1}H NMR spectra offer additional means of probing molecular structure and bonding and the combined study of NMR spectra of all three nuclei imposes the important requirement that interpretation must be consistent with all the NMR parameters. Consequently, we have commenced a study of the NMR spectral characteristics of thallium compounds with alkylthallium derivatives. A necessary first step in a systematic study is the determination of the effects of solvent and concentration changes on the NMR parameters. We report here preliminary results which demonstrate the striking effects of solvent and concentration changes on the spectra of dimethylthallium(III) species, $(CH_3)_2TlX$ (X = NO_3, I, OPh).

Experimental

Preparation of compounds. The compounds $(CH_3)_2TlX$ were prepared by published methods; X = NO_3, OC_6H_5 [6], I [7].

NMR spectra. The 205-isotope (spin, $I = 1/2$; natural abundance, 70.5%) was used for the thallium NMR measurements in preference to the less abundant and slightly less sensitive thallium-203 (spin, $I = 1/2$; natural abundance, 29.5%). Frequency swept thallium spectra were obtained at 34.73 MHz using field modulation on a modified Varian HA-60IL spectrometer fitted with a Varian XL probe. The field was locked using time-shared modulation to the proton resonance of either the solvent or TMS. The latter was sealed in a 5 mm diameter concentric insert in the 12 mm diameter tubes. All spectra were obtained for spinning samples at approximately 29°C. ^{13}C and ^{1}H NMR spectra were obtained at 22.63 MHz on a Bruker HX 90E spectrometer and at 60 MHz in lock mode on a Perkin—Elmer R12B spectrometer respectively. ^{205}Tl, ^{13}C and ^{1}H NMR spectra were determined in several solvents and, where possible, at two concentrations representing, respectively, the limit of solubility and the limit of ^{205}Tl NMR signal detection obtainable in one scan.

Results and discussion

The dimethylthallium group is remarkably stable. The particular derivatives studied were selected as representing three different types of behaviour in solution, hence optimizing the chances of observing variations in NMR parameters. The presence of linear $CH_3—Tl—CH_3^+$ ions in solid $(CH_3)_2TlNO_3$ and in aqueous solution has been established by infrared and Raman spectroscopy [6,8,9]. Conductivity data [10] supports the ionic formulation for $(CH_3)_2TlNO_3$ in aqueous solution but indicates only slight ionization in pyridine. Dimethylthallium iodide is sufficiently soluble for NMR studies only in dimethylsulphoxide and pyridine, reflecting a less ionic nature compared with $(CH_3)_2TlNO_3$. The more polarizable iodide ion is expected to interact with $(CH_3)_2Tl^+$ more strongly than in the case of the nitrate ion. Certainly the crystal structure [11] does not rule out a reasonable degree of covalency in the thallium—iodine interaction. Conductivity studies show [12] that $(CH_3)_2TlI$ is partially dissociated in dimethylformamide. Dimethylthallium phenoxide is dimeric in the solid state with bridging phenoxide groups and slightly bent C—Tl—C units (C—Tl—C angle is approximately 170°) [13]. It seems likely that this structure is largely retained in benzene solution because similar IR spectra are observed for $(CH_3)_2TlOC_6H_5$ in the solid state and in benzene solution [6,14] and molecular weight measurements indicate predominantly dimeric behaviour in benzene [14].

The NMR data are summarized in Table 1. The parameters most sensitive to changes in the environment of thallium are the ^{205}Tl chemical shift and ^1J-(^{205}Tl—C). The ^{205}Tl chemical shifts span approximately 300 ppm and depend on the nature of both the anion, X, and the solvent. The relative shielding effects of dimethylsulphoxide and pyridine are also anion dependent. The chemical shift is concentration dependent in all cases except for $(CH_3)_2TlNO_3$ in aqueous solution. The magnitude and direction of the concentration dependence varies with the anion and the solvent. Anion, solvent and concentration dependent behaviour of chemical shift have previously been observed for several metal nuclei in solutions of salts MX (X = anion, M = ^{205}Tl [1,2,15], ^{7}Li [16,17], ^{23}Na [18—23], ^{39}K, ^{87}Rb, ^{133}Cs [20], ^{45}Sc [24] and ^{113}Cd [25]). By comparison with such studies, it seems likely that the ^{205}Tl chemical shift for $(CH_3)_2TlX$ depends primarily on the degree of contact ion-pair formation between $(CH_3)_2Tl^+$ and X^- and/or the average number of anions and solvent molecules surrounding the cation or ion-pair. Both of these factors depend on solute concentration and hence give rise to concentration dependent chemical shifts. Detailed investigation of these effects is in progress.

Half-height line widths for the components of the ^{205}Tl seven-line multiplet spectra were found to be in the range 5—50 Hz. Broader signals were observed for $(CH_3)_2TlOC_6H_5$ in dichloromethane and toluene (180 Hz and 90 Hz respectively). The methyl resonances in the ^{1}H and ^{13}C NMR spectra of these solutions were also significantly broadened compared to the other solutions studied.

TABLE 1

^{205}Tl, ^{13}C AND ^{1}H NMR PARAMETERS FOR $(CH_3)_2TlX$ ($X = NO_3, I, OC_6H_5$)

X	Solvent [a]	Conc. [b]	Ξ(Tl) [c]	δTl [d]	δ^{13}C-(CH_3) [e]	δ^{1}H-(CH_3) [e]	|^1J(^{205}Tl—^{13}C)| [f]	|^2J(^{205}Tl—^{1}H)| [g]
NO_3	H_2O	0.8	57886757	109	26.9 [h]	1.63 [i]	2459	410
		0.2	57886755	109	26.8 [h]	1.60 [i]	2478	410
NO_3	Pyridine	1.0	57889683	4	22.5	1.44	3018	437
		0.2	57880456	0	22.2	1.50	3080	436
NO_3	DMSO	1.0	57880949	9	25.5	0.89	2905	447
		0.2	57881787	23	25.9	0.70	2903	449
I	Pyridine	0.1	57896617	279	25.5	1.57	3012	415
I	DMSO	0.9	57892660	211	28.0	1.10	2928	440
		0.2	57889756	161	27.5	1.03	2934	441
OC_6H_5	Pyridine	0.9	57891336	188	22.4	1.28	2897	409
		0.2	57891183	185	22.1	1.27	2918	409
OC_6H_5	DMSO	0.8	57889811	162	22.9 [k]	0.90	2928 [j,k]	430
		0.2	57889266	152	22.7 [k]	0.87	2971 [j,k]	430
OC_6H_5	CH_2Cl_2	0.8	57899560	330	22.8 [k]	1.12	2487 [j,k]	372 [j]
		0.2	57899766	334	23.1 [k]	1.16	2475 [j,k]	372 [j]
OC_6H_5	Toluene	0.2	57898826	317	22.8 [k]	1.13	2556 [j,k]	371 [j]

[a] Deuterated solvents were used for ^{1}H and ^{13}C 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. The error is a subjective estimate based on reproducibility over a period of several months. The ^{205}Tl shift in these compounds appears to be temperature dependent and it has subsequently proved necessary to actively control temperature to improve reproducibility enough to take advantage of the measuring accuracy. [d] In ppm (±1). δTl = 0 ppm has been arbitrarily taken as the signal at highest field. [e] In ppm from internal TMS (downfield positive). Errors for δC and δH are ±0.2 and ±0.05 ppm resp. [f] In Hz (±3). [g] In Hz (±2). Determined from ^{1}H NMR spectra. Values previously reported for some of these solutions are in good agreement [6,14,26,28]. [h] Relative to internal TSP. [i] Relative to TMS insert. [j] Signals broadened such that separate coupling to ^{205}Tl and ^{203}Tl was unresolved. [k] Errors; ±10 Hz; ±0.7 ppm.

(Broadened methyl proton resonances for $(CH_3)_2TlOC_6H_5$ in non-polar solvents have previously been observed [14,26].) The broadening probably arises as a result of exchange between monomeric and dimeric forms present in equilibrium. $(CH_3)_2TlOC_6H_5$ is more likely to be present as the dimer in dichloromethane and toluene than in highly coordinating solvents such as pyridine and dimethylsulphoxide where the solvent molecules might compete effectively with $OC_6H_5^-$ for coordination sites around thallium. Signal broadening due to methyl exchange can be ruled out in view of the known kinetic inertness of the dimethylthallium group [27].

Previous reports [6,14,26,28] of ^1H NMR spectra of $(CH_3)_2TlX$ (X = NO_3, I, OC_6H_5) contain few chemical shift data. The methyl proton chemical shifts reported here show little or no dependence on concentration, slight anion dependence and somewhat more solvent dependence (less than ca. 0.3 ppm and 0.8 ppm respectively). Similarly, the methyl carbon chemical shifts are independent of concentration and show slight anion and solvent dependence (<5 ppm in each case). It is noteworthy that there is no evident correlation between the relative shielding effects of the different solvents and anions on the ^1H, ^{13}C and ^{205}Tl nuclei apart from the observation that, in pyridine and dimethylsulphoxide, the largest downfield shifts in all spectra are found when X = I.

The $^2J(^{205}Tl—H)$ values are not significantly concentration dependent but in the two instances where the results allow comparison in the same solvent, the coupling constants show a small (<6%) dependence on the nature of the anion X. The strongest influence on the magnitude of $^2J(^{205}Tl—H)$ is the nature of the solvent and in this the values follow a similar pattern to those previously reported for $(CH_3)_2TlX$. A survey of published values for $^2J(^{205}Tl—H)$ in $(CH_3)_2TlX$ compounds [6,14,26,28—32] reveals that, with few exceptions, they fall into one of two ranges; (1) 400—475 Hz for solutions in polar solvents, with water, pyridine and dimethylsulphoxide producing progressively larger values for a given X; (2) 340—380 Hz for solutions in non-polar solvents. Several solutions of the derivatives with $^2J(^{205}Tl—H)$ in the latter range have been shown to contain dimers and hence this range may well be characteristic of oligomer formation.

The value of $^1J(^{205}Tl—C)$ (= +3456 Hz) for $(CH_3)_2TlBr$ in liquid ammonia appears to be the only previous report [31] of thallium—carbon coupling for dialkylthallium compounds. The magnitudes of the concentration and anion dependences of $^1J(^{205}Tl—C)$ (<2% and <6% respectively) are similar to those observed for $^2J(^{205}Tl—H)$. Also, as in the case of $^2J(^{205}Tl—H)$, the nature of the solvent is the strongest influence on $^1J(^{205}Tl—C)$. The largest solvent dependence was observed for $(CH_3)_2TlNO_3$ (602 Hz between water and pyridine), illustrating the sensitivity of this parameter as a probe for the thallium environment. The values obtained fall into two distinct ranges but do not, however, reproduce completely the pattern observed for $^2J(^{205}Tl—H)$; (1) 2450—2560 Hz for solutions in dichloromethane, toluene and water, (2) 2890—3080 Hz for solutions in pyridine and dimethylsulphoxide. Compared with the $^2J(^{205}Tl—H)$ results, the values for aqueous solutions are anomalously low. Apart from this broad similarity, a plot of $^1J(^{205}Tl—C)$ against $^2J(^{205}Tl—H)$ reveals no detailed correlation. While there appear to be few previous reports of the effects of solvent on metal—carbon coupling constants [33,34], analogous investigations of metal—proton coupling (particularly Sn—H) have received considerable attention [6,33,35—41]. Generally, the same overall pattern of increasing ^2J(M—H) (M = metal) with increasing coordinating ability of the solvent has been found. On the assumption that ^2J(M—H) and ^1J(M—C) are dominated by the Fermi contact mechanism, the results have been discussed in terms of changes in the s-character of the metal—carbon bonds consequent on changes in the coordinating ability of the solvent. This approach is based on the approximate expression for the contact contribution to the coupling constant [42,43];

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

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 solvent effects have been rationalised [6,38—41] by assuming that all terms except α^2(M) are constant and that increasing the coordinating ability of the solvent causes rehybridization at the metal in such a way that α^2(M) increases. The $^1J(^{205}$Tl—C) values for $(CH_3)_2$TlX do not lend support to these simplifying assumptions. Clearly, the factors influencing coupling to thallium are not the same for $^1J(^{205}$Tl—C) and $^2J(^{205}$Tl—H). The assumption of the dominance of the Fermi contact term for $^1J(^{205}$Tl—C) does appear, however, to be reasonable; the orbital contribution is zero in the absence of multiple bonding between thallium and carbon [42] and the spin-dipolar contribution to $^1J(^{205}$Tl—C) has been calculated as 20 Hz [44]. It is worth emphasizing that the solvent-dependent changes in coupling constants for which an explanation is sought are, in the case of $(CH_3)_2$TlX compounds, 25% or less. Given the complexity of the approximate expression for the Fermi contact contribution, it is therefore not surprising that the term(s) responsible for these small changes in the couplings cannot be picked out with certainty. In particular, it does not seem unreasonable to suppose that small changes in ΔE and the s-electron density at the nuclei as well as the more usually invoked changes in s-character of the metal—carbon bond could collectively account for solvent-dependent changes of these magnitudes.

The results obtained so far demonstrate the extra demands and restrictions placed upon interpretation when a range of multinuclear NMR data is available. The dimethylthallium cation system was chosen to test the sensitivity of various NMR parameters to changes in solvent, anion and concentration. Significant changes have been observed which are large enough to warrant further study.

Acknowledgement

We wish to thank the S.R.C. for financial support of this project (to D.G.G. and R.W.M.) and for use of the PCMU ^{13}C NMR facility. P.J.B. is grateful to The Polytechnic of North London for award of a Research Assistantship. We thank Dr. R.E. Burton for helpful discussions and Dr. R.G. Rees for his interest in this work.

References

1 R. Freeman, R.P.H. Gasser, R.E. Richards and D.H. Wheeler, Mol. Phys., 2 (1959) 75.
2 J.J. Dechter and J.I. Zink, J. Chem. Soc. Chem. Commun., (1974) 96; J. Amer. Chem. Soc., 97 (1975) 2937.

3 B.N. Figgis, Trans. Faraday Soc., 55 (1959) 1075.
4 W.G. Schneider and A.D. Buckingham, Disc. Faraday Soc., 34 (1962) 147.
5 G.M. Sheldrick and J.P. Yesinowski, J. Chem. Soc. Dalton, (1975) 870.
6 G.D. Shier and R.S. Drago, J. Organometal. Chem., 5 (1966) 330.
7 H. Gilman and R.G. Jones, J. Amer. Chem. Soc., 72 (1950) 1760.
8 P.L. Goggin and L.A. Woodward, Trans. Faraday Soc., 56 (1960) 1591.
9 G.B. Deacon and J.H.S. Green, Spectrochim. Acta A, 24 (1968) 885.
10 G.B. Deacon, J.H.S. Green and R.S. Nyholm, J. Chem. Soc., (1965) 3411.
11 H.M. Powell and D.M. Crowfoot, Z. Krist., 87 (1934) 370.
12 J.E. Prue and P.J. Sherrington, Trans. Faraday Soc., 57 (1961) 1795.
13 P.J. Burke, D.G. Gillies, P.J.G. Hayward, R.W. Matthews and E.M. McPartlin, to be published.
14 H. Kurosawa, K. Yasuda and R. Okawara, Bull. Chem. Soc. Japan, 40 (1967) 861.
15 H.S. Gutowsky and B.R. McGarvey, Phys. Rev., 91 (1953) 81.
16 J.W. Akitt and A.J. Downs, Chem. Commun., (1966) 222.
17 G.E. Maciel, J.K. Hancock, L.F. Lafferty, P.A. Mueller and W.K. Musker, Inorg. Chem., 5 (1966) 554.
18 M. Herlem and A.I. Popov, J. Amer. Chem. Soc., 94 (1972) 1431.
19 E.G. Bloor and R.G. Kidd, Can. J. Chem., 46 (1968) 3425.
20 C. Deverell and R.E. Richards, Mol. Phys., 10 (1966) 551.
21 R.H. Erlich, M.S. Greenberg and A.I. Popov, Spectrochim Acta A, 29 (1973) 543.
22 R.H. Erlich, E. Roach and A.I. Popov, J. Amer. Chem. Soc., 92 (1970) 4989.
23 R.H. Erlich and A.I. Popov, J. Amer. Chem. Soc., 93 (1971) 5620.
24 G.A. Melson, D.J. Olszanski and E.T. Roach, J. Chem. Soc. Chem. Commun., (1974) 229.
25 R.J. Kostelnik and A.A. Bothner-By, J. Magn. Reson., 14 (1974) 141.
26 A.G. Lee and G.M. Sheldrick, Trans. Faraday Soc., 67 (1971) 7.
27 A.G. Lee, Quart. Rev., 24 (1970) 310.
28 J.V. Hatton, J. Chem. Phys., 40 (1964) 933.
29 A.G. Lee, J. Chem. Soc. A, (1970) 2157.
30 F. Bonati and G. Minghetti, Inorg. Chim. Acta, 3 (1969) 161.
31 K. Hildenbrand and H. Dreeskamp, Z. Phys. Chem., 69 (1970) 171.
32 H. Schmidbaur and F. Schindler, Angew. Chem. Int. Ed., 4 (1965) 876.
33 W. McFarlane, J. Chem. Soc. A, (1967) 528.
34 T.N. Mitchell, J. Organometal. Chem., 59 (1973) 189.
35 J.V. Hatton, W.G. Schneider and W. Siebrand, J. Chem. Phys., 39 (1963) 1330.
36 E.V. Van den Berghe and G.P. Van der Kelen, J. Organometal. Chem., 11 (1968) 479.
37 J.R. Holmes and H.D. Kaesz, J. Amer. Chem. Soc., 83 (1961) 3903.
38 E.V. Van den Berghe, L. Verdonck and G.P. Van der Kelen, J. Organometal. Chem., 16 (1969) 497.
39 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, Bull. Chem. Soc. Japan, 40 (1967) 1566.
40 T.F. Bolles and R.S. Drago, J. Amer. Chem. Soc., 88 (1961) 5730.
41 N.A. Matwiyoff and R.S. Drago, Inorg. Chem., 3 (1964) 337.
42 J.A. Pople and D.P. Santry, Mol. Phys., 8 (1964) 1.
43 H.M. McConnell, J. Chem. Phys., 24 (1956) 460.
44 C.J. Jameson and H.S. Gutowsky, J. Chem. Phys., 51 (1969) 2790.