Thallium-205 Nuclear Magnetic Resonance Spectra of Thallium(I) Alkoxides

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Thallium-205 n.m.r. spectra have been determined for toluene solutions of a series of 11 thallium(I) alkoxides including five previously unreported compounds. The observed spectra are consistent with the predominance of tetrameric species, $[\{Tl(OR)\}_4]$ (R = alkyl group), in solution. The essentially three-line spectra arise from thallium-203–thallium-205 spin–spin coupling with $J(^{203}Tl-^{205}Tl)$ in the range 2 170—2 769 Hz. The thallium-205 chemical shifts span 434 p.p.m. and show some dependence on the nature of the alkyl group. There is no apparent correlation of $J(^{203}Tl-^{205}Tl)$ with the properties of the alkyl groups. The values of $J(^{203}Tl-^{205}Tl)$ are compared with those found for dimeric dimethylthallium(III) derivatives and are discussed in terms of the Fermi-contact contribution to the coupling mechanism.

THE state of aggregation of thallium(I) alkoxides in the solid and in solution has been studied by several investigators. Cryoscopic or ebullioscopic relative molecular-mass determinations have indicated the presence of tetrameric molecules, $[\{Tl(OR)\}_4]$, for R = CH_3, C_2H_5, $CH_2C_6H_5$,[1] or $C(CH_3)_2CH_2CH_3$ [2] in benzene solution and for R = C_2H_5 in ethanol.[1] Corresponding measurements for thallium(I) cyclohexyloxide, $Tl(OC_6H_{11})$, in benzene and thallium(I) methoxide, $Tl(OCH_3)$, in methanol suggest that tri- and mono-meric species, respectively, predominate in these solutions at the concentrations studied.[1] Sidgwick and Sutton [1] proposed a cubic structure for the tetrameric alkoxides in which alternate corners of the cube are occupied by thallium and bridging oxygen atoms respectively. *X*-Ray analysis of thallium(I) methoxide [3] confirmed the tetrameric formulation in the solid state and revealed that the thallium atoms occupied the corners of a regular tetrahedron. Although it was not possible to determine the methoxide positions, Dahl *et al.*[3] proposed that the structure was better represented as a distorted cube in which the O–Tl–O angle is <90°. Raman and i.r. spectra are also consistent with tetrameric structures for liquid thallium(I) ethoxide and solid thallium(I) n-propoxide, $Tl(OC_3H_7)$, and additionally suggest the presence of significant Tl–Tl interactions.[4]

Perhaps the most elegant demonstration of tetrameric species in the liquid state for this class of compound has involved determination of the ^{205}Tl and ^{203}Tl n.m.r. spectra of $Tl(OC_2H_5)$.[5] (^{205}Tl and ^{203}Tl have spin $I = \frac{1}{2}$, and natural abundances of 70.5 and 29.5%, respectively.) The spectra, obtained for both the neat liquid and in cyclohexane solution,[5] can only be satisfactorily accounted for on the basis of symmetrical tetrameric structures. We have studied a range of thallium(I) alkoxides using ^{205}Tl n.m.r. with the purpose of confirming tetrameric behaviour for alkoxides previously studied by other techniques, extending the range of alkyl substituents for which oligomerization has been studied, and investigating possible correlations between $J(^{203}Tl-^{205}Tl)$, $\delta(^{205}Tl)$, and the nature of the alkyl group.

EXPERIMENTAL

Preparation of Thallium(I) *Alkoxides.*—Thallium(I) alkoxides, Tl(OR) [R = n-C_3H_7, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, $CH(CH_3)_2$, $CHCH_3(CH_2)_2CH_3$, $CHCH_3(CH_2)_3CH_3$, $CH_2CH(CH_3)_2$, or $C(CH_3)_2CH_2CH_3$], were prepared by the general method reported by Bradley.[2] The products are all moisture sensitive so all operations were carried out in an atmosphere of dry nitrogen. The preparation of $Tl(OC_3H_7$-n) is typical. n-Propanol (1.45 g, 24.1 mmol) was added to a solution of $Tl(OC_2H_5)$ (Ralph Emmanuel Ltd.; 3.0 g, 12.0 mmol) in light petroleum (b.p. 60—80 °C, 10 cm^3) and the bulk of the solvent removed by distillation. Cooling the solution gave the product as white crystals which were filtered off, dried in a stream of nitrogen, and stored *in vacuo*. For R = n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, $CHCH_3(CH_2)_2CH_3$, and $CHCH_3(CH_2)_3CH_3$ the products were obtained as colourless oils by removing all solvent and ethanol under vacuum. Thallium(I) benzyl oxide, $Tl(OCH_2C_6H_5)$, was obtained as a white precipitate on stirring a mixture of benzyl alcohol and $Tl(OC_2H_5)$ in light petroleum ether (b.p. 60—80 °C), as detailed by Sidgwick and Sutton.[1] The product was recrystallized from light petroleum.

The alkoxides were characterized by comparing their ^{1}H n.m.r. spectra in toluene solutions (1.0 mol dm^{-3}) with spectra of the parent alcohols under the same conditions. In all cases, the formation of the alkoxides in a satisfactorily pure state was confirmed by the absence of signals attributable to $Tl(OC_2H_5)$ and hydroxyl groups, and a downfield shift (in the range 0.38—1.54 p.p.m.) of signals due to protons on α-carbon [except for R = $C(CH_3)_2CH_2CH_3$].

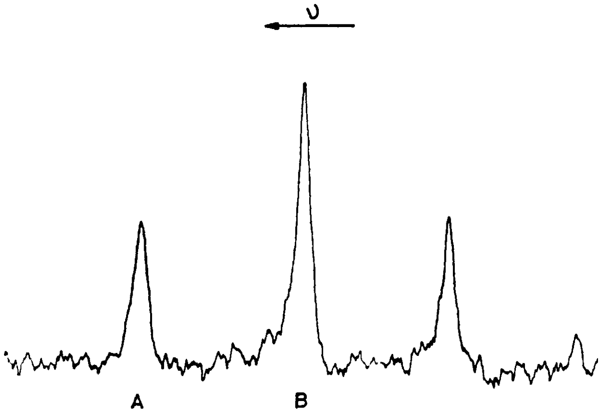
Preparation of Samples for Thallium-205 *N.M.R. Studies.*—Solutions (1.0 mol dm^{-3}) of freshly prepared (<48 h) thallium(I) alkoxides were made up and filtered into n.m.r. tubes (diameter 12 mm) on a vacuum line. Thereafter the n.m.r. tubes were removed from the line and capped under dry nitrogen, and the thallium-205 n.m.r. spectra determined within 24 h. The benzene and toluene solvents were dried over sodium, stored over molecular sieves, and distilled directly onto solutes as required.

N.M.R. Spectra.—Thallium-205 (spin, $I = \frac{1}{2}$; natural abundance, 70.5%) n.m.r. spectra were obtained at 34.7 MHz on a modified Varian HA-60IL spectrometer fitted with a Varian XL probe which accommodated 12 mm spinning samples at 29 °C. Initially, spectra were obtained in continuous-wave (c.w.) frequency-swept mode by detection of the first (usually) upfield side band generated by audiofrequency field modulation at 2 or 6 kHz. The radiofrequency (r.f.) was generated by a Schlumberger FSX 3006S frequency synthesizer which was swept (typically 10 kHz) by a voltage generated from the movement of the recorder.[6] Precise calibration (one part in 10^3 of the sweep width) was quickly achieved (1 s) by counting the interpolation frequency of the synthesizer. All peak positions were measured in this manner which eliminated inaccuracies caused by sweep non-linearity. After initial amplification by a Varian preamplifier, the signals were amplified and detected using a Decca variable-frequency receiver.[6] Some spectra were obtained in pulsed Fourier-transform (p.f.t.) mode. This was achieved using a DEC PDP-11 computer, an Amplifier Research 10LA 10-W broad-band amplifier, and a Polaron 150-W tuned amplifier. The r.f. gate, pulse timers, d.c. amplifier, and low-pass filters were constructed in the laboratory. In both c.w. and p.f.t. modes the field was locked using time-shared modulation with a repetition rate of either 1 or 10 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. stabilized controller, type V4354A.

Continuous-wave spectra using 2 kHz modulation were complicated by overlapping of centre- and side-band features. Increasing the frequency to 6 kHz relieved the situation although there was still overlap of the weak outer features (see Figure). In the p.f.t. spectra (maximum available width 5 kHz), one of these weak features occurred outside the sweep range and was consequently folded back into the spectrum to appear as an out-of-phase signal.

RESULTS

The appearance of the ^{205}Tl n.m.r. spectra for all the thallium(I) alkoxides studied is similar to that shown for thallium(I) hex-2-yl oxide in the Figure, which consists of two resonances at equal frequency separations, within experimental error, from a central more intense signal. The separations between the outer signals are *ca.* 2.5 kHz and half-height linewidths are in the range 120—500 Hz. At the concentrations used (*ca.* 1.0 mol dm^{-3}), these broad signals severely limit the accuracy with which signal intensities can be estimated. Where the quality of the spectra allows reasonable estimates of signal areas [for R = C_2H_5 in benzene and toluene, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, $CHCH_3(CH_2)_2CH_3$, $CHCH_3(CH_2)_3CH_3$, and $CH_2C_6H_5$ in benzene and toluene], the relative intensities of signals A and B (Figure) are in the range 1 : 1.6—2.2. Signal intensities in the spectra of the remaining four compounds qualitatively follow the same pattern.



Continuous-wave thallium-205 n.m.r. spectrum of thallium(I) hex-2-yl oxide, [{Tl[OCH(CH$_3$)(CH$_2$)$_3$CH$_3$]}$_4$], in toluene. The frequency (34.71 MHz) was modulated at 6 kHz and the first upper side band observed. Peak positions were measured individually using a frequency counter to eliminate inaccuracies caused by sweep non-linearity

Thallium-205 chemical shifts * and thallium-203–thallium-205 spin–spin coupling constants derived from these spectra (see below) are given in the Table.

Thallium-205 chemical shifts and ^{203}Tl–^{205}Tl spin–spin coupling constants for thallium(I) alkoxides, Tl(OR)

R [a]	Ξ(Tl) [b]	δ(Tl) [c]	$\|J(^{203}Tl-^{205}Tl)\|$ [d]
C_2H_5 [e]	57 851 998	−605	2 575 ± 15
C_2H_5	57 851 826	−608	2 560 ± 20
n-C_3H_7	57 848 751	−661	2 435 ± 30
n-C_4H_9	57 848 626	−664	2 604 ± 15
n-C_5H_{11}	57 848 582	−664	2 415 ± 20
n-C_6H_{13}	57 848 562	−665	2 550 ± 60
$CH(CH_3)_2$	57 858 116	−500	2 530 ± 20
$CHCH_3(CH_2)_2CH_3$	57 855 964	−537	2 769 ± 30
$CHCH_3(CH_2)_3CH_3$	57 844 926	−728	2 716 ± 15
$CH_2CH(CH_3)_2$	57 842 120	−776	2 394 ± 30
$C(CH_3)_2CH_2CH_3$	57 867 884	−331	2 656 ± 30
$CH_2C_6H_5$ [f]	57 836 069	−881	2 280 ± 20
[g]	57 832 974	−934	2 170 ± 20

[a] Spectra determined in toluene solution (1.0 mol dm^{-3}) unless otherwise stated. [b] Frequency in Hz (±30) of ^{205}Tl signal for a field in which SiMe$_4$ gives a proton resonance at 100 MHz. The error is a subjective estimate based on the uncertainty in determining the centres of the rather broad signals (see text). Some errors are lower than this value. [c] In p.p.m. (±0.6). See footnote on this page for reference standard. [d] In Hz. [e] In benzene; *ca.* 4.0 mol dm^{-3}. [f] 0.5 mol dm^{-3}. [g] In benzene; 1.8 mol dm^{-3}.

DISCUSSION

Schneider and Buckingham[5] observed a symmetrical five-line pattern for the ^{205}Tl n.m.r. spectrum of neat liquid Tl(OC$_2$H$_5$), with relative signal intensities 0.2 : 1 : 2 : 1 : 0.2. The ^{203}Tl n.m.r. spectrum consisted of a symmetrical pattern of seven lines and the line separations were the same (1.28 kHz) in both spectra.[5] Additionally, it was observed[5] that, except for a reduction in overall intensity, the spectra were unaltered by dilution of Tl(OC$_2$H$_5$) in cyclohexane, and no ^{203,205}Tl–^{1}H coupling was detected in the ^{1}H n.m.r. spectra between 20 and −70 °C. These results can only be satisfactorily accounted for in terms of associated molecules within which ^{205}Tl–^{203}Tl spin–spin coupling occurs. The equal signal separations require that, within each oligomer, the ^{205}Tl nuclei which are spin–spin coupled to a ^{203}Tl nucleus (and *vice versa*) must be structurally equivalent. Relative ^{205}Tl n.m.r. signal intensities calculated for the three most intense bands of such oligomeric molecules are: dimer, 1.0 : 4.8 : 1.0; trimer, 1.0 : 2.6 : 1.0; tetramer, 1.0 : 1.9 : 1.0; hexamer, 1.0 : 1.5 : 1.0. Each spectrum consists of a superposition of multiplets arising

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* The reference standard is chosen as the ^{205}Tl chemical shift at infinite dilution for [Tl(CH$_3$)$_2$(NO$_3$)] in water at 41 °C; Ξ(Tl) = 57 887 038 Hz.[7] Unusually among the more easily handled and accessible thallium compounds, aqueous solutions of [Tl(CH$_3$)$_2$(NO$_3$)] show only a very small dependence of δ(Tl) on concentration,[7,8] and this makes it particularly useful in the conversion into a common scale of other ^{205}Tl chemical-shift data, which are not reported in terms of Ξ(Tl).[5,9,10]

from molecules of the type $^{203}Tl_x{}^{205}Tl_{n-x}(OR)_n$ ($n = 2$, 3, 4, or 6; $x = 0$—n), and weighted according to the relative abundances of the isotopically substituted oligomers.[5] The ^{205}Tl chemical shift is given by the position of the central component and component separations are equal to $J(^{203}Tl-^{205}Tl)/2$.

The signal patterns and component intensities of ^{205}Tl n.m.r. spectra for Tl(OR) [R = C_2H_5, n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, $CHCH_3(CH_2)_2CH_3$, $CHCH_3(CH_2)_3CH_3$, or $CH_2C_6H_5$] are consistent with the presence of predominantly tetrameric molecules in solution. Since, however, the relative peak areas could not be determined with sufficient accuracy, the presence of significant proportions of trimeric and/or hexameric molecules in these solutions, and for the remaining thallium(I) alkoxides [R = n-C_3H_7, i-C_3H_7, $CH_2CH(CH_3)_2$, or $C(CH_3)_2CH_2CH_3$], cannot be ruled out. The weak outer pairs of lines were not satisfactorily detected in any of the spectra. In one case, thallium(I) hex-2-yl oxide, the upfield component of one of these pairs was clearly observed, but the downfield component was obscured by some overlap with the out-of-phase centre-band signal (Figure). The results for benzene solutions of $Tl(OC_2H_5)$ and $Tl(OCH_2C_6H_5)$ agree with relative molecular-mass determinations,[1] although it should be noted that the maximum concentrations used in the latter experiments were somewhat lower, 0.7 and 0.4 mol dm^{-3} respectively.[1] The degree of association increases to a maximum of about four with increasing concentration.[1] (Apart from these two samples, all compounds considered in this work were investigated as solutions in toluene.) The remaining results, five of which are for compounds not previously reported, demonstrate that oligomerization and in particular tetramer formation are general features of the chemistry of thallium(I) alkoxides in aromatic hydrocarbon solvents.

The major limitation of the ^{205}Tl n.m.r. technique for study of thallium(I) alkoxides is the broadness of the resonance lines. For this reason the present investigation did not include measurements on solutions at concentrations <*ca.* 1.0 mol dm^{-3}. The broad lines are presumably the result of exchange processes involving the dominant oligomer and possibly other oligomeric species. It follows that the values of δ(Tl) and $J(^{203}Tl-^{205}Tl)$ may represent average values arising from more than one oligomeric species.

The ^{205}Tl chemical shifts of the thallium(I) alkoxides span the range −500 to −934 p.p.m., which represents considerable deshielding relative to the shift range for more ionic thallium(I) compounds [−1 669 to −3 899 p.p.m. for thallium(I) salts in various solvents [9a,9c,10,11]]. The alkoxide shift range also overlaps the low-frequency end of the thallium(III) shift range where the maximum observed span is from *ca.* −1 345 p.p.m. for the $TlCl_3$–water system [9b] to 1 615 p.p.m. for trimethylthallium(III) in pentane.[10] While noting the limitation that contributions to δ(Tl) may arise from more than one oligomeric species, it appears that δ(Tl) depends to some extent on the nature of the alkyl group. Replacing H on C(α) with an alkyl group results in a decrease in shielding of 71—169 p.p.m., and substituting H on C(β) increases shielding by 37—84 p.p.m. Substitution at C(γ) for the straight-chain alkyl derivatives has little effect. However, the result for R = $CHCH_3(CH_2)_3CH_3$ does not fit this pattern and is anomalously low when compared to the value for R = $(CH_2)_2CH_3$.

There appears to be no correlation of $J(^{203}Tl-^{205}Tl)$ with the properties of the alkyl groups in $[\{Tl(OR)\}_4]$, although this parameter is clearly sensitive to the nature of the system. Thus $J(^{203}Tl-^{205}Tl)$ varies over a maximum range of 599 Hz between $[\{Tl(OCH_2C_6H_5)\}_4]$ in benzene and $[\{Tl[OCHCH_3(CH_2)_2CH_3]\}_3]$ in toluene. Apart from the solvent- and/or concentration-dependent values obtained for $[\{Tl(OCH_2C_6H_5)\}_4]$, the values of $J(^{203}Tl-^{205}Tl)$ for the remaining compounds cover a smaller range (375 Hz) and are significantly larger.

The only other $^{203}Tl-^{205}Tl$ spin–spin coupling constants which have been reported are for dimeric dimethylthallium(III) derivatives $[\{Tl(CH_3)_2X\}_2]$ [X = OC_2H_5, $N(CH_3)_2$, or $NHCH_3$],[12,13] and these compounds have values about half those found for the thallium(I) alkoxides. Dimethylthallium(III) ethoxide [$J(^{203}Tl-^{205}Tl) = 1\ 200 \pm 20$ Hz] [12] presumably has a structure similar to those reported [14a] for $[\{Tl(CH_3)_2X\}_2]$ (X = OC_6H_5 or OC_6H_4Cl-*o*) in which the Tl_2O_2 units are coplanar within experimental error,[14a] the Tl–O–Tl angles are in the range 105—109°, the O–Tl–O angles are in the range 70—80°.[14b] The structures of the Tl_2O_2 units are thus similar to that proposed [3] for the alkoxide bridges in the thallium(I) alkoxides, and indeed the thallium–thallium distances (3.77 and 3.84 Å respectively for X = OC_6H_5 and OC_6H_4Cl-*o*)[14b] are close to the value of 3.84 Å found for $[\{Tl(OCH_3)\}_4]$.[3] Assuming that the Fermi-contact contribution dominates the coupling mechanism,* the differences in $J(^{203}Tl-^{205}Tl)$ for the two types of compound may therefore arise from differing amounts of thallium 6*s* character in Tl–O–Tl bonds, or Tl–Tl ' bonds '.[4,16,17] The possibility of interaction between electrons in thallium 6*s* orbitals is presumably greater for $[\{Tl(OC_2H_5)\}_4]$ than for $[\{Tl(CH_3)_2(OC_2H_5)\}_2]$ where it is likely that the 6*s* orbitals are preferentially involved in bonding in the strongly bonded,[18] essentially linear, C–Tl–C unit.[14a]

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* This assumption is made by analogy with the situation for Tl–H and Tl–C coupling where there is evidence for dominance of the contact contribution.[15] More satisfactory evidence for dominance of this term in metal–metal coupling is lacking.

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