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NMR STUDY OF ANION EXCHANGE IN SOME THALLIUM(III) REAGENTS

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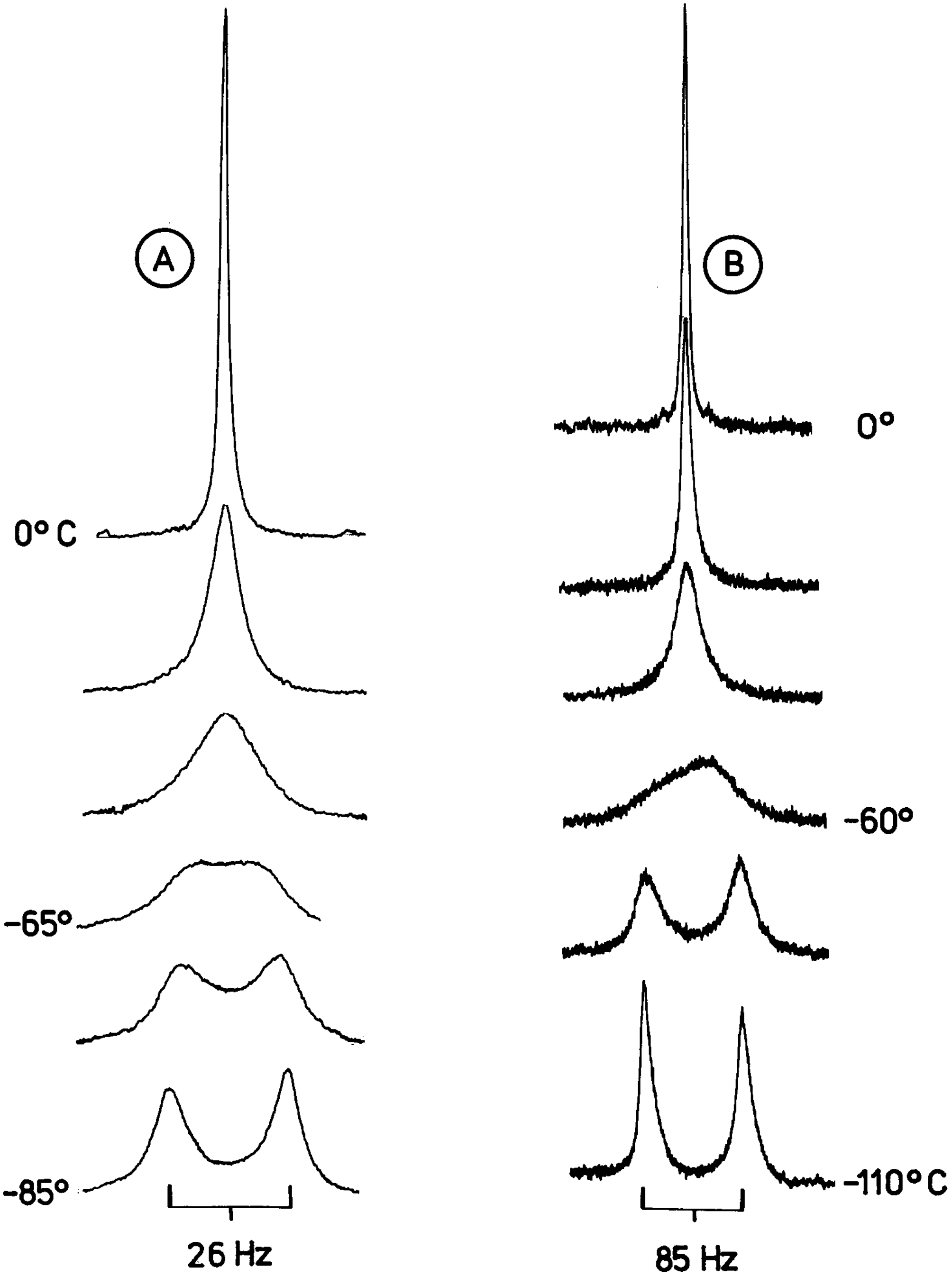
Thallium-proton couplings are often large and extend over many bonds[1] but though Tl-H couplings through a nitrogen atom have been observed[2,3], no coupling through the ester linkage [*e.g.* as in $Tl(OAc)_3$ and $Tl(OCOCF_3)_3$] has been reported. For example, in the case of the ^{13}CMR spectra of arylthallium(III) bis(trifluoroacetates), the absence of any ^{13}C-Tl couplings associated with the trifluoroacetate ligands was presumed to be due to the high ionic character of the Tl-O bonds[4]. We report herein the observation of thallium couplings[5] through the ester linkage, and comment upon some of the consequences of this observation.

During an NMR study of thallium(III) *meso*-tetraphenylporphyrin acetate[3], although the methyl protons of the apical acetate ligand were observed as a sharp singlet at δ -0.03, with no hint of coupling through to the thallium atom, we did not observe either the carbonyl or methyl signals of the acetate ligand in the ^{13}CMR spectrum[6]; all other carbons in the porphyrin were clearly visible. We surmised that this non-observation might be due to broadening of the ^{13}C signals through an exchange process involving the apical ligand. This view was strengthened by the ^{13}C spectrum of thallium(III) acetate (in DMSO-d_6), in which the carbonyl and methyl lines were broad ($\Delta\nu_{\frac{1}{2}}$ *ca.* 16 and 22 Hz respectively) but had the expected chemical shifts (δ 174.8 and 19.9).

In order to confirm this inference we performed a variable temperature ^{1}H and ^{19}F study using $Tl(OAc)_3$, Tl(OAc), and $Tl(OCOCF_3)_3$. On cooling a 0.065 M solution of $Tl(OAc)_3$ in methanol-d_4 (Figure A), the single methyl signal observed at room temperature (δ 2.018) broadened (T_c *ca.* -65°C) and finally split into two peaks with separation 26.3 Hz. The process was completely reversible and experiments



FIGURE; Ⓐ: Temperature dependence of ^{1}HMR spectrum of 0.065 M Tl(OAc)$_3$ in methanol-d$_4$.
Ⓑ: Temperature dependence of ^{19}FMR spectrum of Tl(OCOCF$_3$)$_3$ in tetrahydrofuran.

at 60 and 100 MHz confirmed the separation as a coupling J_{Tl-H} rather than a chemical shift difference.

The line-shape analysis for this rate process may be obtained by treating this spectrum as a simple two-site rate process, i.e. using the coupling as an effective chemical shift difference. Use of the Allerhand-Gutowsky equation[7] and the usual coalescence equation for two site analysis gave consistent results with k_{208} ca. 50 sec.$^{-1}$, which would correspond in a unimolecular rate process to a $\Delta G^{\ddagger}_{208}$ of 10.4 kcal/mole.

The $Tl(OCOCF_3)_3$ investigation (in tetrahydrofuran) gave (Figure B) similar results, the single CF_3 line broadening (T_c ca. -60°C) to give eventually two peaks with separation 85.2 Hz; we ascribe this to Tl-F coupling. The same analysis as for the acetate gave k_{213} ca. 189 sec.$^{-1}$ corresponding to a unimolecular enthalpy of activation of 10.1 kcal/mole.

Interestingly, the low temperature doublet spectra (Figure) of both the acetate and trifluoroacetate are not exactly symmetrical, the two components having slightly different line-widths. This is possibly due to the influence of the two different thallium isotopes (^{203}Tl, ^{205}Tl). A small difference in the Tl-X coupling constant for the two isotopes could be observed as asymmetry in a line-broadened spectrum.

Low temperature studies using thallium(I) acetate in a variety of solvents failed to produce a similar definite coalescence. Some line-broadening of the methyl resonance at ca. -100°C in a methanol/2-methoxyethanol solution was apparent, but we cannot discount the possibility that this was merely a viscosity effect; further cooling caused precipitation of the salt. It therefore appears that the activation energy to exchange is considerably lower in thallium(I) salts.

The nature of the exchange process is not obvious at this stage. Three-fold dilution of the $Tl(OAc)_3$ with methanol-d_4 produced a slight increase in the coalescence temperature, T_c.

For the Tl(III) compounds, the rate determining step could either be the monomolecular dissociation of the complex:

$$Tl(OR)_3 \longrightarrow {}^{+}Tl(OR)_2 + {}^{-}OR$$

or a bimolecular exchange:

$$^{-}OR_a + Tl(OR_b)_3 \longrightarrow (R_aO)Tl(OR_b)_2 + {}^{-}OR_b$$

The thallium(I) acetate would certainly possess a less energetic pathway for bimolecular exchange, and thus (as observed) a much lower activation energy, but the results do not permit a differentiation at this stage.

Anion exchange in heavy metal salts is not a novel observation[8]; for example, lead tetra-acetate in trifluoroacetic acid is as potent as lead tetrakis(trifluoroacetate) in oxidations. However, the observation of the sizeable Tl-H and Tl-F couplings of [illegible].3 and 85.2 Hz in the tri-acetate and tris-trifluoroacetate implies unequivocally that thallium will couple with any magnetic nucleus through an ester linkage, and that the lack of such a coupling is prima facie evidence of an exchange process under those conditions[9]. Particular care must therefore be taken in ^{13}CMR studies because the Tl-^{13}C coupling could be large, and any residual broadening, such as in the thallium(III) porphyrin mentioned above, will result in complete disappearance of the ^{13}C signals.

REFERENCES AND FOOTNOTES

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