Solvent and Anion Dependence of the ^{205}Tl Nuclear Magnetic Resonance Chemical Shift

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Summary The ^{205}Tl chemical shifts, extrapolated to infinite dilution, in water, formamide, DMF, methanol, pyridine, pyrrolidine, and n-butylamine have been determined and are explained in terms of interaction strengths.

BECAUSE of its radius, electronic properties, and nuclear spin, thallium(I) has been shown to have strong potential as both an n.m.r. and electronic spectroscopic probe of the role of potassium in biological systems.[1-3] The thallous ion has been found to substitute effectively for potassium in several potassium-activated enzymes,[1,2] and thallium n.m.r. has been used to examine conformational changes in rabbit muscle pyruvate kinase upon divalent activator ion and substrate binding.[3] There has been no systematic study of the effect of solvents on the chemical shift.

We are currently investigating the solvent dependence of the chemical shift in order to determine whether or not there exist shift regions corresponding to specific donor atoms or groups or a shift correspondence with Lewis basicity of the solvent. Solvents which would serve as models of biologically significant groups were chosen for investigation. The anion dependence of the shift is linear with the perchlorate and fluoride anion concentrations and curvilinear with the formate and acetate anion concentrations. The curvature of the latter shift dependences becomes more marked as the solvent is changed from water to formamide to methanol. All of the anions shift the resonance to low field as the concentration is increased except for the perchlorate which shifts to high field. The only previously reported shifts to high field were in solutions containing the acid of the anion under investigation.[4,5] Contrary to previous work,[5] we do not find curvature in the anion concentration dependence of the thallous fluoride shift.

Previously reported ^{205}Tl anion dependent chemical shift investigations[4,5] involved only aqueous solutions of thallous salts. An ion-pairing mechanism was proposed to explain the curvature in the anion concentration dependence.[5] Thus, the shift extrapolated to zero anion concentration represents the solvated thallous ion.

Because of the linear influence of the fluoride and perchlorate anions, a least squares fit was used in the present study to extrapolate these shifts to zero anion concentration. The extrapolated chemical shifts obtained by this method for the different solvents and representing the purely solvated thallous ion are listed in the Table. The solvent dependence is the most striking feature of the chemical shift. There are two definite regions of shifts, one corresponding to nitrogen co-ordinating solvents and the other region corresponding to oxygen co-ordinators with a maximum separation between them of 1900 p.p.m.

The shifts were measured at a frequency of 32·082 MHz and a field of about 13 kG, using 15 mm n.m.r. tubes with a sealed and degassed 5 mm tube in the centre containing a 5·00 M aqueous solution of $TlCO_2H$ as a reference. Spectra were obtained at ambient probe temperature without spinning. Line widths were about 2 p.p.m. All thallous salts were recrystallised and dried and organic solvents were freshly dried and distilled before use.

TABLE. ^{205}Tl chemical shifts of thallous perchlorate and thallous fluoride extrapolated to infinite dilution in various solvents. Estimated errors in shifts are indicated.

Solvent	Salt	Shift (p.p.m.))
Water	$TlClO_4$	$-233 \pm 1·5$
Water	TlF	$-233 \pm 1·5$
Formamide	$TlClO_4$	$-39 \pm 1·5$
DMF	$TlClO_4$	$-29 \pm 1·5$
Pyridine	$TlClO_4$	432 ± 3
Pyrrolidine	$TlClO_4$	1523 ± 10
n-Butylamine	$TlClO_4$	1662 ± 10

Solvent competition studies show preferential solvation by solvents giving rise to resonances at lower fields. Therefore the more strongly the solvent interacts with the thallous ion, the more the extrapolated shift will be to low field. This shift, as is the anion shift, is probably governed by the paramagnetic or deshielding contribution to the chemical shift.[6] A similar trend was found for ^{23}Na;[7] however, the shift range for sodium was only 25 p.p.m. compared to at least 1900 p.p.m. for Tl^+. The major difference between the reported solvent effect for sodium and that which we observed for thallium is an apparent reversal of water and DMF. Since solvents of intermediate interacting strength are not common to both studies, it is difficult to determine the extent of the reversal. Differences can be expected since thallium, although similar to an alkali metal in chemical behaviour, has a filled *s* shell and is more polarisable than sodium.

(*Received*, 19*th October* 1973; *Com.* 1447.)

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