

ΔH^\ddagger for crystal field contributions.¹⁹ While it appears that σ bonding variation or solvation arguments may accommodate ΔH^\ddagger variations, any discussion of ΔS^\ddagger is complicated by uncertainty as to the extension of the transition state beyond the first coordination sphere. The data in the table indicate that a decrease in ΔH^\ddagger leads to increased ordering in the transition state and that an approximate linear relationship between ΔH^\ddagger and ΔS^\ddagger exists as has been observed for a considerable range of solvent exchange and ligand substitution processes on divalent metal ions.¹⁶ Bennetto and Caldin¹⁸ suggest that ΔS^\ddagger arises largely from solvent reorganization outside the first coordination sphere, and have proposed a mechanism for solvent exchange on $M(\text{solvent})_6^{2+}$, based upon the Frank and Wen²⁰ model for solvated ions, which rationalizes the approximate linear relationship between ΔH^\ddagger and ΔS^\ddagger . This mechanism envisages that if net transfer of solvent from a region of disordered solvent immediately outside the first coordination sphere to the relatively ordered bulk solvent occurs, synchronously with the bond breaking process in the first coordination sphere, then negative contributions to the observed ΔH^\ddagger and ΔS^\ddagger values (and *vice versa*) arise from these processes. If this mechanism is applied to the $Ni(\text{triam})(\text{CH}_3\text{CN})_3^{2+}$ system, it appears

(19) A. L. Companion, *J. Phys. Chem.*, **73**, 739 (1969), and references therein. Crystal field activation energies (CFAE) calculated for a square based pyramid transition state on the basis of the energies of the ${}^3T_{2g} \leftarrow {}^3A_{2g}$ transition are 5.9, 5.6, 6.4, 6.3, 6.6, and 5.9 kcal mol⁻¹, respectively, for $Ni(\text{CH}_3\text{CH})_6^{2+}$, $Ni(\text{trio})(\text{CH}_3\text{CN})_3^{2+}$, $Ni(\text{triam})(\text{CH}_3\text{CN})_3^{2+}$, $Ni(\text{diamol})(\text{CH}_3\text{CN})_3^{2+}$, $Ni(\text{tren})(\text{CH}_3\text{CN})_2^{2+}$, and $Ni(\text{trenol})(\text{CH}_3\text{CN})_2^{2+}$. These values are almost certainly the upper limits of the CFAE contribution to ΔH^\ddagger .

(20) H. S. Frank and Y.-W. Wen, *Discuss. Faraday Soc.*, No. 24, 133 (1957).

that solvent reorganization outside the first coordination sphere is more highly concerted with the bond breaking process than is the case in the $Ni(\text{trio})(\text{CH}_3\text{CN})_3^{2+}$ system which has the more positive ΔS^\ddagger value. As these two species are stereochemically similar, it seems that the mechanistic differences must stem from the electron donating characteristics of the polydentate ligands, which firstly are likely to modify the bond breaking contributions²¹ to ΔH^\ddagger and secondly are likely to result in different charge densities of the first coordination sphere which in turn probably produce differing first coordination sphere-solvent interactions.

The directional characteristics of acetonitrile labilization in $Ni(\text{tren})(\text{CH}_3\text{CN})_2^{2+}$ and $Ni(\text{trenol})(\text{CH}_3\text{CN})_2^{2+}$ suggest that the contributions to ΔH^\ddagger of the bond breaking process in the nonequivalent sites vary, but unfortunately ΔH^\ddagger values were only obtained for one type of site in each species. Nevertheless support for this supposition may be adduced from the observation of different Ni-NCS distances²² in $Ni(\text{tren})(\text{NCS})_2$, which may well indicate differing Ni-NCCCH₃ distances, with consequently different bond breaking contributions to ΔH^\ddagger , in the acetonitrile analog.^{3, 23}

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(21) This mode of variation of ΔH^\ddagger is contrary to the suggestion (ref 16) that ΔH^\ddagger variation arises mainly from solvent reorganization outside the first coordination sphere. It should be noted, however, that ref 16 deals with $M(\text{solvent})_6^{2+}$.

(22) S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

(23) A discussion of the electronic origin of directional effects is given by F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1968.

Nuclear Magnetic Resonance Studies of Thallium(I)-205 in Aqueous Solution¹

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Abstract: The relaxation (longitudinal and transverse) of thallium(I) ions in aqueous solution is observed to be independent of the resonance frequency, isotopic substitution in the solvent (D₂O for H₂O), the resonant spin (²⁰³Tl for ²⁰⁵Tl), the salt concentration, and the nature of the anions. It is, however, very sensitive to dissolved oxygen, and a linear dependence of the relaxation rate on the gas pressure up to 5 atm has been observed. It is concluded that, in oxygen-free solutions, Tl(I) is dominantly relaxed by the transient spin-rotation interaction and, in oxygenated solutions, by the electron-nuclear dipole-dipole interaction with considerable penetration of the hydration sphere by oxygen. No complex between the thallous ion and oxygen molecules appears to form as there is no appreciable increase in oxygen solubility in aqueous thallous solutions nor is there any appreciable shift in the Tl(I) resonance when the solutions are oxygenated. Solvent isotope shifts of thallium ions in light and heavy water have been determined. They are, contrary to other systems studied, rather dependent on the salt concentration and the nature of the anions. These observations are interpreted as a differential competition of various anions and solvent molecules in their interactions with the thallium ion.

Gutowsky and McGarvey^{2a} observed the large chemical and concentration shifts of the thallium

resonances in aqueous solutions. In a later study by Freeman, *et al.*,^{2b} a larger range of concentrations and solutions of thallous salts was studied. Chemical shift measurements were also made by Freeman, *et al.*,^{3a}

(1) This research was generously supported by the National Research Council of Canada in operating grants to L. W. R.

(2) (a) H. S. Gutowsky and B. R. McGarvey, *Phys. Rev.*, **91**, 81 (1953); (b) R. Freeman, R. P. H. Gasser, R. E. Richards, and D. H. Wheeler, *Mol. Phys.*, **2**, 75 (1959).

(3) (a) R. Freeman, R. P. H. Gasser, and R. E. Richards, *Mol. Phys.*, **2**, 301 (1959); (b) T. J. Rowland and J. P. Bromberg, *J. Chem. Phys.*, **29**, 626 (1958).

Rowland, *et al.*,^{3b} and Figgis⁴ in various inorganic thallium salts and by Schneider and Buckingham⁵ in some organothallium systems. A study of the chemical shifts and spin-lattice relaxation of the thallium(I) resonances in aqueous solution with paramagnetic anions by Gasser and Richards⁶ showed that there was no appreciable covalency in the thallos ion-pairs studied.

The recent spin-lattice relaxation measurements by Kayne and Reuben^{7,8} of ²⁰⁵Tl in the presence of the enzyme pyruvate kinase was an attempt to indicate the binding site of the monovalent metal activator.

In a recent communication Bacon and Reeves⁹ reported a strikingly large sensitivity of the thallium(I) spin-lattice relaxation rate (R_1) and spin-spin relaxation rate (R_2) to dissolved oxygen in aqueous solutions. The relaxation rates are, however, within experimental errors, independent of the anions and the concentration and also not affected by isotopic substitution in the solvent (*i.e.*, D₂O for H₂O) or in the resonant nuclei (*i.e.*, ²⁰³Tl for ²⁰⁵Tl). It was pointed out that the T_1 measurements of thallium(I) made earlier^{6,8} reflected the presence of dissolved oxygen. The present work provides a more extensive study of the oxygen dependence of the thallium(I) relaxation rates. In addition, some chemical shift measurements have been made and the effects of added complexing agents (ethylenediamine and *o*-phenanthroline) on the chemical shift and relaxation of thallium(I) in aqueous solution have been included.

Experimental Section

(a) **Chemicals.** Thallos acetate, formate, fluoride, and nitrate were obtained commercially from Alfa Inorganics, Inc., and were further purified by recrystallization from water and subsequent drying in a vacuum desiccator. Dimethylthallium nitrate was prepared¹⁰ by shaking an equivalent amount of silver nitrate in an aqueous suspension of dimethylthallium bromide (from Alfa Inorganics, Inc.). The insoluble silver bromide was precipitated and the solution was filtered, concentrated, and allowed to stand. The crystallized dimethylthallium nitrate was dried in a desiccator under reduced pressure. Ethylenediamine and *o*-phenanthroline, obtained commercially from J. T. Baker Chemical Co., were used without further purification.

(b) **T_1 and T_2 Measurements.** The spin-lattice relaxation rate R_1 was determined by the 90–90° two pulse method. The accuracy is about ±5%. The spin-spin relaxation rate, R_2 , was determined by the Carr–Purcell sequence.¹¹ The precision is to about ±10% because of some pulse imperfections characteristic of the spectrometer, which were difficult to eliminate completely. The pulse spectrometer operates at 7.95 and 15.1 MHz. Most of the measurements were done on ²⁰⁵Tl, the more abundant isotope at 15.1 MHz for a better signal to noise ratio, but a subset of the measurements was also made on the ²⁰³Tl resonance and at the lower frequency, 7.95 MHz, to show isotope independence⁹ and frequency independence of the relaxation of thallium(I) in aqueous solutions. The ambient probe temperature was 26°. For all the measurements made, T_1 and T_2 were approximately equal to each other within experimental errors. Signal averaging, wherever necessary, was done with a Fabritek 1074 signal averager. The memory could be transferred to a PDP11 computer and afterwards to an IBM 360/75 computer for manipulation of the numerical Fourier transform, if necessary.

(4) B. N. Figgis, *Trans. Faraday Soc.*, **55**, 1075 (1959).

(5) W. G. Schneider and A. D. Buckingham, *Discuss. Faraday Soc.*, **34**, 147 (1962).

(6) R. P. H. Gasser and R. E. Richards, *Mol. Phys.*, **2**, 357 (1959).

(7) F. J. Kayne and J. Reuben, *J. Amer. Chem. Soc.*, **92**, 220 (1970).

(8) J. Reuben and F. J. Kayne, *J. Biol. Chem.*, **246**, 6227 (1971).

(9) M. Bacon and L. W. Reeves, *J. Amer. Chem. Soc.*, **95**, 272 (1973).

(10) A. E. Goddard, *J. Chem. Soc.*, 119, 672 (1921).

(11) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

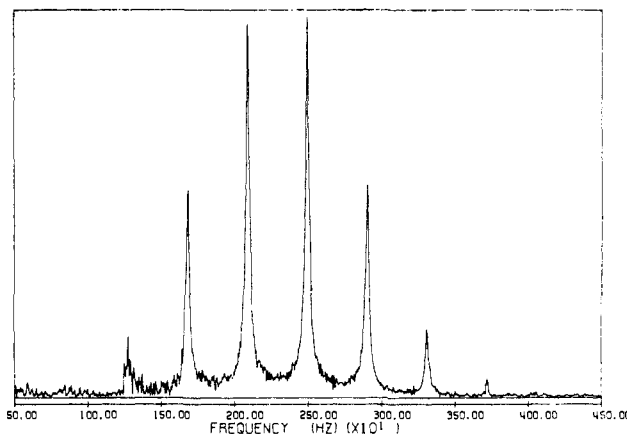


Figure 1. Thallium-205 nmr spectrum of dimethylthallium nitrate in water by Fourier transformation of the free induction decay signal. The center of the septet is about 2.5 kHz off resonance. The deviation of the intensity proportion of the septet from 1:6:15:20:15:6:1 is due to insufficiently intense rf power resulting in progressive reduction of intensity for resonances farther and farther away from the reference frequency. The Tl–H scalar coupling constant is 408 Hz in agreement with the literature value.¹¹

(c) **Chemical Shift Measurements.** The chemical and concentration shifts in the thallium(I) resonance were measured at 15.1 MHz by observing the off resonance beats in the free induction decay signal following a 90° pulse. Measurements were made by interchanging samples in the probe in a constant magnetic field locked by means of a Varian V-3506 magnet flux stabilizer. In the case of dimethylthallium nitrate the free induction signal of the thallium is highly modulated because of the scalar coupling of the thallium to six equivalent protons in the two methyl functions, thus making the counting of the off resonance beats impossible. Resonance shifts were then determined by Fourier transformation of the accumulated free induction decay signals in a constant field. A typical output of the Calcomp plotter for the Fourier transform spectrum of the thallium-free induction decay for dimethylthallium nitrate in water is shown in Figure 1. The very large downfield shift of dimethylthallium nitrate from thallium(I) nitrate by 3450 ppm was determined using a Varian V-4200B wide-line nmr spectrometer driven by a Schomandl ND30M frequency synthesizer.

(d) **Oxygenation and Deoxygenation of Samples.** The oxygenated samples were prepared in specially designed L-shaped sample tubes of 15-mm o.d. The limb with the open end was long enough to extend well outside the magnet assembly while the limb with the closed end takes the normal sample tube position in the probe. The tube was connected by pressure tubing and clamps via a couple of pressure valves to a pure oxygen source and a large mercury manometer 12 ft tall. The manometer was used to measure the pressure of oxygen up to an accuracy of 1 mm of mercury. Equilibration of oxygen dissolved for a given oxygen pressure above a solution was facilitated by a micro magnetic stirrer. At sufficient speed of rotation of the stirrer, the vortex produced in the solution was efficient enough to establish an equilibrium within 1 hr. The micro stirrer in the solution was removed by another bar magnet outside the tube to the other end of the tube remote from the solution before the sample was placed in the probe. Oxygen pressures up to 5 atm were used in the experiments. Oxygen-free samples were obtained by thoroughly purging the samples with high purity nitrogen gas and by subsequent addition of less than 10⁻⁶ M N₂H₄·H₂O to reduce any residual oxygen.

(e) **The Nmr Pulse Spectrometer.** The pulse spectrometer was a homemade one built of modular components on hand in our laboratory. Such a pulse spectrometer is very inexpensive because all of the components making up the machine are either easily available commercially at a reasonable price or are already in existence in many laboratories. The magnet assembly consists of the Varian V-2100A regulated magnet power supply and the V-4012A-HR 12-in. electromagnetic with pole caps and shim coils, field homogeneity control unit V-4365, magnet flux stabilizer V-3506, and slow-sweep unit V-K3507. Varian fixed frequency rf units V-4311 and cross-coil probes V-4331A at 7.95 and 15.1 MHz were used as radiofrequency sources and for phase-sensitive detection of signals. The setup is as shown in the block diagram in Figure 2.

Table I. Variation of the Thallium Spin-Lattice Relaxation Rates (R_1) with the Oxygen Pressure in Various Systems

O pressure, atm	$-R_1 \approx R_2$ (in sec^{-1})					
	2 M HCOOTl aq soln (I)	Solution I with 0.5 M α -phen	Solution I with 0.5 M en	0.8 M Me_2TlNO_3 aq soln	1 M HCOOTl in MeOH	
0.0	0.54	2.0	5.1	1.8	1.1	
0.2	7.8	9.5	13.5	2.5	31.0	
0.6	23.0					
1.0	37.0	40.0	41.5	3.4	147.0	
1.5	61.0					
2.0	73.0	78.0	80.0	4.5	310.0	
2.5	95.0					
3.0	108.0	115.0	120.0	5.4	450.0	
3.5	130.0					
4.0	145.0	148.0	155.0	6.4	615.0	
4.5	167.0					
5.0	190.0	190.0	200.0	7.3	730.0	

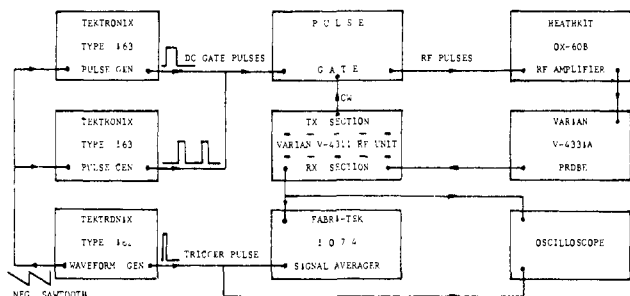
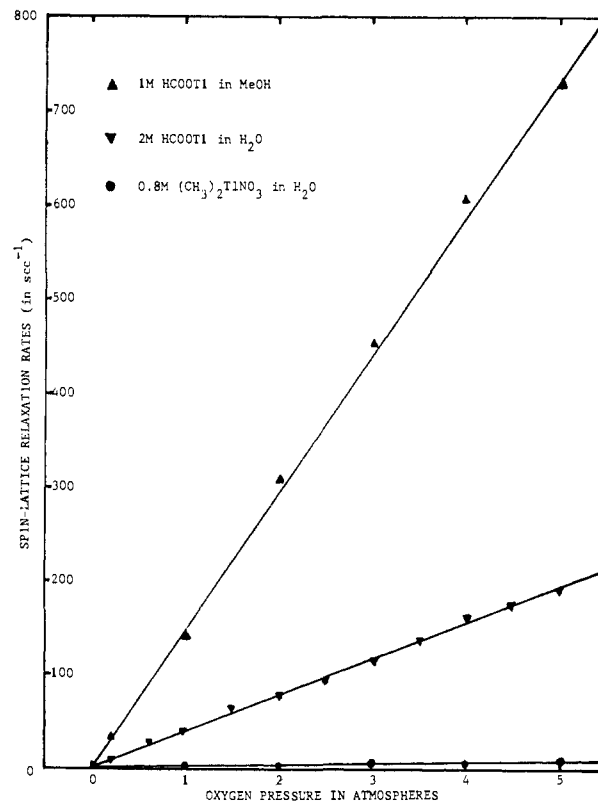


Figure 2. Block diagram of the pulse spectrometer setup.

The pulse gate was constructed using an integrated logic function circuit. Inexpensive rf gates are also readily available commercially. Gate pulses are derived from Tektronix Type 163 pulse generators controlled by a Tektronix Type 162 waveform generator which provides also trigger pulses for the signal averager or the oscilloscope. The pulsed rf is finally amplified by a Heathkit DX-60B rf amplifier before being fed to the transmitter coils in the probe. The phase detected nmr signals are displayed either directly on a Tektronix Type RM35A oscilloscope or digitized and accumulated by a Fabritek 1074 signal averager. The power supplies for the Varian rf units are derived from Lambda C-281M regulated power supply and Electronic Research Associates TR32-4 transistorized power supply.

Results and Observations

(a) **Dependence of Thallium T_1 and T_2 Relaxation on the Oxygen Pressure.** The thallium spin-lattice relaxation rate, R_1 , and spin-spin relaxation rate, R_2 , for all the systems studied and shown in Table I are approximately equal to each other within experimental errors. The rates are independent of the concentration of the solute and the nature of the anion as long as it is not paramagnetic; and for the aqueous solutions studied the thallium relaxation is not affected, within our errors, by isotopic substitution in the solvent (*i.e.*, H_2O for D_2O).⁹ The variation of the thallium spin-lattice relaxation rates, R_1 , with the pressure of oxygen above a solution in equilibrium with the gas is shown in Table I and plotted in Figure 3. Linear dependence of these rates is observed in all the systems. The oxygen effect on the Tl(I) relaxation is unusually large, about 2 to 3 orders of magnitude larger than that commonly known. The even larger effect in methanol solution, about 3.8 times that in aqueous solutions, is explainable by the greater solubility of oxygen in methanol than in water. The oxygen effect on the $(\text{CH}_3)_2\text{Tl}^+$ relaxation is considerably smaller but is still about an order of magnitude larger than that observed before

Figure 3. Spin-lattice relaxation rates *vs.* oxygen pressure.

for other nuclei. In absence of oxygen Tl(I) relaxes at different rates in aqueous and methanol solutions. The faster relaxation in methanol solution is understandable as will be suggested later on. Different complexing agents have different effects on the Tl(I) relaxation in oxygen-free aqueous solution but their effects are all comparatively small and overwhelmed by the oxygen effect in oxygenated solutions. The $(\text{CH}_3)_2\text{Tl}^+$ ion relaxes faster than the Tl^+ ion in aqueous solution as expected since the former has a lower structural symmetry. The oxygen appears to have no observable effect at all on the thallium resonance position as no shift is measurable between pressurized and unpressurized samples. Its effect on relaxation is definitely not just a pressure effect as this can be shown to be practically zero. The relaxation rate determined from a sample with oxygen suddenly released is the same as that corresponding to the initial pressure if the measurement is taken before a new equilibrium is

established between the gaseous and dissolved oxygen. Measurements have also been made on the solubility of oxygen in pure water and in aqueous solutions of thallos salts.¹² No difference in solubility was observed within an experimental error of $\pm 10\%$.

(b) Effects of Complexing Agents on Relaxation Rates R_1 and R_2 of Thallium(I) in Aqueous Solutions. The effects of the complexing agents on the thallium(I) relaxation rates differ somewhat for ethylenediamine and *o*-phenanthroline, and for the same ligand, ethylenediamine, its effect on the thallos ion depends, to a certain extent, on the nature of the counteranion (see Table II). This observation will be discussed in greater detail in the next section.

Table II. Effects of Complexing Agents on the Thallium(I) Relaxation Rates in Aqueous Solutions

Concn of complexing agent (<i>M</i>)	$R_1 \approx R_2$ (in sec^{-1})		
	Ethylenediamine		<i>o</i> -Phen
	0.5 <i>M</i> TlNO_3	1 <i>M</i> HCOOTl	1 <i>M</i> HCOOTl
0	0.54	0.53	0.53
0.25	1.1	2.8	1.2
0.5	2.0	5.4	2.1

(c) Solvent Isotope Shifts of the Thallium Resonance in Aqueous Solutions. The measurements were made at 15.1 MHz on the ^{205}Tl isotope in H_2O and D_2O solutions of the thallos salts. The solvent isotope shift, Δ , is defined as

$$\Delta = (\nu_{\text{H}_2\text{O}} - \nu_{\text{D}_2\text{O}})/\nu_{\text{ref}} \\ = (H_{\text{D}_2\text{O}} - H_{\text{H}_2\text{O}})/H_{\text{ref}}$$

where $\nu_{\text{H}_2\text{O}}$ and $H_{\text{H}_2\text{O}}$ are the resonant frequency and field for ^{205}Tl in H_2O solution, $\nu_{\text{D}_2\text{O}}$ and $H_{\text{D}_2\text{O}}$ are those in D_2O solution, and ν_{ref} and H_{ref} are the reference frequency and field. A positive value, therefore, means resonance occurring at a higher field in a D_2O solution. Table III shows the solvent isotope shifts of the thal-

Table III. Solvent Isotope Shifts of the Thallium Resonance in Aqueous Solutions

Concn (<i>M</i>)	Solvent isotope shift (in ppm)				
	CH_3COOTl	HCOOTl	TlF	TlNO_3	Me_2TlNO_3
2.0	-2.32	0.99	6.88		
1.0	1.59	3.18	7.95		
0.5	2.91	4.70	8.61	7.81	-1.19
0.37	3.23	4.91	8.73	8.24	-0.26
0.25	3.41	5.03	8.82	8.34	2.65

lium-205 resonance in aqueous solutions of a variety of thallium salts at different concentrations. It is worthwhile noting that the solvent isotope shift is dependent on the anion of the salts and varies considerably with the concentration of the solutions. For a particular salt at a certain concentration, the difference between the shifts in the H_2O and D_2O solutions gives the solvent isotope shift. A more extended study on this subject was not the main object of this work.

(d) Effects of Complexing Agents on the Solvent Isotope Shifts of the Thallium Resonance in Aqueous Solutions. Addition of complexing agents to aqueous solu-

(12) L. W. Reeves, unpublished results.

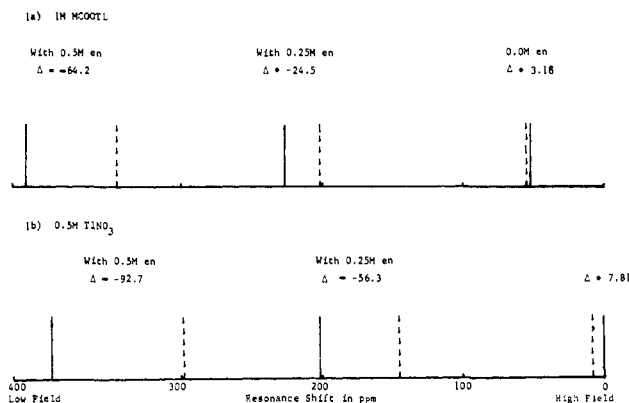


Figure 4. Effects of ethylenediamine on the thallium(I) resonances in H_2O (---) and D_2O (—) solutions.

tions of thallium(I) salts generally produces a large downfield shift of the Tl(I) resonance by hundreds of parts per million. These large shifts are, however, somewhat different for (i) different solvents, (ii) different complexing agents, and (iii) different anion and concentration of the thallos salts. Varying i but keeping ii and iii fixed leads to solvent isotope shift for a particular system, modified by a certain complexing agent. Figure 4 shows the effects of ethylenediamine on the thallium(I) resonance in thallos formate and thallos nitrate in H_2O and D_2O . The large shift is approximately proportional to the amount of the complexing agent added in each solution but the constant of proportionality differs somewhat in different solutions. Generally the downfield shift in the D_2O solution is larger than that in the H_2O solution. In both of the systems studied the solvent isotope shifts are positive in the absence of the complexing agent meaning that thallium(I) ions in D_2O resonate at a higher field. On adding ethylenediamine the solvent isotope shifts change sign and become more and more negative with increasing amount of ethylenediamine added.

Discussion

(a) Relaxation in the Absence of Oxygen. The independence of the Tl(I) relaxation in aqueous solution on (i) resonance frequency (7.95 and 15.1 MHz), (ii) isotopic substitution in the solvent (D_2O for H_2O), (iii) isotopic substitution in the resonant spin (^{203}Tl for ^{205}Tl), (iv) concentration of the solution (0.03–3.5 *M*), and (v) nature of anions is very unusual and interesting. Observations i–iii rule out, as the dominant mechanism for Tl(I) , relaxation by chemical shift anisotropy, ion-solvent intermolecular dipole-dipole interaction and exchange-modulated scalar interaction between ^{203}Tl and ^{205}Tl , respectively. Independence of the concentration and nature of the anion is also contrary to the usual relaxation behavior of ions in aqueous solutions.¹³

It is our belief that the relaxation of Tl(I) in oxygen-free aqueous solution is by a mechanism similar to that suggested for ^{129}Xe in the high-density region.¹⁴ Spin flippings are produced by a fluctuating local magnetic field associated with the rotation of the distorted-from-spherically-symmetric charge clouds during colli-

(13) C. Deverell, *Progr. Nucl. Magn. Resonance Spectrosc.*, **4**, 235 (1969).

(14) E. R. Hunt and H. Y. Carr, *Phys. Rev.*, **130**, 2302 (1963).

sions.^{15,16} This has been known as transient spin-rotation relaxation.¹⁷ Its possible role in the relaxation of ^{129}Xe was first examined by Adrian¹⁸ using Wick's theory¹⁹ of the magnetic field at a nucleus of a diatomic molecule due to rotation. More precise work along the same line was later done by Torrey¹⁵ to explain the density dependence of the chemical shift and relaxation of ^{129}Xe in xenon gas. Eliminating the sum over excited states between the expressions for Ramsey's paramagnetic shielding²⁰ and Wick's magnetic field due to rotation¹⁹ and by appropriate simplification Torrey obtained¹⁵

$$\Delta\sigma = \frac{e H_r}{3mc \omega} \quad (1)$$

where $\Delta\sigma$ is the resonance shift produced by the local field H_r due to rotation at angular velocity ω of the line of centers of two colliding xenon atoms, e and m are the electronic charge and mass, respectively, and c is the velocity of light. To compute the observed shift one has the option of using either a kinetic (time) average or a statistical (ensemble) average. Using a kinetic average the observed shift $(\Delta\sigma)_{\text{obsd}}$ can be expressed as

$$\langle\Delta\sigma\rangle_{\text{obsd}} = \frac{e H_r \tau_c}{3mc \omega \tau_0} \quad (2)$$

where τ_c is the time duration of a collision and τ_0 is the mean time between collisions.

The spin-lattice relaxation rate R_1 is then given, in terms of the observed shift, by

$$R_1 = \frac{1}{T_1} = \frac{3}{2} \left(\frac{mc\gamma}{e} \right)^2 \omega^2 \langle\Delta\sigma\rangle_{\text{obsd}}^2 \tau_0 \quad (3)$$

where T_1 is the spin-lattice relaxation time and γ is the magnetogyric ratio of the resonant spin.

An extension of eq 3 into the dense gas or liquid region has been made by Hunt and Carr¹⁴ using the simple random walk model.^{16,21} An expression, at least accurate to the order of magnitude, is obtained for R_1 as given below

$$R_1 = 36 \left(\frac{mc\gamma}{e} \right)^2 D \langle\Delta\sigma\rangle_{\text{obsd}}^2 / R_m^2 \quad (4)$$

where ω and τ_0 have been replaced by D and R_m , the diffusion constant of the liquid and the hard-sphere diameter, respectively. Equation 4 is consistent with the density-independent relaxation rate observed throughout the liquid range for xenon.

In the case of aqueous solutions of strong electrolytes and if the resonant spin is in the cation, there are three types of collisions that may have effects on the magnetic shielding and relaxation of the spin in question: (i) collisions between cations and water molecules; (ii) collisions between cations and anions, and (iii) collisions between cations and cations themselves. The effects of the collisions are in decreasing order of magnitude as listed. Water as the solvent is the most abundant

species in the system. Interactions between the cations and the solvent usually set up a solvation sphere around each ion. Thus the collisions between cations and water molecules are most frequent, and their contribution to magnetic shielding and relaxation of the spin in the cation is largest. In ii the anions have to penetrate the hydration sphere to make a direct collision with a cation. The individual effect of this type of collision is large because of the close approach on account of their opposite charges. The collisions are, however, less frequent than those in i unless in very concentrated solutions of the electrolyte. The effects of the type iii collisions are practically negligible compared to those of i and ii as the collisions between the cations are made unfavorable by their same electrostatic charges. Neglecting the effects of iii, we have for the spin relaxation in the cation

$$R_{1(\text{obsd})} = R_{1(\text{aq})} + R_{1(\text{anion})} \quad (5)$$

where $R_{1(\text{aq})}$ and $R_{1(\text{anion})}$ are transient spin-rotation relaxation contribution by cation-water and cation-anion collisions, respectively, to the spin-lattice relaxation rate of the spin in the cation and they each have a form of eq 4.

The proposed relaxation, eq 4 and 5, by transient spin-rotation interaction in the liquid phase will explain, at least qualitatively, all the above observations in oxygen-free aqueous solutions of thallos salts. By the proposed relaxation mechanism the spin-lattice relaxation rate R_1 is equal to the spin-spin relaxation rate R_2 in the extreme narrowing limit as observed. The rates are independent of the reference frequency and isotopic substitutions. From eq 5 R_1 observed is made up of two terms $R_{1(\text{aq})}$ and $R_{1(\text{anion})}$. $R_{1(\text{aq})}$, the transient spin-rotation relaxation contribution by cation-water collisions, can be considered as a constant because a change of the anion or concentration (unless comparable to 55.5 M) has negligible effect on it. Even the substitution of H_2O by D_2O does not affect $R_{1(\text{aq})}$ much except a small change explicable in terms of the difference in macroscopic viscosities of H_2O and D_2O .⁹ $R_{1(\text{anion})}$ can also be shown qualitatively to be insensitive to the change of anion and concentration. In eq 4, a change in the anion alters both $\langle\Delta\sigma\rangle_{\text{anion}}$ and R_m in the same direction and to about the same extent as larger anions give large shifts.¹³ Variation in concentration affects D and $\langle\Delta\sigma\rangle_{\text{anion}}$ in such a way so that $D\langle\Delta\sigma\rangle_{\text{anion}}^2$ is approximately constant. Thus $R_{1(\text{obsd})}$ is independent of the concentration and the nature of the anion. Hunt and Carr have also observed transient spin-rotation relaxation of ^{129}Xe in the liquid state to be independent of the density and the temperature.¹⁴

In oxygen-free solution of thallos formate in methanol the relaxation rate of Tl(I) is about twice as large as that in water.

The principal collisions now occur between methanol and thallos ion but the anion collisions are also much more frequent than in water. It is understandable that terms such as $\Delta\sigma$, τ_c , and τ_0 which form the basis of eq 4 influence the overall relaxation rate expressed as in eq 5.

Addition of ethylenediamine and *o*-phenanthroline to oxygen-free solutions of thallos salts both accelerate the Tl(I) relaxation but to a different extent. For the

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same complexing agent, the effect on the Tl⁺ ion depends also on the nature of the anion of the salt. This can be attributed to the fact that the added ligand, the anion, and the solvent molecules compete with each other for sites near the Tl⁺ ion. This situation is indeed, quite complicated, and much more extensive work is required for further elucidation.

(b) Relaxation in Oxygenated Solutions. The fact that $R_1 = R_2$ in oxygenated solutions appears to rule out a mechanism proceeding *via* a scalar coupling between unpaired electrons and the thallium nucleus. Any scalar mechanism in the case of thallium might be unusually efficient because of the very large Fermi contact interaction of the (6s) electron. The dominant mechanism appears to be an electron dipole–nuclear dipole interaction between oxygen unpaired electrons and the thallium nuclei. The magnitude of the effect, which derives from molecular oxygen in solution only, is at least 2 orders larger than any other system previously studied. The effect of nitric oxide is similar²² as is the influence of ferricyanide ion^{6,9} but the increased relaxation rate in the presence of copper(II) is considerably smaller.⁹

The solubility of oxygen and gases in general is smaller in ionic solutions than in pure water by a well documented salting out effect.²³ There are exceptions for solutions of organic ions such as sodium dodecylsulfate, potassium oleate, and tetraalkylammonium salt solutions.²³ The enhanced oxygen solubility is in these cases associated with the presence of hydrocarbon chains. The measurements of oxygen solubility in this work are not sufficiently precise to indicate a change of less than $\pm 10\%$ but certainly indicate no significant salting in of the gas. Any strong tendency for the dissolved gas to congregate at the thallium ion in preference to the bulk aqueous solution would indicate a complex and increase the solubility. If the nitric oxide and oxygen gas effect can be compared with any previous result it is the one reported by Gasser and Richards⁶ for the ferricyanide ion. In this case too, there is no chemical shift change of the Tl-205 resonance, and Gasser and Richards rule out the possibility of covalency between the ion pairs in solution.

The oxygen effect on the $(\text{CH}_3)_2\text{Tl}^+$ relaxation observed in aqueous solution of 0.8 M $(\text{CH}_3)_2\text{TlNO}_3$ is much smaller than that for Tl(I) ions in aqueous solution. However, it is still about an order of magnitude larger than that commonly observed in other nuclei.

(c) Chemical Shift Changes of the Thallium Ion. The observed concentration and anion-dependent shift of the Tl(I) resonance can be computed by the transient spin–rotation interaction model as for the Tl(I) relaxation by summing up the contribution of each type of collision. Thus we get

$$\langle \Delta\sigma \rangle_{\text{obsd}} = \langle \Delta\sigma \rangle_{\text{aq}} + \langle \Delta\sigma \rangle_{\text{anion}} \quad (6)$$

where $\langle \Delta\sigma \rangle_{\text{aq}}$ and $\langle \Delta\sigma \rangle_{\text{anion}}$ are the paramagnetic shifts of the hydrated ion relative to the “free ion” and the experimentally observed shift due to interactions with the anion, respectively, and each has the form of eq 2. This expression is identical with that of Deverell¹³ obtained by a different approach.

At this stage it may be worth noting that the reso-

nance shift derived from the transient spin–rotation interaction model is consistent with that derived from the Kondo–Yamashita theory²⁴ of chemical shift which is based on the short range repulsive forces (overlap effects) between the ions originally in alkali halide crystals.

The anion, concentration, and solvent dependence of the chemical shift is quite common in all electrolyte solutions.¹³ The observed shifts in the thallium resonances are, however, another order of magnitude larger than the largest shift observed in the alkali metals. The thallium(I) ion has a large temperature-independent paramagnetism and polarizability. The observed shift of the fluorine-19 resonance from isotopic substitution in the solvent from light to heavy water²⁵ has been interpreted in terms of alterations in the vibrational energy of the hydrated fluoride ion, which leads to a change of the average excitation energy occurring in the paramagnetic term of the nuclear magnetic shielding constant in Ramsey’s formula. The solvent isotope shift observed is insensitive, within a few per cent, to changes in the salt concentration and in the nature of the counter ion. This leads to the conclusion that the effect is primarily due to replacement of H₂O by D₂O in the solvation shell of the fluoride ion. In our present case of the thallium resonance the situation is quite different. The observed solvent isotope shift is very concentration-dependent and differs considerably from one anion to another. This is probably due to the instability of the solvated thallium ion and the differential penetration of the solvation sphere by the different anions. If the penetration of the solvation sphere by an anion produces a downfield shift (from concentration-dependent resonance shift measurements) the hydration sphere made up of D₂O is more easily penetrated than that of H₂O. Thus for the thallium resonance a complete study of the solvent isotope shift has to include two complete concentration shift measurements in two isotopic substituted solvents for each salt. Such studies are still lacking.

The approximate proportionality of the thallium shift observed on the amount of the complexing agent added can be accounted for using the same proposed model for the dependence of the shift on anion concentration by adding a third term to eq 6. Thus

$$\langle \Delta\sigma \rangle_{\text{obsd}} = \langle \Delta\sigma \rangle_{\text{aq}} + \langle \Delta\sigma \rangle_{\text{anion}} + \langle \Delta\sigma \rangle_{\text{ligand}} \quad (7)$$

where $\langle \Delta\sigma \rangle_{\text{ligand}}$ is the paramagnetic shift resulting from interaction between the thallium ion and the ligand added and has a form of eq 2. This last term is expected to be proportional to the concentration of the ligand as is required by eq 2. The different effect of the complexing agent on the Tl(I) shift with different thallous salts is interpreted as the differential relative strength of interaction of the ligands (*i.e.*, the anion and the added complexing agent) with the Tl⁺ ion. From the two systems studied, the formate ion appears to interact more strongly than the nitrate ion with the Tl⁺ ion. Thus when ethylenediamine is added the formate competes more efficiently than the nitrate with the strong complexing agent and renders

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the effect of the added ligand slightly smaller. H₂O also competes more efficiently than D₂O with ethylenediamine in the interactions with the TI⁺ ion; thus the effect of the added ligand is somewhat smaller in the H₂O solution than in the D₂O solution resulting in the

change in sign of the solvent isotope shifts as ethylenediamine is added.

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A Nuclear Magnetic Resonance Study of the Conformations of Six-Membered Chelate Rings in Metal Carbonyl Complexes of Di(tertiary arsines)

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Abstract: The complexes $(\text{CO})_4\text{MAs}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{R})\text{CH}_2\text{As}(\text{CH}_3)_2$ (R = H, CH₃, C(CH₃)₃; M = Cr, Mo, and W, but not all combinations) which contain six-membered chelate rings were prepared and their nuclear magnetic resonance spectra investigated. In order to solve the spectra it was necessary to prepare selectively deuterated analogs. When R = H the rings are undergoing fast conformational inversion between symmetric chair forms. When R = C(CH₃)₃ the rings are locked in a chair conformation with R in an equatorial position.

Numerous conformational analyses on carbocyclic and heterocyclic six-membered ring systems have been documented and reviewed in the literature.² Recently, there has been an interest in the stereochemistry of metal complexes containing six-membered chelate rings.³⁻¹⁵ In contrast to the carbocyclic systems that have only a tetrahedral arrangement of atoms, a site exists that can have a square planar or octahedral configuration, introducing interactions not formerly encountered.

Although X-ray studies give conformations of metal complexes in the solid state, it is apparent that the structures may be distorted by such factors as intermolecular hydrogen bonding and crystal packing.^{3,16} Furthermore, since most chemical reactions are carried

out in solution, it is important to establish conformations in this state. We have initiated a program of nuclear magnetic resonance studies directed toward elucidating the effects of such factors as ring size, ring substituents, central metal size, and central metal geometry, on chelate ring conformations. We have chosen the nmr method because of its unique ability to give the desired information provided that the ligands are suitably designed.

The study of di(tertiary arsine) chelate complexes of metals for the investigation of factors influencing conformation in solution has some advantages over the use of the more conventional diamine-metal compounds. With the latter, one is hindered by the necessity of deuterating the N-H bonds when present and by the commonly encountered need to use such solvents as D₂O and DMSO-*d*₆, with high dielectric constants and hydrogen bonding and complexing capabilities.¹⁷ Furthermore, the possible broadening resulting from the coupling of the proton nuclei with the nitrogen atoms is obviated with the use of diarsine complexes.

There also exists a distinct simplification in the study of six-membered rings as opposed to the much studied five-membered ring systems.^{3,16} Whereas in the latter a number of conformers can have quite similar energies, it has been calculated¹⁸ that, in octahedral systems, the symmetric chair form of the six-membered ring is the highly favored configuration relative to the symmetric

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(17) While studies in these media can produce interesting results such as the apparent axial preference of the hydroxy and chloro groups in the platinum complexes of the diamine H₂NCH₂CHXCH₂NH₂ (X = OH, Cl)⁴ (which contrasts with the equatorial preference of those groups in cyclohexane derivatives), it seems important to first establish conformational preferences in less polar solvents using spectra of well-defined complexes. A further necessity is that the spectra must be of a quality to allow complete and unambiguous assignments to be made.

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