JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 97, NUMBER 11 MAY 28, 1975

Solvent Dependence of the ^{205}Tl(I) Nuclear Magnetic Resonance Chemical Shift

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Contribution No. 3359 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received July 22, 1974*

Abstract: The solvent dependence of the ^{205}Tl nmr chemical shift of the thallous ion is over 2600 ppm. The chemical shift is discussed in terms of changes in the site symmetry of the Tl^+ ion. The Ramsey equation is used to estimate the extent of orbital hybridization resulting from this change of symmetry. The effect of the dielectric constant and basicity of the solvent on the chemical shift is discussed. A limited substituent effect is found for the chemical shift when substituted pyridines are used as solvents. A linear correlation of the chemical shift with the uv absorption wavelength is found in methanol when the anion concentration is varied over a moderate range. Because of the sensitivity of the chemical shift to the nature of the environment of Tl^+, the chemical shift should be a powerful probe of the function of monovalent ions in biological systems.

In recent years, the use of the thallous ion as a probe of biological systems has received much attention in the literature.[1-5] Changes in the electronic absorption spectrum have been suggested as one means of investigating the role of the thallous ion in these systems[2] and ^{205}Tl NMR has been shown to be another.[3] Elsewhere, we report the results of our investigation of electronic absorption spectroscopy as a probe of the environment of Tl^+.[6] In this paper we report the sensitivity of the solvent dependence of the chemical shift and describe this dependence in terms of the change in the Tl^+ site symmetry. A preliminary account of this work has been published.[7]

The solvent dependent chemical shift for ^{205}Tl is over 2600 ppm (vide infra). In comparison, the known solvent dependent shift for ^{7}Li is only 5 ppm,[8,9] for ^{23}Na it is only 23 ppm,[10-12] and for ^{133}Cs it is only 120 ppm.[13] Previously reported ^{205}Tl anion dependent chemical shift investigations involved primarily aqueous solutions of thallous salts.[14-16] The greater sensitivity of the thallous chemical shift to the environment of the ion makes it a better probe than the alkali metal ions of subtle changes in that environment.

A large number of enzymes have been found to have an absolute requirement for monovalent ions.[17,18] Of the ones showing a requirement for K^+, four have been found to be activated by Tl^+. Kayne determined the number of monovalent binding sites in rabbit muscle pyruvate kinase through substitution of Tl^+ for K^+ and also found Tl^+ to activate yeast pyruvate kinase and AMP aminohydrolase.[4] Williams found that Tl^+ activated 1,2-propanediol dehydrase.[2] Krasne and Eisenman have used Tl^+ to investigate the type of ligand groups responsible for binding ions in biological ion carriers.[5]

The chemical shift is described by the Ramsey shielding formula[19] which has been separated into three independent contributions to the shielding tensor,[20] eq 1, where σ_d is the shielding of the nucleus by electrons in the ground state, σ_p

$$\sigma = \sigma_d + \sigma_p + \sigma_o \tag{1}$$

is the deshielding caused by the mixing of excited states and the angular momentum associated with them into the ground state, and σ_o is remote shielding arising from distant atoms. Unless one is considering proton shifts, σ_o can be ignored. For the heavier nuclei, σ_p is so much larger than σ_d that the latter term can be ignored.[21] This will be especially true for a single ion in the absence of covalent interactions. The σ_p term is amenable to analysis based on the decrease in site symmetry of the Tl^+ ion and the average ionic excitation energy (vide infra). The symmetry of the solvated ion can be changed by anion penetration of the solvation sphere or by changes in the geometry of the solvation sphere when the solvent is varied. Our analysis of the solvent dependence of the ^{205}Tl(I) chemical shift is based on these ideas.

Experimental Section

NMR chemical shifts were obtained using an HR-60 spectrometer operating at a fixed frequency of 32.082 MHz. The magnetic field was approximately 13,060 G and was varied by sweeping the super stabilizer with a slow sweep unit. NMR tubes (15 mm o.d.) were spun by means of a homemade precision spinner. Spectra were recorded on a strip chart recorder with the instrument operating in center band mode. Modulation of the center band could be varied using an audio oscillator and was usually about 2500 Hz. Both high-field and low-field sweeps were recorded in order to correct for field drift and the average deviation for the shifts obtained in this manner varies from 0.1 to 0.4% of the measured shift.

A 5 mm o.d. degassed, sealed, NMR tube containing a 5.00 *M* aqueous solution of TlCOOH was used as an external reference. It was held in place concentric with the large tube by a Teflon plug. The chemical shift was calculated using this reference sample and

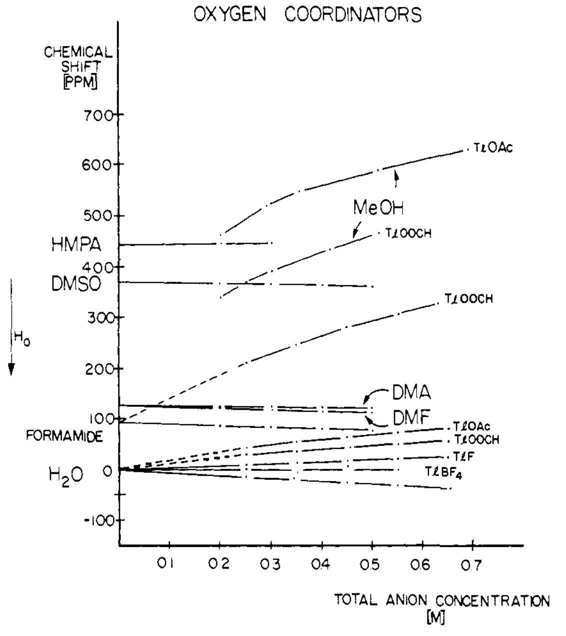

Figure 1. The chemical shift vs. the total anion concentration for the solvents that coordinate via an oxygen atom. Unless labeled otherwise, the anion is perchlorate.

the side band separation. In order to make a uniform chemical shift scale more accessible to other workers, we report the chemical shifts using the infinite dilution extrapolated value of the anion dependence of the chemical shift in water as zero. Downfield shifts are positive. Line widths at half-height without spinning were approximately 60 Hz; peak widths of about 10-15 Hz were observed with spinning.

Thallium salts were obtained commercially and were recrystallized and dried before use. Sodium salts were dried and used without further purification. Organic solvents were freshly dried and distilled before use; water was distilled and deionized. No special attempts were made to exclude atmospheric moisture during sample preparations.

Results

Thallium Shifts in Pure Solvents. The solvents that were investigated can be separated into those that normally coordinate a cation through an oxygen atom and those that normally coordinate through a nitrogen atom. Figure 1 shows the shift in the oxygen coordinators as a function of anion concentration. Figure 2 shows the anion dependence of the shift in the nitrogen coordinators. These shifts are plotted versus total anion concentration. The thallous ion concentration is constant at either 0.20 or 0.25 *M* while the anion concentration is varied by adding the sodium salt of the anion. It can be easily seen that the ClO_4^-, BF_4^-, and F^- anions have a linear influence on the chemical shift. The shift dependence on the acetate and formate anions is curved at low concentrations but becomes linear at much higher concentrations. Because of the linear nature of the anion dependence for the former group, a least-squares linear regression of the shift to zero anion concentration was performed. These extrapolated shifts are unique for each solvent. The three extrapolations in water yielded the same value within 1 ppm.

For the perchlorate ion in water, the infinite dilution curve (i.e., the plot of concentration of $TlClO_4$ vs. shift) and the curve in Figure 1 have the same slope and intercept. In DMSO, the slopes are different but the intercepts are the same within experimental error. The above curves are linear in water to 0.05 *M* and in DMSO to 0.10 *M*, the limit of observability in these solvents.

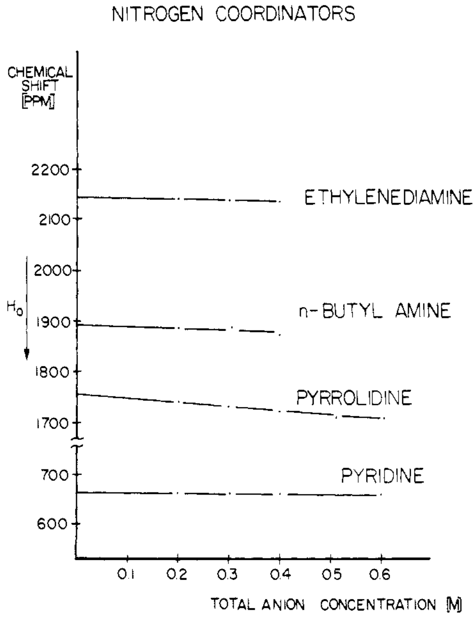

Figure 2. The chemical shift of $TlClO_4$ vs. the total anion concentration for solvents that coordinate via nitrogen atom.

Table I. Selected Solvent Properties and Experimental Chemical Shift Values

Solvent	Dielectric^{a} constant	pK^{b}	Molar polarizability^{c}	Shift^{d}
Ethylenediamine	14.2^{e}	6.84 10.96	54.4	2147 (0.90)
n-Butylamine	5.3^{e}	10.64	56.4	1896 (6.33)
Pyrrolidine	8.30^{e,f}	11.3^{g}	59.2	1757 (5.00)
Pyridine	12.3	5.28^{g}	63.6	664 (1.65)
HMPA	30^{b}		158	443^{h}
DMSO	46.7^{b}	−2.78^{g}	66.6	369 (0.25)
DMF	36.7^{b}	−0.01	71.4	126 (0.52)
DMA	37.8^{b}	−0.39^{g}	86.0	126 (1.00)
Formamide	111.0^{b,e}	−0.48	38.6	96 (1.00)
Water	78.5	7.00	17.3	0 (1.24)
Methanol	32.6	−1.5	37.0	
Pyrrole	7.5^{e}	−4.4^{g}	47.5	−505^{h}

[a] A. A. Maryott and E. R. Smith, *Natl. Bur. Stand. (U.S.), Circ.*, No. 514 (1951). Dielectric constants, unless otherwise noted, are at 25°. [b] J. A. Riddick and W. B. Bunger, "Organic Solvents", "Techniques of Chemistry", Vol. II, A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1970. [c] Calculated from: $P_M = [(\epsilon - 1)/(\epsilon + 2)](M/\rho)$. [d] Shifts are obtained by a least-squares linear regression to zero anion concentration and are in units of ppm from water; a downfield shift is positive; standard deviation from the mean for the extrapolated shift obtained from the fit is given in parentheses. [e] Dielectric constant at 20°. [f] F. Buckley and A. A. Maryott, *Natl. Bur. Stand. (U.S.), Circ.*, No. 589 (1958). [g] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution: Supplement", Butterworths, London, 1972. [h] Insufficient data for a least-squares fit.

Table I lists the extrapolated values of the chemical shift for the different solvents that were studied. Selected solvent properties and the standard deviation from the mean for each extrapolated shift are also listed. The most striking feature of the solvent dependence of the chemical shift is the 2600-ppm range. Another important feature of the shifts is the separation into two regions, one of nitrogen coordinators and one of oxygen coordinators. With the sole exception of pyrrole, we have found no overlap between them. Methanol cannot be placed properly in the table since the salts of anions with a linear influence are not sufficiently soluble; however, there is reason to believe it lies below water (vide infra).

In an effort to determine the effect of solvent basicity on the Tl^+ chemical shift, a series of methyl-substituted pyridines was used as the solvent. The second and fourth columns of Table III show the p*K*'s and chemical shifts for the

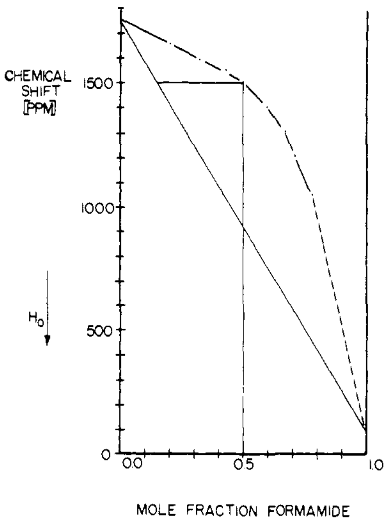

Figure 3. Mole fraction dependence of the chemical shift for a binary mixture of pyrrolidine and formamide.

compounds studied. There is no correspondence between the shift and p*K*. However, we have found a limited correspondence between the type of substitution and the shift (vide infra).

Thallium Shifts in Binary Mixtures. The preferential solvation of the thallous ion was investigated for several binary mixed solvent systems using the NMR chemical shift. Figure 3 shows a plot of the chemical shift versus the mole fraction of formamide for a formamide and pyrrolidine mixture containing 0.20 *M* $TlClO_4$. In this system, the shift varies through a range of over 1600 ppm. If there were equal solvation of Tl^+ by the two solvents, a linear behavior between the two shift extremes would be expected as is illustrated in Figure 3. This would mean that the solvation sphere composition is the same as the bulk solvent mixture composition. In the case of preferential solvation, the composition of the solvation sphere can be estimated by comparing the experimental curve in Figure 3 to the ideal curve. For example, for the observed shift at a bulk mixture composition of $X_{form} = 0.50$, the solvation sphere composition can be found by moving horizontally to the ideal curve giving a solvation sphere composition of $X_{form} = 0.15$. The fact that the experimental curve in Figure 3 has supraideal behavior indicates that pyrrolidine competes more stongly for the solvation sphere than formamide.[22]

An example of subideal behavior is shown in Figure 4 which illustrates the shift dependence on mole fraction of water in a water and methanol mixture containing 0.20 *M* TlOAc. The shift dependence indicates that water competes better than methanol for the Tl^+ solvation sphere. For this reason, methanol was placed below water in Table I. In an attempt to correct for the difference in size of the solvent molecules, the partial molar volume fraction was tried instead of the mole fraction in plots of the type shown in Figure 4. For the formamide–pyrrolidine system, curvature in the shift dependence was reduced while the curvature for the water–methanol system was increased. It has been shown thermodynamically that the mole fraction is the correct function to plot.[23]

The point on the curve midway between the shift extremes has been termed the "iso-solvation" point,[24] i.e., the point where the solvation sphere mole percent is 50. Iso-solvation values greater than and less than 50 correspond respectively to supra- and subideal behavior. For the formamide–pyrrolidine system the iso-solvation value is 80 mol % formamide and for methanol–water the value is 15 mol % water.

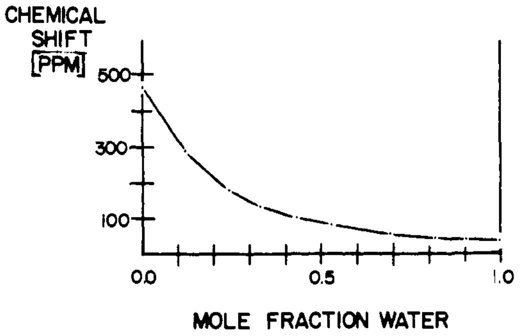

Figure 4. Mole fraction dependence of the chemical shift for a binary mixture of methanol and water.

Discussion

Investigations of the effect of solvent on the chemical shift for the alkali metal ions usually involved an attempt to correlate shift with some bulk solvent property or some measure of solvent polarity. ^7Li solvent dependent shifts were described in terms of Kosower's *Z* parameters for aprotic solvents.[8] ^{23}Na shifts were correlated with the solvent p*K*[10] and with Gutmann's donor numbers.[12,25] In contrast, we have found no simple correlation of the solvent dependence of the Tl^+ chemical shift with measures of solvent polarity such as Kosower's *Z* parameter[26] or with measures of solvent basicity such as p*K*, Gutmann's donor numbers,[27] or Drago's *E* and *C* numbers.[28]

Ion pairing has been proposed as a possible shift mechanism for ^7Li,[9] ^{23}Na,[12,25] and ^{133}Cs.[13] Because Li^+ and Na^+ have quite small ionic radii compared to Tl^+ or Cs^+, it might be expected that solvation would be more important in determining the shift. Cs^+ and Tl^+ have larger ionic radii, and since they are less strongly solvated, ion pairing would be expected to be more important, especially in nonaqueous solvents with low dielectric constants. Since overall shift ranges increase with increasing atomic number, Tl^+ should be the most sensitive of the four to the extent of ion pairing that occurs in solution.

Site Symmetry and the Ramsey Equation. The chemical shift can be explained in terms of changes in the electronic distribution of the Tl^+ by the Ramsey shielding formula. As previously mentioned, this shielding expression can be divided into three contributions. Only σ_p is important (vide infra). Schneider and Buckingham[21] developed an "atom in a molecule" model and used it to calculate the possible range of variation of σ_d and σ_p for Tl^{3+}. For σ_p, they obtained the following expression.

$$\sigma_p = -\frac{e^2 h^2 L(L+1)}{12\pi^2 m^2 c^2 \Delta E}\langle\psi_0|r^{-3}|\psi_0\rangle \qquad (2)$$

By evaluating the r^{-3} expectation value in terms of the effective atomic number, they obtained

$$\sigma_p = -7.67 \times 10^{-16}\frac{(Z_0 Z)^{3/2} L(L+1)}{n^3 l(l+1)(l+\frac{1}{2})\Delta E} \qquad (3)$$

where for Tl^+, $Z_0 = 5.35$, $Z = 81$, $n = 6$, $l = 1$, and ΔE is in ergs. With eq 3, it is possible to calculate the total shift range in parts per million due to σ_p.

Orgel[29] has explained the magnetic susceptibility and chemical shift of ions with $d^{10}s^2$ configuration in terms of extensive mixing of $d^{10}sp$ and $d^{10}p^2$ configurations into the ground state due to a decrease in the symmetry of the environment. When the symmetry is less than cubic, this s–p mixing in noncentrosymmetric environments can be described as

$$\psi_0 = \alpha\psi_s + (1 - \alpha^2)^{1/2}\psi_{p_z} \qquad (4)$$

Table II. Calculated Hybridization of Tl^+

Solvent	Absorption[a] wavelength	$(1 - \alpha^2)$[b]
Ethylenediamine	2375	0.494
n-Butylamine	2356	0.449
Pyrrolidine	2432	0.409
HMPA	2373	0.162
DMSO	2435	0.114
DMA	2481	0.0963
Formamide	2370	0.0949
Water	2128	0.0848

[a] Wavelength in angstroms of the transition to the $^3P_1$ level arising from the d^{10}sp excited state electronic configuration of the ion pair reported in ref 6 except for water where no ion-pair absorption is observed. [b] Calculated from eq 5.

Table III. Additive Substituent Effect of Substituted Pyridines

Solvent	Exptl[a] p*K*	Δp*K*	Exptl[b] shift	Δδ
Pyridine	5.28		662	
2-Picoline	6.00	0.72	480	−182
3-Picoline	5.75	0.47	662	0
4-Picoline	6.06	0.78	758	96
		Calcd p*K*		Calcd shift
2,4-Lutidine	6.85	6.78	526	576
2,5-Lutidine	6.55	6.47	487	480
3,5-Lutidine	6.19	6.22	651	662

[a] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution: Supplement", Butterworths, London, 1972. [b] Shifts are reported for solutions 0.20 *M* in $TlClO_4$.

In order to obtain the paramagnetic contribution to the chemical shift, we substitute the quantity $4(1 - \alpha^2)$ for $L(L + 1)$ in eq 3. Substituting the other necessary quantities, we obtain

$$\sigma_p = -4.29 \times 10^{-14}[(1 - \alpha^2)/\Delta E] \qquad (5)$$

If this formalization is sufficient, then as the quantity $(1 - \alpha^2)$ varies from zero to its maximum value of 0.500 (indicative of sp hybridization), the Tl^+ chemical shift should vary through its full possible shift range.

Hafner and Nachtrieb[30] approximated the shift of the free ion (i.e., $\sigma_p = 0$) as the highest field shift observed experimentally. For the shift scale used here, the free ion value is about −390 ppm. The values of $(1 - \alpha^2)$ for the various solvents calculated from the shift data and the uv absorption wavelengths reported elsewhere[6] are listed in Table II.

Several aspects of the above discussion need to be considered in more detail. First, pyrrole, which produces a Tl^+ shift at −505 ppm, does not fall within the range of shifts that can be calculated from eq 5. This may be due to some form of specific interaction between the Tl^+ and the solvent which greatly affects σ_d such as an interaction with the π cloud of the pyrrole ring. If σ_d is not fairly constant, then eq 5 will not completely describe the change in the shift.

Second, eq 5 was derived using the assumption that only one level arising from the d^{10}sp configuration is significant in producing a paramagnetic contribution to the shift. No reasonable degree of change in the energy of that level can produce the magnitude of a chemical shift that is observed for Tl^+ in the solvents that we have examined. Therefore, we could not expect in general to find a linear correlation between the shift and the absorption wavelength as was found for ^{59}Co resonances.[31]

Third, the treatment we have used here has neglected spin-orbit coupling. In the free ion, the spin-orbit coupling constant for the d^{10}sp configuration of Tl^+ is calculated from atomic spectral data[32] to be 8182 cm^{-1}. A coupling of this magnitude cannot be ignored. Therefore, it is quite likely that in addition to a molecular or temperature independent paramagnetism that there is an actual residual paramagnetism produced by mixing electron spin from the formally triplet states of the d^{10}sp configuration intc the ground state.

Qualitative Aspects of Interactions in Solution. A Tl^+ ion in a spherically symmetric electrostatic field formed by the solvation sphere will have no paramagnetic contribution to the shielding tensor and should have a shift of about −390 ppm.[30] If anion penetration of the solvation sphere occurs, the effect on the shift will depend on the degree to which the symmetry is lowered, i.e., how much the solvent "looks" like the anion. In the case where the field strength of the anion and solvent are identical and there is no geometric distortion, the paramagnetic contribution will remain zero. A large difference between the field strengths of the anion and solvent ligands will cause extensive sp hybridization and result in a large chemical shift to low field. In mixed solvent systems, a Tl^+ ion possessing two different types of solvent molecules in the solvation sphere will experience sp hybridization to the extent that the solvent field strengths are dissimilar.

The hybridization of Tl^+ caused by a nonspherically symmetric solvation sphere is not related to any single bulk property of the solvent. The thallous ion has a molar polarizability of 9.2.[33] Pearson classifies Tl^+ as a soft acid.[34] The ion is not large enough to be a solvent structure breaker and should lack specific interactions such as hydrogen bonding or covalent interactions. The main solvent-cation interaction should be ion dipole in nature, which will vary with the dielectric constant of the solvent.[35] The main effect of the solvent on cation-anion interactions is its ability to shield the cation from the charge of the surrounding anions and the thickness of the solvation sphere. The former may be related to the bulk dielectric constant of the solvent, although there certainly is a saturation of the dielectric effect under these conditions. The latter is probably related to solvent size.

The dielectric constant of the solvent has an important physical effect on the chemical shift but is not the only important factor as is shown by a plot of $(\epsilon - 1)/(\epsilon + 1)$ of the solvent[36,37] versus the thallium chemical shift for the oxygen coordinating solvents (Figure 5). Although the agreement found here is as good as that found elsewhere for protons,[36] it is not sufficiently good to provide a one-parameter characterization of the shift. Furthermore, the scatter is much more severe for the nitrogen coordinating solvents since they are much stronger bases and their dielectric constants are lower. However, their basicities as measured by p*K* values do not correlate with the shifts. Whether a combination of these two or other bulk properties will be successful in characterizing the shifts is presently unknown.

Solvent Basicity and Additive Solvent Substituent Effects. In order to minimize the number of bulk properties contributing to the shift and to ascertain the importance of solvent basicity, the thallous ion chemical shift was measured using a series of substituted pyridines as the solvent. From the data listed in Table III, it is evident that there is no correlation between p*K* and the shift. However, for both the p*K* and the shift, there is a limited additive substituent effect.

Fischer et al.[38] found a linear correlation between Taft's inductive substituent constant, σ^0,[39] and the p*K* value for a series of substituted pyridines. The change in p*K* between any substituted pyridine and pyridine will therefore be directly proportional to the change in σ^0 between the substituted pyridine and pyridine. Since the σ^0 of pyridine is 0.00,

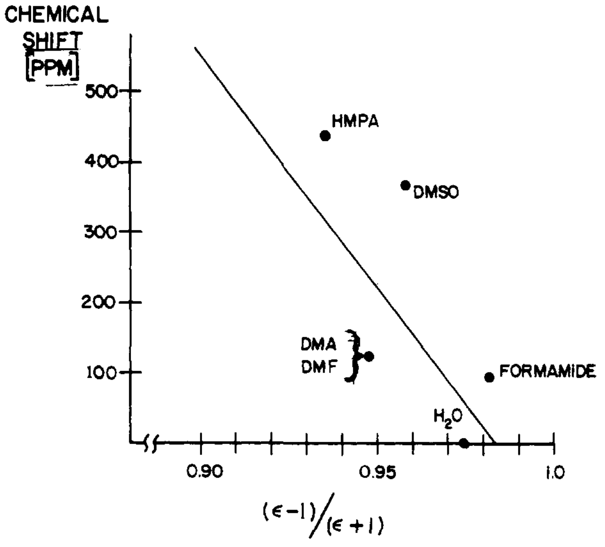

Figure 5. Plot of the chemical shift vs. a function of the dielectric constant for the oxygen coordinating solvents illustrating the failure of the dielectric constant to adequately characterize the shift.

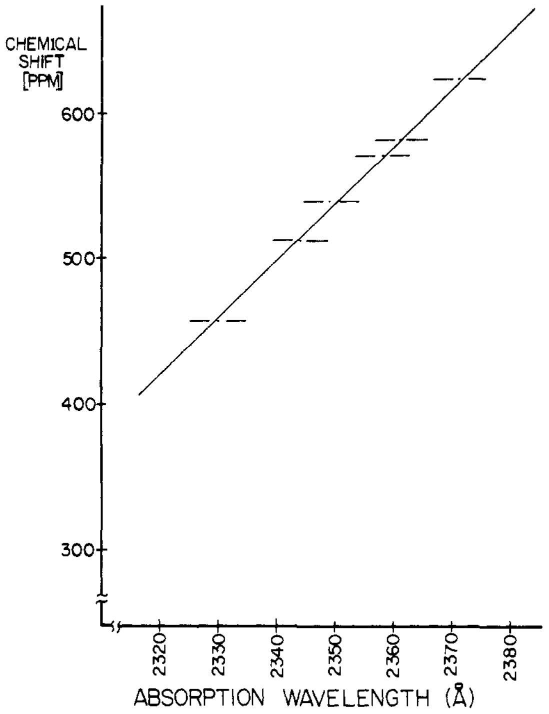

Figure 6. Correlation of the anion dependence of the chemical shift with the anion dependence of the electronic absorption wavelength for TlOAc in methanol.

the change in pK will be directly proportional to the σ^0 of the substituted pyridine. After the ΔpK values for different substituents and positions have been calculated, then, similar to the assumption that σ^0 values are additive, the pK for polysubstituted pyridines can be calculated by adding the appropriate ΔpK values. The success of this method indicates that the effect of substituents on the ionization of benzoic acid and on the basicity of pyridine are the same. The calculated and experimental pK's for several substituted pyridines are listed in the second and third columns of Table III.

Consider the analogous process for Tl^+ chemical shifts when the solvent is a substituted pyridine. If $\Delta\delta$ is defined as the shift difference between Tl^+ in the substituted pyridine and Tl^+ in pyridine, then substituent $\Delta\delta$ values can be found for each combination of substituent and position. By simply adding $\Delta\delta$ values, the chemical shift of Tl^+ in any polysubstituted pyridine can be calculated. Solubility problems severely limit the number of substituted pyridine systems that can be investigated, but the agreement between the calculated and experimental values for three disubstituted pyridines can be seen in the last two columns of Table III. The success of this method indicates that there is definitely an inductive substituent effect on the shift but that there are other important effects (vide infra) which are included in the $\Delta\delta$ values and not in the ΔpK values. Otherwise, the $\Delta\delta$ values would correlate with the ΔpK values.

There are several results that warrant further discussion. First, the ΔpK values for the ortho and para positions are almost identical while the $\Delta\delta$ values are not. Since steric effects will not influence the pK, the discrepancy in the ortho and para $\Delta\delta$ values must be due to the steric effect of an ortho methyl group on the ability of the nitrogen to coordinate to the Tl^+. Second, the calculated shifts for 2,5-lutidine and 3,5-lutidine agree well with the experimental shifts but 2,4-lutidine causes a Tl^+ chemical shift 50 ppm to high field from where it is calculated to be. Since the experimental pK agrees quite well with the calculated pK for this compound, and since electronic effects due to the 2,4 disubstitution might be expected to influence the pK's as well as the shifts, it is quite likely that there is an increase in the steric hindrance by the ortho methyl group.

Correlation of the Anion Dependence of the Uv Absorption with the Chemical Shift. When the concentration of the anion is varied in a given solvent, ion pairing should be the predominant process in determining changes in the shift. The uv absorption spectrum of the thallous ion can be used to independently measure the degree of ion pairing.[40] As ion pairing increases, the absorption band of the ion pair increases in intensity and that of the solvated ion decreases in intensity. The measured absorption band widths are sufficiently large to be incompletely resolved, causing an apparent shift of the observed absorption to longer wavelength. The shift of the band maximum is related to the degree of ion pairing.

Changes in the chemical shift in the above system will reflect changes in the average site symmetry caused by increased ion pairing. These changes should be paralleled by changes in the absorption wavelength. As a test, we chose the system with the largest changes in the absorption wavelength and the chemical shift as a function of anion concentration: thallous acetate in methanol. As shown in Figure 6, a linear correlation is observed. The change in shift is at least ten times larger than can be accounted for simply by the change in energy in the denominator of eq 5. The percent p character increases from 16.7 to 20.3% reflecting the increase in ion pairing. The acetate ion in methanol was the only system causing sufficiently large changes in the absorption wavelength to allow this type of study.

In summary, the chemical shifts are very large and sensitive to the environment of the thallous ion. The shifts can be profitably described by a simplified form of the Ramsey equation. No single bulk property of the solvents adequately characterizes the shifts.

Acknowledgment. We gratefully acknowledge the National Science Foundation for support of this work.

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Magnetic Resonance Studies. I. Investigation of Phosphorus Compounds by ^{13}C and ^{31}P Nuclear Magnetic Resonance for Phosphonium Salts Containing Saturated Groups

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Received July 26, 1974

Abstract: It is found that the dominant effects observed for ^{13}C chemical shifts are also operative in the ^{31}P chemical shifts of alkyl substituted triphenylphosphonium salts. In this study β and γ effects are established in the ^{31}P NMR of the title compounds; steric effects are also evaluated in light of perturbations of the ^{31}P and ^{13}C chemical shifts. The influence of the triphenylphosphonium group on the ^{13}C chemical shifts for several types of alkyl groups including cycloalkanes is discussed. It is found that there is a relationship between phosphorus–carbon nuclear spin coupling and the hybridization of the carbon. Electronegativities of the substituents are also found to be reflected in ^{31}P–^{13}C coupling.

There have been few studies of the effect of the phosphonium substituent on ^{13}C chemical shifts.[1,2] Also structural and electronic effects on phosphorus–carbon nuclear spin coupling have not been well understood. In this study one substituent to phosphorus is varied in a systematic manner. By these minor structural variations the influence of phosphorus on ^{13}C chemical shifts and ^{31}P–^{13}C couplings can be examined.

The value of ^{31}P NMR for establishing structures of phosphorus containing molecules has been well documented.[3-5] However, the influence of the electronic environment on ^{31}P chemical shifts is not entirely clear. Totally empirical relationships have been developed which allow an accurate prediction of chemical shifts for phosphines, phosphine oxides, and phosphonium salts.[6] These relationships allow predictions of ^{31}P chemical shifts with a fair degree of accuracy; however, they do not clarify the mechanisms by which minor structural changes affect shifts in ^{31}P NMR. Quin and Breen[7] have shown that tetraalkylphosphonium salts exhibit α, β, and γ methyl substituent effects. They suggested that the factors influencing ^{31}P chemical shifts might have the same basis as those affecting ^{13}C NMR. It is interesting to note that the two theories of ^{31}P chemical shifts do not account for the β and γ substituent effects. For example, in going from $Me_4P^+I^-$ (25.3 ppm) to $Et_4P^+I^-$ (40.1 ppm) a 14.8 ppm decrease in shielding is observed.[8,9] Purdela's theory of ^{31}P chemical shifts is related only to changes in the bond angles around phosphorus,[10] and since all of the C–P–C bond angles in these two phosphonium salts must be tetrahedral because of symmetry, this theory cannot possibly account for the change in chemical shifts. Utilization of the computer program for the Van Wazer–Letcher theory of ^{31}P chemical shifts[11] predicts chemical shifts for Me_4P^+ of 31.3 ppm and Et_4P^+ of 29.3 ppm. In other words, a 2 ppm increase in chemical shift is predicted on going from $Me_4P^+I^-$ to $Et_4P^+I^-$, whereas a 14.8 ppm downfield shift is observed. The Van Wazer–Letcher approach has also been criticized because unrealistic assumptions must be made to deal with steric perturbations on ^{31}P chemical shifts for dioxaphosphorinanes.[12] In the present study factors influencing ^{31}P chemical shifts, particularly those of steric origin, are examined for a series of alkyl substituted triphenylphosphonium salts.

Results and Discussion

The results for the ^{31}P chemical shifts for compounds having the general structure Ph_3P^+–R X^-, where R is a saturated alkyl group and X is a chloride, bromide, or iodide anion, are presented in Table I. It should be noted that the counteranion has little, if any, influence on the ^{31}P chemical