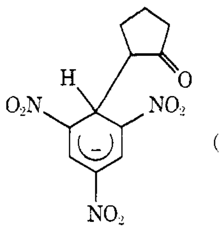
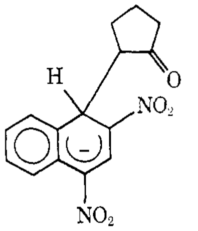
cyclopentanone + TNB + NEt$_3$ $\longrightarrow$  (8)

7

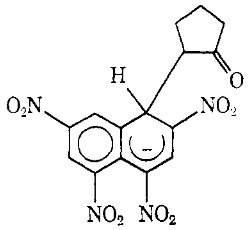
$\Delta H_8 = -27.2$ kcal

cyclopentanone + DNN + NEt$_3$ $\longrightarrow$  (9)

8

$\Delta H_9 = -6.2$ kcal

cyclopentanone + TNN + NEt$_3$ $\longrightarrow$

 (10)

9

$\Delta H_{10} = -28.2$ kcal

4 + cyclopentanone $\longrightarrow$ **8** + acetone

$$\Delta H_{11} = -6.2 - (-2.3) = -3.9 \text{ kcal} \quad (11)$$

6 + cyclopentanone $\longrightarrow$ **9** + acetone

$$\Delta H_{12} = -28.2 - (-24.2) = -4.0 \text{ kcal} \quad (12)$$

5 + cyclopentanone $\longrightarrow$ **7** + acetone

$$\Delta H_{13} = -27.2 - (-5.1) = -22.1 \text{ kcal} \quad (13)$$

The second bracketed quantity can be evaluated from literature data[50] as -3 kcal/mol if it is assumed that the heats of solution of the two ketones in DMSO are comparable. With this assumption, the difference in enthalpies of formation between the acetone complexes of DNN and TNN, as well as the difference in enthalpies of formation of the cyclopentanone complexes of these two aromatics, is only about 1 kcal/mol in each case.

The situation is quite different for the competitive reaction involving TNB. Comparison of ΔH_{13} with ΔH_{11} and ΔH_{12} shows an enhanced enthalpic stability of some 18 kcal/mol for **7**. In an earlier report[28] we have commented about the unusual pmr characteristics of **7** which provided considerable evidence for some sort of interaction between the ketonic moiety and adjacent NO$_2$ groups. In that report we considered the possibility of steric repulsion of the carbon framework of the cyclopentanone ring and the adjacent NO$_2$ groups. Such a barrier may in fact result from a strong and *stabilizing* dipole attraction between the carbonyl and one of the two NO$_2$ functions. Such an explanation is supported by the unusual enthalpic stability of **7**.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Army Research Office at Durham, the National Aeronautics and Space Administration, and the National Science Foundation for support of this work.

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(50) J. D. Cox and G. Pilchen, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London, 1970.

Solvation of Ions. XXI.[1] Solvation of Potassium Cation in Nonaqueous Solvents

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Abstract: The free energies of transfer of potassium cation from water to 14 nonaqueous solvents are reported. The values are derived from measurements in an electrochemical cell assumed to have a negligible liquid junction potential and are compared with existing literature values based on the assumption that $\Delta G_{tr}(\text{Ph}_4\text{As}^+) = \Delta G_{tr}(\text{BPH}_4^-)$. The essentially electrostatic nature of its solvation allows potassium cation to be used as a model for nonspecific solvent–ion interactions. A comparison of $\Delta G_{tr}(\text{Ag}^+)$ with $\Delta G_{tr}(\text{K}^+)$ detects some specific interactions of the silver cation with solvents. *Especially noteworthy in this regard is the striking difference between* $\Delta G_{tr}(\text{Ag}^+)$ of -23.8 kcal mol^{-1} and $\Delta G_{tr}(\text{K}^+)$ of $+6.4$ kcal mol^{-1} for transfer from water to dimethylformthioamide at 25°.

As with other simple spherical univalent cations of closed electron shells, the solvation of potassium cation is best described in terms of the electrostatic interaction between the ion and polar solvent molecules, modified by the effect of the ion on solvent–solvent interactions (solvent structure). The potassium cation is "hard" in the Pearson sense,[2] having a size (r_c = 1.33 Å) intermediate between that of the very small lithium ion (r_c = 0.68 Å) and the large cesium ion (r_c = 1.67 Å). The ion–solvent interactions, of course, are modified somewhat by the effect of the ion on the solvent–solvent interactions, *i.e.*, by the solvent structure. Because covalent interactions between potassium cation and sol-

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(1) Part XX: J. W. Diggle and A. J. Parker, *Electrochim. Acta*, **18**, 975 (1973).

(2) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

vent molecules are of relatively minor importance,[3] this ion may serve favorably in modeling some of the more important nonspecific electrostatic and structural effects which influence the general solvation of cations. Thus it is of interest to determine and to interpret $\Delta G_{tr}(K^+)$, the change in the standard chemical free energy (molar scale) of potassium cation on transfer from water to a variety of other solvents at 25°.[4]

Values of $\Delta G_{tr}(Ag^+)$ for transfer of silver cation from water to other solvents have been reported previously.[5,6] It is well known that the silver cation, a Lewis acid of d^{10} electronic configuration, experiences strong specific covalent interactions with certain basic solvents[4] (*e.g.*, acetonitrile). Because potassium cation does not have specific interactions with most solvents, deviations from linearity of a plot of $\Delta G_{tr}(Ag^+)$ *vs.* $\Delta G_{tr}(K^+)$ for a series of solvents will indicate the contribution of specific ion–solvent interactions to the over-all solvation free energy of silver cation.

Several values of $\Delta G_{tr}(K^+)$ have been calculated by applying to solubility data the assumption that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$ (assumption abbreviated as TATB).[5] Solubility measurements are subject to uncertainties because of possible solvate formation, ion association in saturated solutions, and ionic strength effects.[6]

An alternative approach to solubility measurements which avoids these problems has been used in this work. This involves direct measurement of the potential of half-cell A in a particular solvent *vs.* a suitable reference

$$\begin{array}{l|l||l} K(Hg) & KClO_4 & NEt_4Pic \\ & 0.01\ M & 0.01\ M \end{array}$$
A

electrode at 25°. The half-cell consists of a dilute potassium amalgam in contact with a dilute solution of a selected potassium salt in the solvent of interest. The preferred potassium salt, when solubility permits, is the perchlorate, so that ion association is minimized. The choice of tetraethylammonium picrate as the salt bridge electrolyte is made because of the high solubility of this salt in most of the solvents studied, because of the absence of strong specific interactions between the ions and the solvent molecules, and because of the similar mobility of the tetraethylammonium cation and the picrate anion.[7]

The choice of a reference electrode to be coupled with half-cell A presents some problems. The saturated calomel electrode in water is unsuitable without prior knowledge of the liquid junction potentials between aqueous saturated KCl and 0.1 M NEt_4Pic in the various nonaqueous solvents.[8] Although the ferrocene electrode (Pt|ferrocene, 0.02 M NEt_4ClO_4|) in the same nonaqueous solvent as half-cell A would eliminate solvent junctions, its use is precluded by its instability over the extended time period required to make a potentiometric measurement.[1] However, the Pleskov electrode (Ag|0.01 M $AgClO_4$|) in the same solvent as half-cell A would overcome both difficulties.[8] Measurements on cell B in a variety of solvents S would yield values of

$$\begin{array}{l|l||l||l|l} K(Hg) & 0.01\ M\ KClO_4 & 0.1\ M\ NEt_4Pic & 0.01\ M\ AgClO_4 & Ag \\ & \text{solvent S} & \text{solvent S} & \text{solvent S} & \end{array}$$
B

$\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+)$. Furthermore, since values of $\Delta G_{tr}(Ag^+)$ (based on the TATB assumption) are known independently,[5] the values of $\Delta G_{tr}(K^+)$ based on the TATB assumption would be readily calculable.

The Pleskov electrode, however, is not the one of choice because of its susceptibility to trace impurities which interact strongly with silver cation in certain solvents.[6] It is also difficult to reproduce precisely the amalgams, so that there are variations of up to 10 mV in the potential of cell B through a series of measurements. Hence, cell C was devised for the series of measurements.

$$\begin{array}{l|l||l||l|l} K(Hg) & 0.01\ M\ KClO_4 & 0.1\ M\ NEt_4Pic & 0.1\ M\ KClO_4 & K(Hg) \\ & \text{solvent S} & \text{acetonitrile} & \text{acetonitrile} & \end{array}$$
C

In this cell, the same amalgam is streamed through the two solutions of $KClO_4$, so that there is no need to reproduce precisely or to characterize the amalgam. The streaming electrode can be designed so that the amalgam has a very short contact time with the solvent, thus minimizing errors due to corrosion of the amalgam.

An alternative to potentiometry in cells B and C is to determine $E_{1/2}(K^+)$ by polarographic techniques.[1] In principle, $E_{1/2}(K^+)$ can often be equated with $E°(K^+)$, but the polarographic method requires that the system be reversible and that there be a relatively high concentration of some supporting electrolyte with the potassium salt. This introduces complications arising from ion association and salt effects, so that the potentiometric method in cell B or C is preferred.

Experimental Section

Apparatus. The apparatus used consisted of three major parts: (1) an amalgam generating cell, (2) an amalgam receiving reservoir in which concentrated amalgams could be diluted with pure mercury, and (3) a liquid junction electrochemical cell. These components were arranged vertically to allow for gravity feed of the amalgam from one cell to that below. Each cell could be flushed simultaneously and continuously with oxygen-free dry nitrogen (see Figure 1). The cells, as well as the gas and solution delivery tubes, were constructed of Pyrex glass. Teflon taps were used throughout. A nylon Swagelok union was used for joining the amalgam generating cell to the diluting cell; Teflon Swagelok unions were used for connecting the diluting cell to the liquid junction cell. Platinum wires sealed through the glass walls of the cells served to establish electrical contact between the amalgam and external leads.

Although the basic cell design resembles that described by Bennetto and Willmott,[9] several aspects of the liquid junction cell design are of particular interest. Amalgam delivery to each half-cell was by means of 0.4-mm i.d. capillaries of 18-cm length. Contact time of the amalgam with solution was reduced to a minimum by allowing the spent amalgam to fall free of the solution into a separate waste chamber beneath each half-cell. A bridge compartment separated the two half-cells. A removable Teflon seal on each side isolated the bridge solution from the solutions in the half-cells. Electrical contact with minimal diffusion across these boundaries was achieved by having four cotton threads (0.2-mm diameter) extending through each Teflon seal (see Figure 1). In addition, each half-cell was fitted with a glass frit type bridge to allow for the measurement of the potential of either half-cell against an external reference. (Emf values for cell B were obtained in this manner.)

Materials. **(a) Solvents.** All of the solvents were dried and

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(3) U. Mayer and V. Gutmann in "Structure and Bonding," No. 12, Springer-Verlag, Berlin, 1972.

(4) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(5) Part XIX: B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, submitted for publication.

(6) R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, **94**, 1148 (1972).

(7) B. G. Cox, A. J. Parker, and W. E. Waghorne, *J. Amer. Chem. Soc.*, **95**, 1010 (1973).

(8) J. W. Diggle and A. J. Parker, *Aust. J. Chem.*, submitted for publication.

(9) H. P. Bennetto and A. R. Willmott, *Quart. Rev., Chem. Soc.*, **25**, 501 (1971).

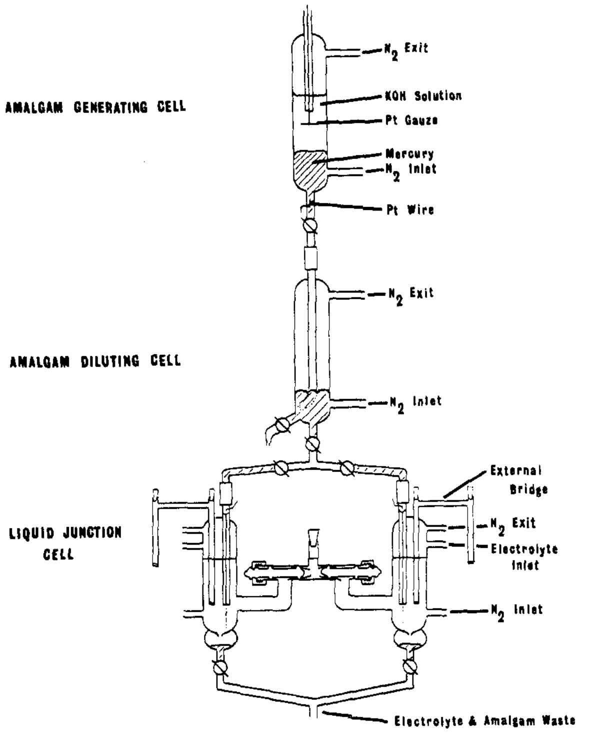

Figure 1. Amalgam cell C.

fractionally distilled at least twice before use. Karl Fischer determinations of water content and conductivity measurements were used to gauge the efficacy of the purification methods. 2,2,2-Trifluoroethanol, TFE (Eastman Kodak), was dried on potassium carbonate followed by two fractional distillations at atmospheric pressure (bp 74° at 715 Torr; water content 198 ppm; specific conductivity 3.9 × 10^{-7} ohm^{-1} cm^{-1}). Dimethylformthioamide, SDMF, was prepared from dimethylformamide (Mallinckrodt analytical reagent) and phosphorus pentasulfide (BDH laboratory reagent) according to the method of Willstatter and Wirth[10] (bp 70° at 1.0 Torr; water content 350 ppm; specific conductivity 2.32 × 10^{-6} ohm^{-1} cm^{-1}). Nitromethane, $MeNO_2$ (Ajax Unilab laboratory reagent), was dried on calcium sulfate, passed successively through columns of basic, acidic, and neutral alumina, and then refluxed over silver perchlorate for several hours. Careful distillation off the perchlorate was followed by two fractional distillations (bp 99° at 715 Torr; water content 49 ppm; specific conductivity 2.70 × 10^{-6} ohm^{-1} cm^{-1}). Ethanol, EtOH, and methanol, MeOH (both Ajax Univar analytical reagents), were dried by refluxing each with their respective magnesium alkoxide salts, prior to fractionally distilling each twice (EtOH, bp 78° at 715 Torr, water content 50 ppm, specific conductivity 4.1 × 10^{-7} ohm^{-1} cm^{-1}; MeOH, bp 64° at 715 Torr, water content 41 ppm, specific conductivity 2.64 × 10^{-6} ohm^{-1} cm^{-1}). Acetonitrile, An (Ajax Univar analytical reagent), was subjected to the benzoyl chloride–potassium permanganate treatment described by O'Donnell, Ayres, and Mann[11] (bp 80.5° at 715 Torr; water content 59 ppm; specific conductivity 1.9 × 10^{-7} ohm^{-1} cm^{-1}). Propylene carbonate, PC (Aldrich), was dried on calcium sulfate before fractional distillation (bp 96° at 3.0 Torr; water content 36 ppm; specific conductivity 1.5 × 10^{-7} ohm^{-1} cm^{-1}). Sulfolane, TMS (Eastman Kodak), was purified by the hydrogen peroxide–sulfuric acid treatment followed by granular sodium hydroxide as described by Jones.[12] Two final fractionations of powdered calcium hydride completed the procedure (bp 80° at 0.5 Torr; water content 145 ppm; specific conductivity 5.2 × 10^{-8} ohm^{-1} cm^{-1}). Formamide, $HCONH_2$ (Ajax Unilab laboratory reagent), was initially dried on calcium sulfate followed by fractional distillation. The resulting material was further purified by the method of Notley and Spiro[13] (bp 68° at 1.0 Torr; water content 627 ppm; specific conductivity 34.74 × 10^{-6} ohm^{-1} cm^{-1}). Deionized water was distilled from an all glass still. Dimethylformamide, DMF (Mallinckrodt analytical reagent), after drying over Linde 4A activated molecular sieves, was passed through a basic alumina column as recommended by Moe.[14] The product was subsequently fractionally distilled (bp 34° at 3.2 Torr; water content 207 ppm; specific conductivity 3.2 × 10^{-7} ohm^{-1} cm^{-1}). *N*-Methyl-2-pyrrolidone, NMePy (Aldrich), was dried on calcium sulfate and then twice fractionally distilled (bp 40° at 0.2 Torr; water content 200 ppm; specific conductivity 3.9 × 10^{-7} ohm^{-1} cm^{-1}). *N*,*N*-Dimethylacetamide, DMA (Aldrich), was dried on Linde 4A activated molecular sieves prior to fractionation (bp 58° at 9.0 Torr; water content 87 ppm; specific conductivity 7.1 × 10^{-7} ohm^{-1} cm^{-1}). Dimethyl sulfoxide, DMSO (Merck), was fractionally distilled after drying on calcium hydride (bp 56° at 3.0 Torr; water content 41 ppm; specific conductivity 3.7 × 10^{-7} ohm^{-1} cm^{-1}). Hexamethylphosphorotriamide, HMPT (Aldrich), was fractionally distilled without initial drying, twice fractionally crystallized (mp 7°), dried on Linde 4A activated molecular sieves, and redistilled (bp 84° at 2.0 Torr; water content 230 ppm; specific conductivity 1.9 × 10^{-7} ohm^{-1} cm^{-1}).

(b) Mercury. The mercury used for amalgam preparations was purified by ultrasonic cleaning once with Freon TF, twice with 10% nitric acid, and three times with distilled water.[15]

(c) Silver. Silver electrodes were in the form of silver wires (purity >99.99%) and were mechanically abraded before each use.

(d) Salts. Potassium hydroxide (Ajax Univar analytical reagent) was used without further purification. Potassium iodide (BDH analytical reagent) was dried *in vacuo* at 130° for 24 hr prior to use. Potassium perchlorate (Merck) was recrystallized from water and dried *in vacuo* at 135° for 72 hr. Potassium tetraphenylboride was prepared by metathesis of potassium chloride (Ajax Univar analytical reagent) with sodium tetraphenylboride (Fluka) and then recrystallized.[16] Silver perchlorate (BDH laboratory reagent) was used after drying *in vacuo* at 80° for 24 hr. Tetraethylammonium picrate was prepared by neutralizing 10% aqueous tetraethylammonium hydroxide (Eastman Kodak) with picric acid (Ajax Univar analytical reagent) in methanol. The resulting tetraethylammonium picrate was recrystallized from methanol.

(e) Gas. Nitrogen (CIG, high purity) was purified by passage over the following sequence of materials: Pyrex glass cotton, Linde 4A activated molecular sieves, soda lime, copper foil ribbons at 300°, soda lime, molecular sieves, and glass cotton.

Procedures and Measurements. Prior to each measurement the apparatus was thoroughly cleaned (successive rinses with distilled water, chromic acid, distilled water, analytical grade acetone), dried, and purged with oxygen-free dry nitrogen.

Amalgams were generated electrochemically using a Beckman Electroscan power supply. A carefully weighed quantity of mercury was placed in the upper cell of the apparatus along with an aqueous potassium hydroxide solution (containing 5–10 times excess potassium over that required for the desired amalgam concentration). With the mercury pool as cathode and the platinum gauze as anode, a constant current (140 mA) was passed and the coulombs were measured. Normally, the current was stopped when the amalgam was of the desired concentration (assuming 100% efficiency for the cathodic electron transfer), thus eliminating the need for diluting the amalgam. All amalgams were originally believed to contain 0.045% w/w potassium, but subsequent analysis revealed the cathodic electron transfer process to be only 50–80% efficient. Hence, amalgam concentrations were always less than 0.045% w/w potassium. Nitrogen flow was maintained through the cell during amalgam generation.

The two half-cells of the liquid junction cell were filled with their complements of electrolyte solutions in appropriate solvents by means of a nitrogen pressure loading system. Once within the half-cells, the solutions were purged with purified nitrogen. The bridge was filled manually, using a dropper. After the amalgam was generated and the solutions were purged with nitrogen, the streaming electrodes were set in operation by manipulating the taps to establish amalgam flow through the capillaries.

All measurements were conducted at a constant temperature of 25 ± 1°. Potentials were monitored using a Radiometer pH Meter 26 with an expanded scale facility. Potentials were recorded as soon as the amalgam was flowing, and values were stable to ±5 mV

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(10) R. Willstatter and T. Wirth, *Chem. Ber.*, 42, 1908 (1909).

(11) J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, 37, 1161 (1965).

(12) J. F. Jones, *Inorg. Chem.*, 5, 1229 (1966).

(13) J. M. Notley and M. Spiro, *J. Chem. Soc. B*, 362 (1966).

(14) N. S. Moe, *Acta Chem. Scand.*, 21, 1389 (1967).

(15) *Sci. Glassblowers Soc. Aust. J.*, 1, 12 (1971).

(16) R. W. Kunze and R. M. Fuoss, *J. Phys. Chem.*, 67, 385 (1963).

Table I. Emf (mV) of Cells B, C, and D at 25° in Solvents and Free Energies of Transfer (kcal/g-ion) $\Delta G_{tr}(M^+)$ (negl E_{1j}) Based on the Assumption of Negligible Liquid Junction in Cells C and D (Reference Solvent Acetonitrile at 25°)

$\mathrm{K(Hg)}^{b}|\mathrm{KClO_4}\ 0.01\ M,\ \mathrm{S}\|\mathrm{TEAPic}^{a}\ 0.1\ M,\ \mathrm{S}\|\mathrm{AgClO_4}\ 0.01\ M,\ \mathrm{S}|\mathrm{Ag}$
cell B

$\mathrm{K(Hg)}^{b}|\mathrm{KClO_4}\ 0.01\ M,\ \mathrm{S}\|\mathrm{TEAPic}^{a}\ 0.1\ M,\ \mathrm{An}\|\mathrm{KClO_4}\ 0.01\ M,\ \mathrm{An}|\mathrm{K(Hg)}$
cell C

$\mathrm{Ag}|\mathrm{AgClO_4}\ 0.01\ M,\ \mathrm{S}\|\mathrm{TEAPic}^{a}\ 0.1\ M,\ \mathrm{An}\|\mathrm{AgClO_4}\ 0.01\ M,\ \mathrm{An}|\mathrm{Ag}$
cell D

Solvent[a] S	$E_B(S)$, mV	$E_C(S)$, mV	$E_D(S)$, mV	$E_C(S) - E_D(S)$, mV	$E_B(S) - E_B(An)$, mV	$\Delta G_{tr}(Ag^+)$ cell D[i] (negl E_{1j})	$\Delta G_{tr}(K^+)$ cell C[j] (negl E_{1j})
TFE		267[c]	686[h]	−419		15.9	6.2
SDMF	−1.288	130[d]	−855	985	993	−19.8	3.1
$MeNO_2$		102[e]	423[h]	−321		9.8	2.3
EtOH		51[c]	243	−192		5.6	1.3
MeOH		26[f]	265[g]	−239		6.1	0.6
An	−2.281	0	0	0	0	0.0	0
PC	−2.748	−43[e]	414	−457	−467	9.6	−1.0
TMS 30°		−68[e]	288	−356		6.7	−1.6
$HCONH_2$		−120	68[g]	−188		1.6	−3.0
H_2O	−2.595	−139[f]	185[g]	−324	−314	4.3	−3.3
DMF	−2.527	−207	43	−250	−246	1.0	−4.8
NMePy		−207[e]	−26	−181		−0.6	−4.8
DMA		−235	−30	−205		−0.7	−5.5
DMSO	−2.382	−256	−152[g]	−104	−101	−3.5	−6.0
HMPT	−2.370	−320	−230[g]	−90	−89	−5.3	−7.3

[a] Pic is picrate, TEA is NEt_4, TFE is 2,2,2-trifluoroethanol, SDMF is dimethylformthioamide, PC is propylene carbonate, TMS 30° is tetramethylene sulfone at 30°, NMePy is *N*-methyl-2-pyrrolidone, DMA is dimethylacetamide, HMPT is hexamethylphosphorotriamide, An is acetonitrile. [b] Amalgam is −0.0445 wt % potassium. [c] 0.01 *M* KI was in solvent S in cell C. [d] 4×10^{-4} *M* $KClO_4$ was used in both SDMF and An in cell C. The same emf was obtained with 10^{-2} *M* $KBPh_4$ in SDMF and An. [e] 10^{-2} *M* $KBPh_4$ was in solvent S in cell C. [f] 10^{-3} *M* $KClO_4$ was used in S and in An in cell C. [g] Reference 6. [h] 10^{-3} *M* $AgClO_4$ was in the solvents in cell D. [i] Calculated from the emf of cell D. [j] Calculated from the emf of cell C.

over 5 min. As expected, the cell potential was found to be independent of the concentration of potassium in the amalgam since the same dilute amalgam, split into two streams, flowed simultaneously through the solvent in each half-cell. Effects attributable to decomposition of the amalgam were minimized by employing streaming capillary electrodes to provide a continually regenerated amalgam surface (see Figure 1).

Results

Values of E_B, E_C, and E_D, the emf's of cells B, C, and D, are in Table I. Values of $\Delta G_{tr}(K^+)$(negl E_{1j}) and

$$\mathrm{Ag}|\mathrm{AgClO_4}\ 0.01\ M,\ \text{solvent S}\|\mathrm{NEt_4Pic}\ 0.1\ M,\ \text{acetonitrile}\|\mathrm{AgClO_4}\ 0.01\ M,\ \text{acetonitrile}|\mathrm{Ag}$$
D

$\Delta G_{tr}(Ag^+)$(negl E_{1j}) for transfer from acetonitrile to a variety of other solvents are also in Table I. They were calculated as $23.1E_C$ and $23.1E_D$ kcal/g-ion, respectively (E, V), by assuming negligible liquid junction potential in these cells.[6]

If one accepts the TATB assumption that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$, then cells C and D do have a liquid junction potential E_{1j}(TATB).[1] However, E_{1j}(TATB) is virtually the same in cells C and D, because most of E_{1j}(TATB) is associated with the 0.1 *M* NEt_4Pic, acetonitrile–solvent S junction in each cell and the junctions only differ in having 0.01 *M* Ag^+ rather than 0.01 *M* K^+[7] in solvent S. That the junction is virtually the same is confirmed in Table I by the observation that $E_B(S) - E_B(An)$, for cell B, which has no liquid junction potential, is virtually the same as $E_C(S) - E_D(S)$, in those cases where data are available. Thus, either $E_B(S) - E_B(An)$ or $E_C(S) - E_D(S)$ can be used to calculate $\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+)$ for transfer of these cations from acetonitrile to solvent S. This difference is free of any assumptions.

Acetonitrile was chosen as reference solvent because E_{1j}(TATB) is small between acetonitrile and most solvents except water.[7] However, having obtained values of $(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))An \rightarrow S$ it is more convenient to convert to values for transfer from water to other solvents. Thus in Table II values of $(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))H_2O \rightarrow S$ have been calculated from $(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))An \rightarrow S$ in Table I through eq 1.

$$\begin{aligned}(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))H_2O \longrightarrow S = \\ (\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))An \longrightarrow \\ S - (\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))An \longrightarrow H_2O \quad (1)\end{aligned}$$

Values of $\Delta G_{tr}(K^+)$(TATB) for transfer from water to other solvents, based on the TATB assumption, are calculated by adding $\Delta G_{tr}(Ag^+)$(TATB), from part XIX,[5] to the values of $(\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+))H_2O \rightarrow S$ in Table II. $\Delta G_{tr}(K^+)$(TATB) *via* cells B and C are compared in Table II with those previously reported[5] from solubility measurements. The new values are believed more reliable.

Table II also contains $\Delta G_{tr}(K^+)$(negl E'_{1j}) for transfer from water to other solvents. These values assume negligible liquid junction potential in cell C and have been algebraically manipulated from data in Table I ($\Delta G_{tr}(K^+)$(negl E_{1j}) An $\rightarrow$ S − $\Delta G_{tr}(K^+)$(negl E_{1j})An $\rightarrow$ H_2O) for transfer from water.

It was not possible to apply the TATB assumption to solvation of ions in 2,2,2-trifluoroethanol (TFE) because of the instability of the BPh_4^- anion in this acidic solvent. Nor was the TATB assumption applied to solvation in dimethylformthioamide (SDMF) because of the high solubility (>0.1 *M*) of $AgBPh_4$ in SDMF. Hence, $\Delta G_{tr}(K^+)$(negl E_{1j}) was equated to $\Delta G_{tr}(K^+)$(TATB) for transfer from water both to TFE and to SDMF. This approximation is probably valid to within 1 kcal/g-ion in view of the good correspondence between $\Delta G_{tr}(K^+)$(negl E_{1j}) and $\Delta G_{tr}(K^+)$(TATB) for the majority of other solvents in Table II.

The free energies of solvation, $\Delta G_s K^+$, for transfer of potassium cation from the gas phase to solvent S are also contained in Table II. These are based on a value of

Table II. Free Energies of Transfer from Water $\Delta G_{tr}(M^+)$ (kcal/g-ion), Free Energies of Solvation ($\Delta G_s(M^+)$), and Standard Electrode Potentials (volts *vs.* nhe, H_2O) of Potassium and Silver at 25° (Assumption $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$(TATB))

Solvent[a]	$\Delta G_{tr}(K^+) - \Delta G_{tr}(Ag^+)$[b]	$\Delta G_{tr}(Ag^+)$ (TATB)[c]	$\Delta G_{tr}(K^+)$ (TATB)	$\Delta G_{tr}(K^+)$ (negl E_{lj})[f]	$-\Delta G_s(Ag^+)$ (TATB)[g]	$-\Delta G_s(K^+)$- (TATB)[g]	$E°$(Ag,S) nhe, H_2O (TATB)	$E°$(K,S) nhe, H_2O (TATB)
TFE	−2.2	(11.7)[d]	(9.5)[d]	9.5	102.8	71.1	1.31	−2.50
SDMF	+30.2	(−23.8)[d]	(6.4)[d]	6.4	138.3	74.2	−0.23	−2.64
$MeNO_2$	0.1	5.7	5.8	5.6	108.8	74.8	1.05	−2.67
EtOH	3.0	1.6	4.6	4.6	112.9	76.0	0.87	−2.72
MeOH	2.0	1.8	3.7 (2.4)[e]	3.9	112.7	76.2	0.90	−2.75
An	7.5	−5.2	2.3 (1.9)[e]	3.3	119.7	78.3	0.57	−2.82
PC	−3.2	3.8	0.6 (1.4)[e]	2.3	110.7	80.0	0.96	−2.90
TMS 30°	−0.7	−0.9	−1.6 (−1.0)[e]	1.7	115.4	82.2	6.76	−2.99
$HCONH_2$	3.1	−3.7	−0.6 (−1.5)[e]	0.3	118.2	81.2	0.64	−2.94
H_2O	0.0	0.0	0.0 (0.0)[e]	0.0	114.5	80.6	0.80	−2.92
DMF	1.9	−4.1	−2.2 (−2.3)[e]	−1.5	118.6	82.8	0.62	−3.01
NMePy	3.3	−7.2	−3.9 (−3.3)[e]	−1.5	121.7	84.5	0.49	−3.09
DMA	2.7	−5.8	−3.1	−2.2	120.3	83.7	0.55	−3.05
DMSO	5.1	−8.0	−2.9 (−2.9)[e]	−2.7	122.5	83.5	0.45	−3.05
HMPT	5.4	−9.4	−4.0	−4.0	123.9	84.6	0.39	−3.09

[a] Abbreviations as in Table I. [b] Calculated from $E_C - E_D$ in Table I after converting from acetonitrile to water as reference solvent, see text. [c] From ref 5. [d] Assuming that $\Delta G_{tr}(M^+)$(negl E_{lj}) = $\Delta G_{tr}(M^+)$(TATB), see text. [e] From ref 5, based on solubilities of potassium salts and $\Delta G_{tr}(Ag^+)$(TATB). [f] From Table I after conversion to water as reference solvent, assuming negligible liquid junction potential in cell C. [g] Calculated from a value of −80.6 kcal/g-ion for the free energy of hydration (ΔG_h) of K^+, which gives −114.5 kcal/g-ion for the free energy of hydration of Ag^+. *Cf.* $\Delta G_s(M^+) = \Delta G_h(M^+) + \Delta G_{tr}(M^+)$.

−80.6 kcal/g-ion for the hydration of potassium cation[17] and are calculated from the relationship $\Delta G_s(K^+) = -80.6 + \Delta G_{tr}(K^+)$(TATB).

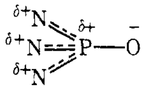
The final two columns of Table II record the standard electrode potentials, $E°$(Ag,S)(TATB) and $E°$(K,S)(TATB), of silver and potassium, respectively, *vs.* the normal hydrogen electrode (nhe) in water. These are based on the TATB assumption and are calculated from eq 2 in which M represents Ag or K and W is water.

$$E°(M,S)(TATB) = E°(M,W) + [\Delta G_{tr}(M^+)(TATB)/23.1] \quad (2)$$

Discussion

Solvation of K^+. Most of the solvents listed in Table II interact with potassium cation by means of their oxygen atoms. Exceptions are acetonitrile (An) and dimethylformthioamide (SDMF) which interact through N and S, respectively. The most strongly solvating solvents for potassium cation are hexamethylphosphorotriamide (HMPT), *N*-methyl-2-pyrrolidone (NMePy), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), formamide, and sulfolane (TMS). In a free energy sense, all solvate potassium more strongly than does water, despite the more favorable entropic contribution to the solvation free energy in water compared to that in these less structured dipolar aprotic solvents.[5] The process of transferring potassium cation from water to each of these solvents is quite exothermic,[5] in an enthalpic sense, and this outweighs any effects due to unfavorable entropies of transfer.

The strong enthalpic interaction between potassium cation and each of the solvents HMPT, NMePy, DMA, DMSO, DMF, $HCONH_2$, and TMS and the strong ordering of solvent about potassium ion is thought to be primarily electrostatic in nature. These solvents alone, of the 15 listed in Table II, contain an oxygen atom which carries extensive negative charge and which is relatively free of groups which might interfere with its structuring about the potassium cation. The phosphorus–oxygen, sulfur–oxygen, and carbon–oxygen bonds in these phosphoramides, sulfoxides, and amides have less than full double bond character; indeed, their structures in the first solvation sphere about potassium cation may well be more like I, II, and III than IV, V, and VI. The oxygens of the alcohols, water, propylene carbonate (PC), and nitromethane ($MeNO_2$) are more shielded and carry less partial negative charge than do the oxygens of the phosphoramides, sulfoxides, and amides. Thus, the former set of solvents are weaker solvators of potassium cation than the latter, although relative to the gas phase, *i.e.*, $\Delta G_s(K^+)$ (Table II), all the solvents would be classed as strong solvators. Despite substantial differences in dielectric constant, solvent structure, and solvent polarity, values of $\Delta G_{tr}(K^+)$ and $\Delta G_{tr}(Ag^+)$, *i.e.*, the transfer free energies, account for no more than 15% of the total solvation energy of these ions in solvents of dielectric constant 25–100. Electrostatic solvation as envisaged by Born[4] is still considered the major type of solvation.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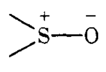
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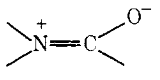
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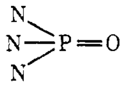
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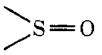
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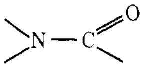
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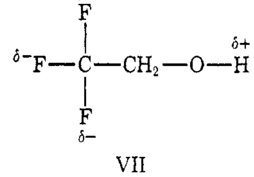
Some of the $\Delta G_{tr}(K^+)$(TATB) values deserve special comment. 2,2,2-Trifluorethanol (TFE), VII, is the weakest solvator of potassium cation of the solvents studied. Although trifluoroethanol and ethanol have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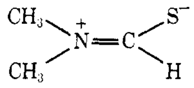
VIII

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(17) D. R. Rosseinsky, *Chem. Rev.*, 65, 469 (1965).

similar dielectric constants (26 and 24, respectively) the $\Delta G_{tr}(K^+)$(TATB) value for transfer from water to trifluoroethanol is +9.5 kcal/g-ion whereas transfer from water to ethanol is only +4.6 kcal/g-ion. The strongly electron withdrawing CF_3 group reduces the negative charge density and hence the basicity at the oxygen of trifluoroethanol, thus decreasing its ability to interact with cations.

Dimethylformthioamide (SDMF), VIII, of dielectric constant 48[18] is also a relatively poor solvator of potassium cation despite its high dielectric constant. There is considerable localized negative charge on sulfur, but this is a "soft" center in the Pearson sense.[2] According to the HSAB principle[2] the interaction between the "soft" sulfur atom of dimethylformthioamide and the "hard" potassium cation is weak. Indeed the value of $\Delta G_{tr}(K^+)$(TATB) + 8.6 kcal/g-ion for transfer "hard" dimethylformamide to "soft" dimethylformthioamide is indicative of the preference of class a cations to interact with negative oxygen, rather than sulfur, in otherwise similar coordinating solvents.

Methanol and ethanol are weaker solvators in a free energy sense of potassium cation than is water. One might expect a somewhat greater negative charge density on oxygen in the alcohols, but in water the oxygen experiences less shielding by other atoms or groups. The enthalpies of transfer favor the alcohols over water.[5] More important, though, is the more favorable entropic interaction which potassium cation has with water[5] compared to the alcohols. This favorable entropic effect arises through the unique structure of water and the structure breaking effect on this structure of forming a solvation sheath about the potassium cation. With less capacity for polymeric hydrogen bonding, alcohols have less well developed liquid structures for potassium cation to break up than does water, *i.e.*, K^+ is a strong structure maker in the alcohols and $\Delta S_{tr}(K^+)$ from water to the alcohols is negative. Thus, $\Delta G_{tr}(K^+)$ from water becomes endoenergetic, despite the more basic oxygen of the alcohols, relative to water, leading in part to an exothermic enthalpy of transfer from water to the alcohols.[5]

Comparison of K^+ Solvation and Ag^+ Solvation. It is necessary to distinguish between those ion–solvent interactions which are purely electrostatic in nature and those which are primarily of covalent character. Both types of interactions will be influenced by changes induced by the ion itself on the solvent structure (first solvation sphere effects) and by the solvent-coordinated ion on the solvent structure (second and subsequent solvation sphere effects).[5] As noted previously, potassium cation with its closed electronic shell and moderate size (r_c = 1.33 Å) is expected to respond almost exclusively to electrostatic solvation effects, whereas silver cation, as a transition metal of d^{10} electronic configuration, is expected to be capable of experiencing a variety of covalent interactions, including back-bonding to suitable ligands. Because of its smaller size (r_c = 1.26 Å) and poorly shielded nucleus, silver cation may also have stronger electrostatic interactions with all the solvents studied than has potassium ion. Such an interpretation is certainly consistent with the data in Table II; all $\Delta G_s(K^+)$ values listed are less than 85 kcal/g-ion but all values of $\Delta G_s(Ag^+)$ are greater than 100 kcal/g-ion.

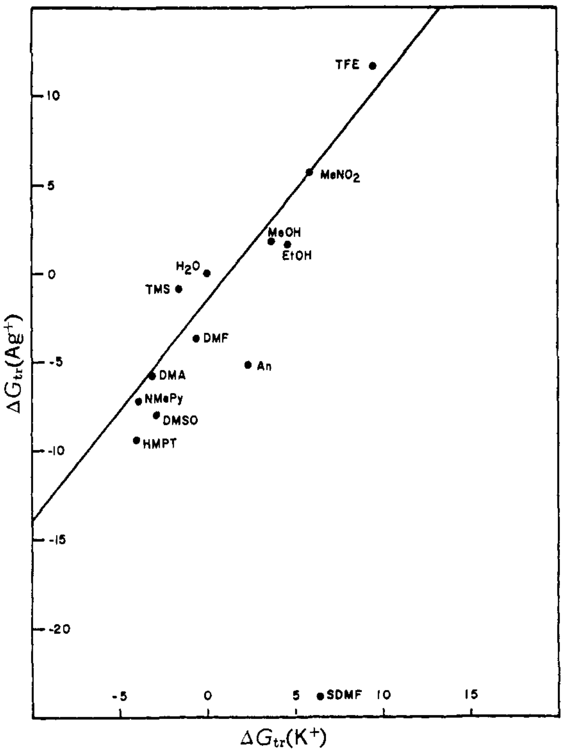

Figure 2. Plot of free energies of transfer $\Delta G_{tr}(Ag^+)$ *vs.* $\Delta G_{tr}(K^+)$ for transfer from water to other solvents at 25°. Assumption $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$.

Figure 2 is a plot of $\Delta G_{tr}(Ag^+)$(TATB) *vs.* $\Delta G_{tr}(K^+)$-(TATB). There is a quite good linear correlation between these quantities for transfer to solvents which interact through oxygen with the cations. The slope of 1.24 indicates that, as expected, silver cation responds more to solvent transfer than does potassium cation. Indeed, for all of the solvents which solvate cations through oxygen, the main factors influencing solvation of potassium and silver cations seem to be nonspecific electrostatic interactions, modified by structural effects due to solvent–solvent interactions. The electrostatic interactions are greater for silver cation than for potassium cation.

A remarkably striking illustration of the effect of covalent interactions with silver cation but not with potassium cation is seen in the position of transfer to dimethylformthioamide (SDMF), VIII, in Figure 2. The silver cation is better solvated by SDMF, *i.e.*, by 30 kcal/g-ion more than would be expected from the $\Delta G_{tr}(K^+)$(TATB) plot in Figure 2. The covalent interaction of silver with the "soft" sulfur atom of SDMF is apparently responsible for the strong solvation.

Similarly, acetonitrile, which is known to have specific covalent interactions with d^{10} cations, such as Cu^+, Ag^+, and Au^+,[4] solvates silver cation some 6 kcal/g-ion more strongly than might be expected from the Figure 2 correlation. Furthermore, solvation of the silver cation by dimethyl sulfoxide and by hexamethylphosphorotriamide is a little stronger than one might predict from Figure 2. This effect is thought to arise from weak covalent bonding or possibly the influence of the "soft" sulfur and phosphorus centers, respectively, in these two solvents, relative to water and related solvents.

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[18] J. W. Diggle and D. Bogsanyi, *J. Phys. Chem.*, submitted for publication.

Advocacy of Negl E_{1j} Extrathermodynamic Assumption. The assumption that there is a negligible liquid junction potential in cells C and D leads to values of $\Delta G_{tr}(M^+)$(negl E_{1j}) which in most cases are within 1 kcal/g-ion of the corresponding $\Delta G_{tr}(M^+)$(TATB) values. Considering the relative ease of performing experiments in cells C and D compared with the several steps, including solubilities, involved in applying the TATB assumption, the potentiometric measurements are to be recommended for semiquantitative estimates of $\Delta G_{tr}(M^+)$.

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Microwave Spectrum, Structure, and Dipole Moment of Biphosphine-4

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Abstract: The microwave spectra in the *K* and *R* bands of four isotopic species of biphosphine, P_2D_4, P_2D_3H(C), P_2D_3H(B), and P_2H_4, have been measured. The following structural parameters have been determined from a least-squares analysis of the observed moments of inertia: $r(P{-}D_1) = 1.414 \pm 0.002$ Å, $r(P{-}D_2) = 1.417 \pm 0.002$ Å, $r(P{-}P) = 2.2191 \pm 0.0004$ Å, $\angle DPD = 92.0 \pm 0.8°$, $\angle D_1PP = 94.3 \pm 0.2°$, $\angle D_2PP = 99.1 \pm 0.1°$, and ϕ(dihedral) = $74.0 \pm 2.2°$. The values for the dipole moments obtained from Stark splittings are: P_2D_4, $|\mu_c| = 0.928 \pm 0.005$ D; P_2D_3H(C), $|\mu_a| = 0.02 \pm 0.007$, $|\mu_b| = 0.15 \pm 0.02$ D, $|\mu_c| = 0.91 \pm 0.01$ D, $|\mu| = 0.92 \pm 0.01$ D; P_2D_3H(B), $|\mu_a| = 0.008 \pm 0.007$ D, $|\mu_b| = 0.92 \pm 0.1$ D, $|\mu_c| = 0.04 \pm 0.02$ D, $|\mu| = 0.92 \pm 0.01$ D. The values of the structural parameters are discussed and the conformation is compared with those previously determined for similar molecules.

The symmetry of molecules which have the general formula X_2Y_4 has been the subject of many recent studies.[1-11] The possible structures for the X_2Y_4 type molecules include planar (D_{2h} symmetry), staggered with a twist angle of 90° (D_{2d}), and the three symmetries arising from the nonplanar arrangement of the XY_2 moiety: trans (C_{2h}), gauche (C_2), and cis (C_{2v}). It has been found that for molecules in which the central pair of atoms is a group VA element, N, P, or As, the structures determined have been either trans or gauche. These structures correspond to a pyramidal arrangement of the neighboring atoms and nonbonded electron pairs about the central group VA atoms. The relative amounts of the trans or gauche isomers will depend upon the interactions of the two nonbonded electronic clouds, the steric repulsions of the substituent atoms, the exchange forces electrostatic interactions, and other less important forces.[12] The factors which are expected to be the most important in determining the conformations of these X_2Y_4 molecules are the X–X bond length and the electronegativity of the Y substituent. Work has shown that an increased X–X bond length favors a greater percentage of the trans isomer.[13] These results can be rationalized on the basis of exchange forces which have a very high power dependence ($1/r^6$) on the X–X bond length, whereas the electrostatic forces are expected to have a relatively small power ($1/r^2$) dependence on this distance. Thus, for long X–X bond lengths, the electrostatic factors are expected to be dominant and, therefore, favor the trans isomers as has been found for these molecules.

The importance of the electronegativity factor can best be demonstrated by considering the isomeric composition of the $P_2(CH_3)_4$ (40% trans) and P_2Cl_4 (95% trans) molecules.[3,4] Since the P–P distance is expected to be nearly the same and the methyl group is about the same size as a chlorine atom, the substituent steric forces should be about the same for these two compounds. However, the electronegativity of the methyl group (~2.0) is considerably smaller than that of the chlorine atom (3.0). Thus, it appears that the increased electronegativity of the substituent favors the trans conformer for the phosphines.

Hydrazine has received more attention by spectroscopists than any of the rest of the simple X_2Y_4 molecules of the group VA elements. In the early attempts to assign all of the observed frequencies in the infrared and Raman spectra of hydrazine, various models were

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(1) F. G. Baglin, S. F. Bush, and J. R. Durig, *J. Chem. Phys.*, **47**, 2104 (1967).

(2) J. R. Durig and J. W. Clark, *J. Chem. Phys.*, **48**, 3216 (1968).

(3) J. R. Durig and J. S. DiYorio, *Inorg. Chem.*, **8**, 2796 (1969).

(4) J. R. Durig, J. E. Saunders, and J. D. Odom, *J. Chem. Phys.*, **54**, 5285 (1971).

(5) J. R. Durig and J. M. Casper, *J. Chem. Phys.*, **55**, 198 (1971).

(6) J. D. Odom, J. E. Saunders, and J. R. Durig, *J. Chem. Phys.*, **56**, 1643 (1972).

(7) J. R. Durig, J. E. Saunders, and J. D. Odom, *J. Cryst. Mol. Struct.*, **2**, 169 (1972).

(8) J. R. Durig, J. W. Thompson, and J. D. Witt, *Inorg. Chem.*, **11**, 2477 (1972).

(9) K. H. Rhee, A. M. Snider, Jr., and F. A. Miller, *Spectrochim. Acta, Part A*, **29**, 1029 (1973).

(10) B. Beagley, A. R. Conrad, J. M. Freeman, J. J. Monogham, and B. G. Norton, *J. Mol. Struct.*, **11**, 371 (1972).

(11) S. G. Frankiss, *Inorg. Chem.*, **7**, 1931 (1968).

(12) W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934); *Trans. Faraday Soc.*, **30**, 898 (1934).

(13) J. R. Durig, B. M. Gimarc, and J. D. Odom in "Vibrational Spectra and Structure," Vol. II, J. R. Durig Ed., Marcel Dekker, New York, N. Y., 1973.