sition state the four phosphorus atoms are coplanar with the central metal atom, and the $H_4$ tetrahedron was twisted through 45° with respect to the $P_4$ tetrahedron so that the former is staggered with respect to the latter. The transition state has $S_4$ symmetry. There was no indication in the solution nmr spectra of the departure from $D_{2d}$ symmetry observed in the X-ray crystal structure. The deviation from $D_{2d}$ symmetry is small, and even if the solution structure exhibited the same distortion the effective nmr Hamiltonian would probably have $D_{2d}$ symmetry due to rapid intramolecular processes averaging the deviations to zero on the nmr time scale. In this physical process, the PP repulsions are maximized in the transition state, whereas they are minimized in the transition state for the tetrahedral jump mechanism.[29]

**Acknowledgment.** We wish to acknowledge the assistance of M. A. Cushing with the synthetic work, of L. F. Lardear with the X-ray work, and of G. Watunya and L. J. Rizzardi in obtaining some of the nmr spectra.

[29] The $MP_4$ skeleton in $H_4Mo[P(C_6H_5)_2CH_3]_4$ is about midway between a regular tetrahedron and a square plane. Hence the tetrahedral jump mechanism and this one physical alternative require phosphorus atom motions that are antipodal in character.

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# Nature of Phosphorus(V) Chloride in Ionizing and Nonionizing Solvents[1-3]

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*Contribution from the Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.* *Received May 2, 1972*

**Abstract:** Laser Raman spectra in conjunction with freezing point depression measurements provide evidence for two competing equilibria in the ionizing solvents $CH_3CN$, $CH_3NO_2$, and $C_6H_5NO_2$, (1) $2PCl_5 \rightleftarrows PCl_4^+ + PCl_6^-$ and (2) $PCl_5 \rightleftarrows PCl_4^+ + Cl^-$, with (1) being predominant above about 0.03 *m* and (2) being predominant at lower concentrations. These observations resolve earlier conflicting reports on the ionization scheme in acetonitrile and nitrobenzene. The nature of phosphorus(V) chloride has also been studied in nonionizing solvents. When cryoscopic data are treated in the usual manner (neglect of possible solid solution formation) the apparent molecular weight in $C_6H_6$ supports the monomeric formulation $PCl_5$, while in $CCl_4$ the apparent molecular weight supports the dimeric formulation $P_2Cl_{10}$. This study has shown, however, that solid solution formation does occur in the carbon tetrachloride–phosphorus(V) chloride system and that it cannot be neglected. Application of the experimentally determined coefficient for the distribution of solute between solid and liquid phases (mole fraction of solute in solid phase : mole fraction of solute in liquid phase = 0.50 ± 0.02 at infinite dilution) to correct for solid solution formation gives an apparent molecular weight which is in excellent agreement with monomeric $PCl_5$.

Phosphorus(V) chloride is known to show a varied structural nature which depends upon the environment in which it is found. In the solid state[4-7] it is $[PCl_4^+][PCl_6^-]$ and molecular $PCl_5$ in the molten[8] and vapor[9-11] states. In polar solvents such as acetonitrile and nitrobenzene it is ionized while in nonpolar solvents such as benzene and carbon tetrachloride it is molecular in character.[9,12]

The nature of phosphorus(V) chloride in solution as a function of solvent has been a matter of contention in the literature. Conflicting reports have been given for its properties in both ionizing and nonionizing solvents.

In acetonitrile and in nitrobenzene, phosphorus(V) chloride is electrically conducting.[14] Although it seems certain that the tetrachlorophosphonium cation, $PCl_4^+$, exists in such solutions, the presence of the hexachlorophosphate anion, $PCl_6^-$, has been a source of dispute. Payne[14] has interpreted electrolysis experiments in nitrobenzene and acetonitrile to indicate that in these solvents $PCl_5$ is in equilibrium with $PCl_4^+$ and $PCl_6^-$. On the other hand, Fialkov and Buryanov[15] have interpreted the results of similar experiments in terms of an alternative scheme in which $PCl_5$ is in equilibrium with $PCl_4^+$ and $Cl^-$. Critical comments[16] on the proposals of Payne[14] and Fialkov and Buryanov[15] have claimed that phosphorus(V) chloride is in fact completely ionized as $PCl_4^+$ and $PCl_6^-$ in acetonitrile and nitrobenzene. However, the presence of a "small" amount of molecular $PCl_5$ in solution was later acknowledged.[13]

An infrared study by Schmulbach and Ahmed[17] indicated the presence of $PCl_5$, $PCl_4^+$, and $PCl_6^-$ in $CH_3CN$.

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[1] V. P. Petro, J. Howatson, and S. G. Shore, Abstracts, presented in part at the 150th Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1965, p 33-O.

[2] R. W. Suter, Ph.D. Thesis, The Ohio State University, 1969.

[3] H. C. Knachel, Ph.D. Thesis, The Ohio State University, 1971.

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[5] G. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963).

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[8] A. Voigt and W. Blitz, *Z. Anorg. Allg. Chem.*, **133**, 277 (1924); J. H. Simons and G. Jessop, *J. Amer. Chem. Soc.*, **53**, 1278 (1931); H. Moureu, M. Magot, and G. Witroff, *C. R. Acad. Sci.*, **205**, 545 (1937); *ibid.*, **203**, 257 (1935); *ibid.*, **205**, 276 (1937); K. Moedritger, L. Maier, and L. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962).

[9] M. Roualt, *Ann. Phys. (Leipzig)*, **14**, 78 (1940).

[10] J. D. Wilmshurst and H. J. Bernstein, *J. Chem. Phys.*, **27**, 661, 217 (1957).

[11] I. R. Beattie and G. A. Ozin, *J. Chem. Soc. A*, 1691 (1969).

[12] M. J. Taylor and L. A. Woodward, *J. Chem. Soc.*, 4670 (1963); M. J. Taylor, Ph.D. Dissertation, Oxford, 1961, as cited by Beattie.[13]

[13] I. R. Beattie, R. Gilson, K. Livingston, V. Fawcett, and G. A. Ozin, *J. Chem. Soc. A*, 712 (1967).

[14] D. S. Payne, *J. Chem. Soc.*, 1052 (1953).

[15] Ya. A. Fialkov and Ya. B. Buryanov, *J. Gen. Chem. USSR*, **26**, 1141 (1956).

[16] I. R. Beattie and M. J. Webster, *J. Chem. Soc.*, 38 (1963).

[17] C. D. Schmulbach and I. Y. Ahmed, *ibid.*, 3008 (1968).

However, their phosphorus-31 nmr spectra at −40° revealed only resonances characteristic of the $PCl_4^+$ and $PCl_6^-$ ions.[17] Conductivity data at ambient temperature and high dilution suggested to them that the primary species in solution at high dilution is molecular $PCl_5$.

In the nonionizing solvents, benzene and carbon tetrachloride, vibrational spectra of phosphorus(V) chloride are consistent with the $D_{3h}$ symmetry expected for monomeric $PCl_5$.[9,12,13] However other results imply that the nature of phosphorus(V) chloride in carbon tetrachloride might be more complicated than suggested by the spectroscopic data. While the apparent molecular weight from the boiling point elevation of carbon tetrachloride favors monomeric $PCl_5$,[18] cryoscopic molecular weights point to associated species which are markedly concentration dependent.[19]

The objective of this investigation has been to resolve these questions concerning the nature of phosphorus(V) chloride in ionizing and nonionizing solvents.

## Results and Discussion

**Ionizing Solvents. Identification of $PCl_5$, $PCl_4^+$, and $PCl_6^-$ in Solution.** Based upon a shoulder on the solvent band in the Raman spectrum of an acetonitrile solution of phosphorus(V) chloride, the presence of a "small" amount of $PCl_5$ has been reported.[13] However it was maintained that the primary species in this solution were $PCl_4^+$ and $PCl_6^-$. We examined the Raman spectrum of phosphorus(V) chloride in acetonitrile and acetonitrile-$d_3$ over the concentration range 0.03–0.4 *m* and also observed $PCl_4^+$ (456 cm$^{-1}$), $PCl_6^-$ (354 cm$^{-1}$), and $PCl_5$ (393 cm$^{-1}$)[20] (Figure 1a). In acetonitrile-$d_3$ the solvent band is shifted to 348 cm$^{-1}$ clearly revealing the presence of molecular $PCl_5$ as a prominent band in *fresh* solutions. However, at room temperature, within 2 hr the band assigned to molecular $PCl_5$ disappeared from the spectrum. This is in accord with a report[21] which shows that phosphorus(V) chloride reacts with acetonitrile to produce $PCl_6^-$ and a complex cation. This reaction could be responsible for conclusions drawn[13] concerning the presence of a "small" amount of molecular $PCl_5$ in solution. In the present investigation the effect of this reaction was minimized by working with fresh solutions which were not more than 0.5 hr old at the conclusion of a particular experiment. Electrical conductivity studies[3,22] of solutions as a function of time at 25° showed that significant deterioration did not occur in the time intervals required to obtain the spectroscopic data reported herein.

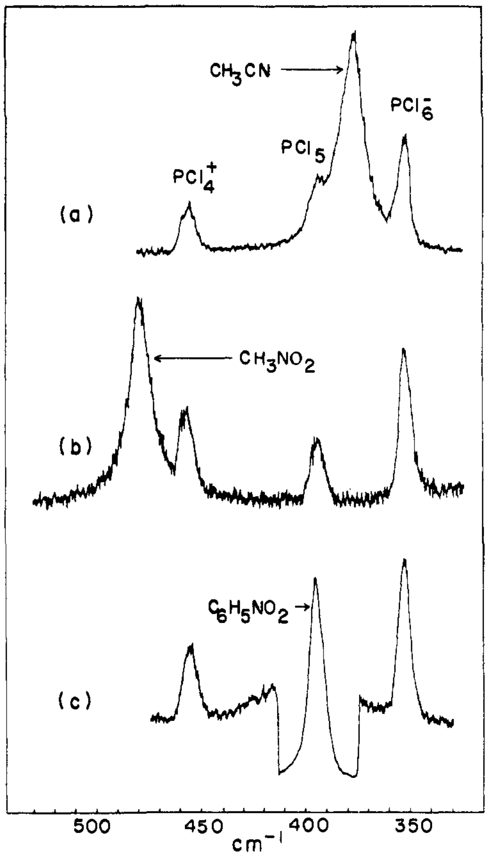

Figure 1. Raman spectra of phosphorus(V) chloride in solution.

The species spectroscopically identified in fresh solutions are in accord with the ionization scheme first proposed by Payne.[14]

$$2PCl_5 \rightleftarrows PCl_4^+ + PCl_6^- \qquad (1)$$

Relative amounts of these species are reversibly temperature dependent in solution. Raman spectra of acetonitrile and acetonitrile-$d_3$ solutions revealed that the intensity of the band assigned to molecular $PCl_5$ diminishes with decreasing temperature, effectively disappearing below −15°, while the bands assigned to $PCl_4^+$ and $PCl_6^-$ correspondingly increase in intensity. This is consistent with phosphorus-31 nmr spectra reported by Schmulbach and Ahmed[17] as a function of temperature. This temperature dependence shows that the forward (ionization) step of (1) is exothermic.

Equilibrium 1 is also considered to be operative in nitromethane and nitrobenzene. The Raman spectrum of phosphorus(V) chloride in nitromethane (Figure 1b) clearly shows the presence of $PCl_4^+$ (456 cm$^{-1}$), $PCl_6^-$ (354 cm$^{-1}$), and $PCl_5$ (395 cm$^{-1}$). The $PCl_5$ appears to be a significant component of the system. In nitrobenzene the Raman spectrum of phosphorus(V) chloride (Figure 1c) reveals $PCl_4^+$ (456 cm$^{-1}$) and $PCl_6^-$ (354 cm$^{-1}$), but the solvent band (398 cm$^{-1}$) masks the most intense band of $PCl_5$ (393 cm$^{-1}$). In this figure the solvent band has been attenuated. However, three weaker bands of $PCl_5$ (262, 273, and 280 cm$^{-1}$) were observed.[5,13] We also observed these

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(18) G. Oddo and E. Serra, *Gazz. Chim. Ital.*, 343 (1890), as cited in Mellor's "A Comprehensive Treatise on Inorganic and Theoretical Chemistry;" Moles, *An. Soc. Espan. Fis. Quim.*, 10, 30 (1912), as cited in the "International Critical Tables," Vol. 3, McGraw-Hill, New York, N. Y., 1928, p 330.

(19) L. Kolditz and D. Hass, *Z. Anorg. Allg. Chem.*, **294**, 191 (1958).

(20) These assignments are based upon earlier work of Carlson,[5] Wilmshurst,[10] and Taylor[12] as well as that found in the following articles: R. H. Condrate and K. Nakamoto, *Bull. Chem. Soc. Jap.*, **39**, 1108 (1966); F. A. Miller, *Pure Appl. Chem.*, 7, 125 (1963); H. Gerding and J. C. Duinker, *Rev. Chim. Miner.*, 3, 815 (1966).

(21) H. P. Latscha, W. Weber, and M. Becke-Goehring, *Z. Anorg. Allg. Chem.*, 367, 40 (1969).

(22) It is of interest to note that the conductance values reported by Schmulbach and Ahmed[17] are an order of magnitude less than those observed by Payne.[14] We were able to duplicate Payne's values by taking care to exclude moisture from the conductivity cell. We could[3] reproduce the low values[17] only by "doping" the solutions with trace amounts of water. This is consistent with the fact that one of the hydrolysis products, $POCl_3$, is essentially nonconducting in acetonitrile while the other hydrolysis product HCl has been shown to have an equivalent conductance of only 0.2 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in acetonitrile.[23]

(23) G. Janz and S. S. Danyluk, *J. Amer. Chem. Soc.*, **81**, 3584 (1959).

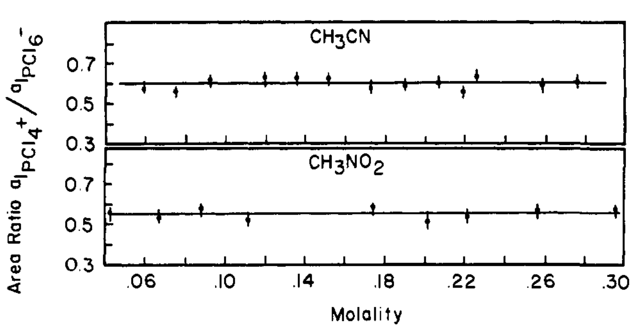

Figure 2. Area ratios of $a_{1,PCl_4^+}/a_{1,PCl_6^-}$ Raman bands as a function of concentration.

bands of molecular $PCl_5$ in a solution of phosphorus(V) chloride in benzene. Carlson's[5] assignment of the band at 263 cm$^{-1}$ is uncertain, but appears to be due to $PCl_5$ rather than the $POCl_3$ impurity he suggested since the much more intense $POCl_3$ band at 488 cm$^{-1}$ is absent from our spectrum.

**Evidence for Competing Equilibria.** If equilibrium 1 were the only reaction or the dominant reaction occurring in solution, the ratio of the relative amounts of $PCl_4^+$ and $PCl_6^-$ would be independent of concentration. From the Raman data it is possible to examine this point.

Figure 2 presents the ratios of the areas of the $PCl_4^+$ (456 cm$^{-1}$) and $PCl_6^-$ (354 cm$^{-1}$) $a_1$ bands in acetonitrile and nitromethane as a function of concentration.[24] The ratio for each solvent is essentially independent of the concentration and therefore favors equilibrium 1 as at least the predominant equilibrium in the concentration range studied (*ca.* 0.05–0.3 *m*). That the area ratios appear to differ for the two solvents by about 10% (0.60 ± 0.04 for $CH_3CN$ and 0.55 ± 0.03 for $CH_3NO_2$) might be due to systematic errors in estimating area ratios or it might be due to solvent differences[25] which involve a second competing equilibrium which is discussed and described below.

It was not practical to obtain relative areas of the $PCl_4^+$ and $PCl_6^-$ $a_1$ bands below 0.04 *m* concentrations because of unfavorable signal to noise ratios; however, it was desirable to examine the nature of phosphorus(V) chloride at lower concentrations. Accordingly, the apparent molecular weight was determined as a function of concentration to concentrations as low as 0.005 *m* using cryoscopic techniques. Recall equilibrium 1

$$2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^- \qquad (1)$$

If this were the sole equilibrium involved, the apparent molecular weights in the ionizing solvents $CH_3CN$, $CH_3NO_2$, and $C_6H_5NO_2$ would be equal to the formula weight and be independent of concentration because the number of solute species is independent of the extent of ionization. We found that the apparent molecular weight closely approximates the formula weight to within ±5% of the theoretical value and shows only slight concentration dependence above concentrations of about 0.03 *m* in $CH_3CN$, 0.04 *m* in $CH_3NO_2$, and 0.06 *m* in $C_6H_5NO_2$. At 0.1 *m* the apparent molecular weights are 215 in $CH_3NO_2$, 220 in $C_6H_5NO_2$, and 195 in $CH_3CN$, compared to a formula weight of 208. These results are consistent with the invariance of the area ratios of the $PCl_4^+$ and $PCl_6^-$ $a_1$ bands shown in Figure 2.

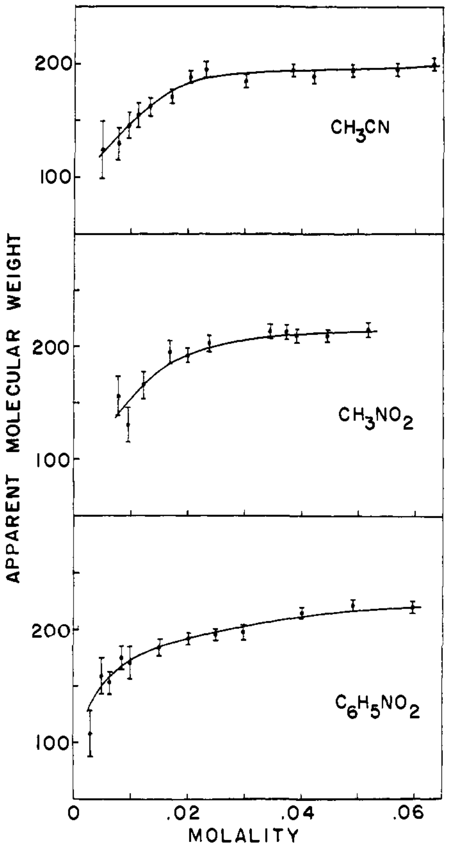

Figure 3. Cryoscopic apparent molecular weights of phosphorus(V) chloride in ionizing solvents as a function of concentration.

Figure 3 gives apparent molecular weights from about 0.005 *m* to about 0.06 *m*.[28,29] At concentrations below about 0.02 *m*, the apparent molecular weight falls off markedly and approaches a value of about half the formula weight of $PCl_5$. Clearly such concentration dependence of the apparent molecular weight suggests that in this concentration range, equilibrium 1 no longer predominates. A second equilibrium (2) is believed to

$$PCl_5 \rightleftharpoons PCl_4^+ + Cl^- \qquad (2)$$

predominate in this range. This equilibrium accounts for the observed concentration dependence of the apparent molecular weight. Indeed the observed concentration dependence is typical for that of a uniunivalent electrolyte in a solvent of relatively high dielectric constant.[30]

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(24) Investigation of the concentration-dependent Raman spectra of phosphorus(V) chloride–nitrobenzene solutions was not carried out.

(25) It is of interest to note that it has been suggested that there is negligible interaction between $PCl_4^+$ and $CH_3CN$ based upon invariance of the $a_1$ (456 cm$^{-1}$) band in solution compared to this band in solid $[PCl_4^+][PCl_6^-]$. Invariance of nmr chemical shift data in $CH_3CN$ has also been cited as lack of evidence for interaction.[26] We have observed independent evidence to support this contention. We find that the $a_1$ band observed under high resolution in $CH_3CN$ and $CH_3NO_2$ shows the appropriate isotopic splitting for a structure involving four equivalent chlorines in the natural isotopic abundance.[27] If the $PCl_4^+$ were distorted from a regular tetrahedral structure in solution the relative intensities of the splittings would be altered.[27]

(26) I. Y. Ahmed and C. D. Schmulbach, *Inorg. Chem.*, **11**, 228 (1972).

(27) H. J. Clase and H. W. Kroto, *Mol. Phys.*, **15**, 167 (1968).

(28) The results given herein are more reliable and supercede earlier reports[1,29] which did not extend to such low concentrations.

(29) V. P. Petro, *Diss. Abstr.*, **21**, 6218 (1965).

(30) E. Z. Egan and S. G. Shore, *J. Amer. Chem. Soc.*, **83**, 4717 (1961); L. D. Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

We believe that (1) and (2) are competing equilibria in solution with equilibrium 1 predominating at concentrations above about 0.03 *m*, while equilibrium 2 predominates below 0.03 *m*.

It was noted above that the ratio of the area of the $a_1$ band of $PCl_4^+$ to that of $PCl_6^-$ is some 10% larger for $CH_3CN$ than $CH_3NO_2$. This difference might be due to an artifact. On the other hand, it is of interest to consider the implication if this difference is real.

If equilibrium 2 is more significant at higher concentrations in $CH_3CN$ than in $CH_3NO_2$, this would account for the difference in the ratios. Indeed, the apparent molecular weight data are consistent with this suggestion in that the apparent molecular weight in $CH_3CN$ is less than that in $CH_3NO_2$ at equivalent concentrations, which implies a greater influence of equilibrium 2 in $CH_3CN$. In addition, for solid phosphorus(V) chloride, $[PCl_4^+][PCl_6^-]$, the area ratio of the $a_1$ bands is 0.48 ± 0.02. This value is some 12% less than the ratio in $CH_3NO_2$ and 20% less than the ratio in $CH_3CN$. In part these differences might reflect a contribution of equilibrium 2 in the concentration range in which the area ratios for the solutions were determined. Nevertheless, equilibrium 1 would still be the predominant equilibrium in this region and the relative contribution of equilibrium 2 would have to be essentially constant in this region by virtue of the apparent independence of the ratio as a function of concentration (Figure 2).

**Nonionizing Solvents. Cryoscopic Molecular Weights.** The apparent molecular weight of phosphorus(V) chloride in benzene and in carbon tetrachloride as a function of concentration is depicted in Figure 4. In benzene solution the apparent molecular weight is essentially concentration independent with a value of 204 ± 4, in good agreement with the value of 208 for a monomeric entity $PCl_5$ in solution. In carbon tetrachloride the apparent molecular weight shows some concentration dependence, but it is not as pronounced as that reported by Kolditz and Hass.[19] Further comparison cannot be made, however, because two of the four values of molecular weights reported cannot be calculated from the freezing point depressions and concentrations given.[19]

Our molecular weight data extrapolated to infinite dilution (415 ± 12) very strongly suggest that the predominant solute species is dimeric. It has been reported that a complex of the composition $CCl_4 \cdot 2PCl_5$ precipitated when a saturated solution of phosphorus(V) chloride in carbon tetrachloride was cooled.[31] Such a complex could account for the apparent molecular weight; however, we have been unable to duplicate this observation.[2]

While cryoscopic data point to monomeric and dimeric forms of phosphorus(V) chloride in benzene and carbon tetrachloride, its vibrational spectrum is identical in both solvents and is best interpreted in terms of a monomer of $D_{3h}$ symmetry.[20] We have found the infrared spectrum in carbon tetrachloride to be invariant from ambient temperature (24°) to the freezing point of the solution (−23°).

The apparent molecular weight of phosphorus(V) chloride in carbon tetrachloride was also determined from vapor pressure depression measurements, the results of which are described elsewhere.[2] For the present discussion, it is sufficient to note that the vapor pressure depression measurements indicated that the predominant species in carbon tetrachloride is monomeric. For example, the apparent molecular weight was 225 ± 10, obtained from a 0.072 *m* solution at 25°, thus differing sharply from the cryoscopic apparent molecular weight.

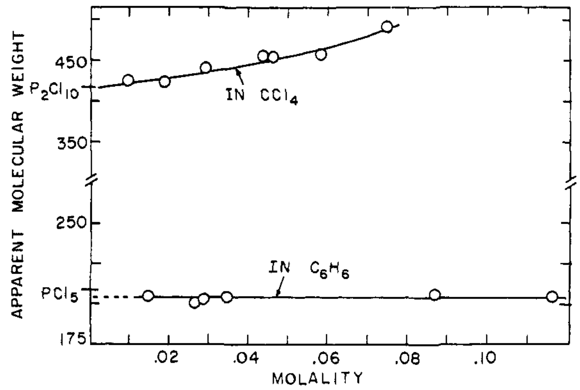

Figure 4. Cryoscopic apparent molecular weights of phosphorus(V) chloride in benzene and carbon tetrachloride as a function of concentration.

**Reevaluation of Cryoscopic Apparent Molecular Weights.** Conclusions drawn from the vapor pressure depression study and the infrared investigation require reconsideration of the apparent molecular weights obtained by cryoscopy.

Assumption of ideal solution behavior and dilute solution approximations are inherent in the well-known[32] equation for calculating apparent molecular weight from cryoscopic data. Values presented in Figure 4 were obtained assuming the validity of this equation. However, an inherent assumption which is not commonly recognized is that the solute does not form a solution with the solid solvent which separates during the freezing process. In the event that solid solution formation does occur, the equation takes the form[33]

$$M = \frac{W_2K_f(1 - k)1000}{W_1\Delta T}$$

where $M$ is the apparent molecular weight, $W_1$ the weight of the solvent, $W_2$ the weight of the solute, $K_f$ the molal freezing point depression constant, $\Delta T$ the depression of solvent freezing point, and $k$ the solute distribution coefficient (ratio of the activity of the solute in the solid phase to the activity of the solute in the liquid phase, but often approximated by the ratio of respective mole fractions[34]).

The formation of an unrecognized solid solution would lead to an apparent molecular weight which is calculated to be higher than the actual value because $k$ would be assumed to be zero. However, if the existence of the solid solution is recognized and the solute distribution coefficient $k$ determined, then the equation can be used to calculate the correct apparent molecular weight for the solute species.

It seems unlikely that solid solution formation is a factor in our cryoscopic studies in $CH_3CN$, $CH_3NO_2$,

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[31] S. Krakawiecki, *Rocz. Chem.*, **10**, 197 (1930).

[32] S. Glasstone, "Textbook of Physical Chemistry," 2nd ed, Van Nostrand, New York, N. Y., 1946, p 646.

[33] Reference 32, p 650.

[34] Reference 32, p 736.

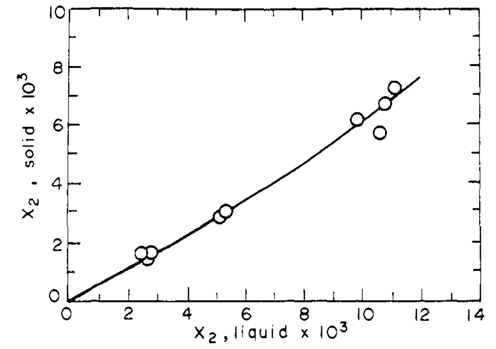

Figure 5. Mole fraction of phosphorus(V) chloride in the solid phase as a function of the mole fraction of phosphorus(V) chloride in the liquid phase, for solutions in carbon tetrachloride.

$C_6H_5NO_2$, and $C_6H_6$ because the largest apparent molecular weights observed exceeded the formula weight of $PCl_5$ by only several per cent. On the other hand, in view of the difference between vapor pressure depression and cryoscopic results, solid solution formation appeared to be a distinct possibility in $CCl_4$.

We have found that the phosphorus(V) chloride–carbon tetrachloride system forms a solid solution upon freezing. Solid and liquid phases were separated from partially frozen systems and analyzed. The distribution coefficient, $k$, was obtained from the slope of a plot of mole fraction of solute in the solid phase *vs.* mole fraction of solute in the liquid phase (Figure 5). At high dilution the distribution coefficient is 0.50 ± 0.02. Using this value to correct the apparent molecular weight of phosphorus(V) chloride at infinite dilution (Figure 4) gave a value of 205 ± 7. Thus proper interpretation of the cryoscopic data leads to an apparent molecular weight for phosphorus(V) chloride in carbon tetrachloride which is in excellent agreement with a monomeric formulation for this solute ($PCl_5$ = 208).

## Experimental Section

**Materials.** Solutions containing phosphorus(V) chloride were prepared in a dry atmosphere from Baker-Adamson reagent grade phosphorus(V) chloride which had been freshly sublimed under vacuum at 70–80° onto an air-cooled (30°) cold finger.

Acetonitrile (Matheson, Coleman and Bell spectroquality) and $CD_3CN$ were treated according to the method of Osa and Kuwana.[35] They were vacuum distilled and either stored under vacuum or dry nitrogen. All distilled samples of acetonitrile used in the investigation were no more than 1 week old.

Nitrobenzene (Matheson, Coleman and Bell) was washed twice with 5 $N$ sulfuric acid, twice with distilled water, and then with saturated NaOH solution until the aqueous layer was essentially colorless. It was washed finally with distilled water until the aqueous layer was neutral to pH paper. The light yellow material was subsequently dried over calcium chloride for approximately 1 week, then over Drierite for a similar period, and then finally drawn through approximately 12 in. of neutral alumina (Woelm-Grade I) packed in a column of 1 in. i.d. The dry nitrobenzene was then fractionally distilled (middle fraction bp 209.5–210.5°), through a 3-ft column packed with $^1/_4$-in. glass beads, into a glass storage bulb. During all drying processes and the final storage, the solvent was maintained under dry nitrogen and protected from light.

Spectroquality nitromethane obtained from Matheson, Coleman and Bell was treated with molecular sieves and neutral alumina after the procedures of Fuoss and Coplan[36] and Osa and Kuwana[35] followed by distillation under dry nitrogen at atmospheric pressure. The purified solvent was stored under vacuum and protected from light.

Reagent grade naphthalene (J. T. Baker Chemical Co.) was sublimed under vacuum just prior to use.

Spectroquality benzene (Matheson, Coleman and Bell) was stored over two charges of "Drierite" for approximately 1 week. It was then decanted under dry nitrogen onto $CaH_2$, refluxed for approximately 48 hr, and then slowly distilled under vacuum.

Spectroquality carbon tetrachloride (Matheson, Coleman and Bell) was dried prior to use according to the following procedure. It was stirred for 1 week over silica gel, filtered under dry nitrogen onto 4A molecular sieves, stirred another week, and then distilled. The middle fraction of this distillate was then stirred over $P_2O_5$ for about 1 day before the final fractionation. The final fractionation was monitored by vapor-phase chromatography which was sensitive to chloromethanes in concentrations as low as about 10 ppm. First fraction takeoff was continued at a reflux ratio of greater than 10:1, until both chloro- and dichloromethane were barely or no longer detectable and the trichloro- to tetrachloromethane ratio was constant at 1:$10^4$. This required the removal of about 20% of the original pot volume in the first fraction. The second fraction was then collected at full takeoff and was vapor transferred before use. The solvent was stored under dry nitrogen in the dark until required.

**Apparatus and Procedures. Raman Spectra.** A Jarrell Ash 25-300 laser Raman spectrometer with a Spectra-Physics He–Ne laser, operating at about 88 mW, was employed. The detection system consisted of an ITT FW-130 photomultiplier tube cooled to about −30° and a photon counting system of Hamner components. Spectra at room temperature were obtained using a Perkin-Elmer multipass cell (2.5 ml volume) with approximately 30 passes of the laser beam. Low-temperature sample cells were made from 5-mm Pyrex tubing which had been flattened on the end. After introduction of the solution the tubes were sealed off under vacuum. Half-silvering was accomplished using a standard silvering technique. The low-temperature cell holder is described elsewhere.[3]

Areas of the Raman bands were determined using a polar planimeter. Where a band overlapped the solvent band ($PCl_6^-$ band overlapped the $CH_3CN$ band and $PCl_4^+$ band overlapped the $CH_3NO_2$ band), the overlapping wing of the solvent band was estimated from the appearance of the band in the spectrum of the pure solvent. Area ratios from an individual spectrum could be determined to ±5% of the value based upon three determinations per spectrum. A linear least-squares treatment of area ratio *vs.* concentration (Figure 2) gave intercepts of 0.60 and 0.55 in $CH_3CN$ and $CH_3NO_2$, respectively. Maximum deviations of experimentally determined ratios from the values of the intercepts were ±0.04 and ±0.03, respectively. Respective slopes of 0.041 and 0.025 attested to the effective concentration independence of the area ratios in the concentration range studied (0.05–0.3 $m$). Area ratios of the $a_1$ bands for solid $[PCl_4^+][PCl_6^-]$ were determined to ±2% of the value based upon three determinations per spectrum. An average ratio of 0.48 was obtained from four different spectra of the solid. The maximum deviation from the average was ±0.02.

**Cryoscopy. Freezing Points.** Apparent molecular weights were determined cryoscopically. Freezing point measurements were carried out in a cell (Figure 6) which provided for isolation of the sample from atmospheric moisture and permitted continuous stirring of the sample. Before using the cell it was cleaned in alcoholic KOH and rinsed with dilute HCl. Then hot distilled water was allowed to remain in the cell for approximately $^1/_2$ hr, after which it was rinsed with double distilled demineralized water and placed in an air-circulating oven at 120° for at least 2 hr. After the cell cooled to room temperature, it was assembled, evacuated, and baked out at 200° with a heat gun. When cooled, it was filled with dry nitrogen.

In a typical experiment, a 15-ml sample of either pure solvent or solution was introduced into the freezing point cell from a glass tipped syringe through a Teflon needle which extended to within several centimeters above the final liquid level. The cell was then immersed in an evacuable dewar to allow for the control of the rate of thermal leak (thermal contact was provided by $n$-hexane between the cell and dewar) and the entire assembly was immersed in a bath appropriate for the particular solvent studied. A chloroform slush bath (−63.5°) was used for studies in acetonitrile, an ice slush for nitrobenzene, a 1,2-dichloroethane slush (−35.6°) for the nitromethane and carbon tetrachloride solutions, and a potassium chloride–ice–water slush (−8°) in the case of benzene solutions. With the exception of the benzene solutions, temperature was measured using an NBS calibrated platinum resistance thermometer in conjunction with a Muller, Type G-2 temperature bridge. Corre-

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sponding data for the benzene system were obtained as automatically recorded temperature *vs.* time plots given by a thermistor thermometer used in conjunction with a Sargent, S-81601, Model SR, recorder. Calibration of the thermistor was obtained from the freezing point depressions of solutions of azobenzene in benzene.

Freezing points of samples were obtained from cooling curves. Supercooling was minimized by dropping a small Teflon pellet or bit of platinum wire (cooled to −196°) into the liquid when it was at a temperature of several hundredths of a degree above the projected freezing measurement. Cooling curves initially were treated according to the method of Rossini[37] and yielded freezing points to a precision of better than ±0.003°. Freezing point depressions were determined to a precision of better than ±0.005°. It was discovered that the small curvature of these time–temperature plots allowed visual extrapolation which have freezing points in good agreement with those obtained by the graphical extrapolation method of Rossini. Consequently the less tedious visual extrapolation method was used in treating most the of data.

The following values of $K_f$ in units of deg kg mol$^{-1}$ were used in calculating apparent molecular weights: $CH_3CN$, 2.22; $CH_3NO_2$, 3.13;[38] $C_6H_5NO_2$, 6.85;[38] $C_6H_6$, 5.09;[39] $CCl_4$, 29.8.[38] These values were experimentally verified from freezing point studies using naphthalene as the solute. For acetonitrile a significant discrepancy was observed between the theoretical[40] value of 1.97 deg kg mol$^{-1}$ and the experimental value of 2.22 ± 0.01 deg kg mol$^{-1}$ which we determined from a plot of observed depression of freezing point *vs.* concentration of solutions which contained either naphthalene or benzene solute. The constant $K_f$ was obtained as the slope of the linear plot.

**Solid Solution Investigation.** A 15-ml sample of a solution of $PCl_5$ in $CCl_4$ was added to a freezing point cell modified[2] from that shown in Figure 6. Conditions for freezing the solution were the same as those described above and for a solution initially at room temperature usually required 90 min to show the first crystals of the solid phase and an additional 25–30 min to solidify completely, if allowed to do so. In practice the liquid phase was withdrawn as thoroughly as possible with a clean, dry, syringe at some point in the freezing process. The solid phase was allowed to melt and then similarly withdrawn. The two phases were separately analyzed for chloride ion content by hydrolysis of the solute in solution with 2 *N* KOH. After separation of the aqueous and $CCl_4$ phases, the chloride content of the aqueous phase was determined by standard gravimetric analysis.

Separation of solid phase from liquid phase in the freezing point cell was incomplete due to physical hold-up of liquid on the surface of the separated crystals. The quantity of solute and solvent which appeared with the solid phase due to retained liquid phase was determined assuming such hold-up was primarily a function of the quantity and size of the crystals of the separated solid phase. Using rates of cooling and stirring identical with those employed in the $PCl_5$ distribution determination, $CCl_4$ solutions of *n*-hexane were studied for solute distribution after it was first shown that *n*-hexane gives the expected molal depression of the $CCl_4$ freezing point and therefore does not form a solid solution. Four samples of a solution, 5.3 × 10$^{-2}$ *m*, in *n*-hexane were frozen to progressively greater extents in the cell. In each case the phases were separated as previously described and analyzed by vapor-phase chromatography for hexane content. The per cent of liquid phase held-up on the solid phase was calculated on the bases that the hexane present in this sample was due only to unseparated liquid phase. A plot of this percentage as a function of total weight of the solid-phase aliquot was used to determine the hold-up corrections for the $PCl_5$–$CCl_4$ solid solution studies. The probable hold-up of liquid phase was obtained from a plot of the percentage of retained liquid on the solid phase *vs.* weight of the solid aliquot removed from the cell. From this and the liquid-phase analysis, the number of moles of each constituent retained from the liquid phase was calculated. These were then subtracted from the experimental mole composition of the total solid-phase aliquot, yielding the actual composition of just the solid phase.

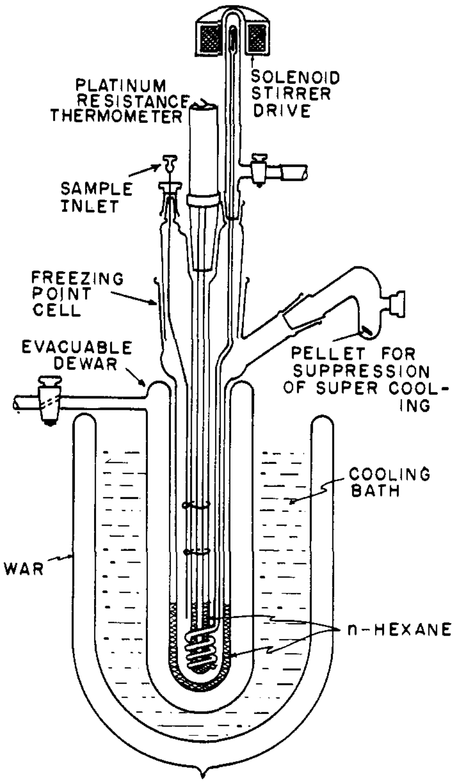

Figure 6. Freezing point cell.

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