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THE NEUTRAL ORGANOPHOSPHORUS COMPOUNDS AS EXTRACTANTS

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THE NEUTRAL ORGANOPHOSPHORUS COMPOUNDS AS EXTRACTANTS

L. L. Burger*

Introduction

The neutral organophosphorus compounds comprise an extremely large number of structures. For discussion it has been customary to categorize them according to the parent inorganic compound. Thus, most of the compounds of interest will be seen to be esters of the simple oxyacids of phosphorus or derivatives of phosphine. The preparation and properties of organophosphorus compounds has been the subject of several reviews⁽¹⁻⁵⁾. The most recent of these, Van Wazer's text, includes a survey of all the classes of compounds of interest.

The present paper is concerned with the properties of these compounds as solvents; in particular, solvents which form solvation complexes with inorganic molecules. For information on the preparation and chemical reactions, the excellent reviews just cited should be consulted.

Table I lists the basic structures of interest in this paper. Other nomenclatures have been proposed but will not be discussed here. Actually, since we are interested in these molecules as structural entities rather than their method of preparation, we could justifiably name them all as phosphines and phosphine oxides. "R" may of course be an aryl group as well as an alkyl group. If, in addition, one considers all the possible compounds in which the R group attached to the phosphorus atom is replaced by a hydrogen atom, the number is greatly increased. Many, however, are unknown or rapidly convert to more stable species. Actually compounds of type 2) and 3) are sufficiently rare that they could be omitted.

*General Electric Company, Richland, Washington. Work performed under Contract No. AT(45-1)-1350 for the U.S. Atomic Energy Commission.

TABLE I

NOMENCLATURE OF NEUTRAL ORGANOPHOSPHORUS COMPOUNDS*

1	$\begin{array}{c} \text{RPR} \\ \text{R} \end{array}$	Trialkyl phosphine
2	$\begin{array}{c} \text{RPOR} \\ \text{R} \end{array}$	Dialkyl alkoxy phosphine
3	$\begin{array}{c} \text{ROPOR} \\ \text{R} \end{array}$	Alkyl dialkoxy phosphine
4	$\begin{array}{c} \text{ROPOR} \\ \text{O} \\ \text{R} \end{array}$	Trialkoxy phosphine (trialkyl phosphite)
5	$\begin{array}{c} \text{O} \\ \text{RPR} \\ \text{R} \end{array}$	Trialkyl phosphine oxide
6	$\begin{array}{c} \text{O} \\ \text{ROPOR} \\ \text{H} \end{array}$	Dialkyl hydrogen phosphonate
7	$\begin{array}{c} \text{O} \\ \text{ROPOR} \\ \text{R} \end{array}$	Dialkyl alkylphosphonate
8	$\begin{array}{c} \text{O} \\ \text{ROPR} \\ \text{R} \end{array}$	Alkyl dialkylphosphinate
9	$\begin{array}{c} \text{O} \\ \text{ROPOR} \\ \text{O} \\ \text{R} \end{array}$	Trialkyl phosphate

* In this table, R denotes any alkyl group. It may also be considered an aryl group with, of course, appropriate changes in nomenclature.

The polyphosphorus compounds such as the diphosphonates, diphosphine oxides and other polyfunctional compounds could well be included since they are chemically stable, form complexes similar to those formed with the compounds in Table II and offer very interesting structural variations. They are, however, the subject of another paper⁽⁶⁾ in this symposium. Likewise, the acid organophosphorus derivatives will be treated elsewhere.⁽⁷⁾

Physical Properties

The physical properties are characteristic of high polar organic compounds; that is, low vapor pressure, high viscosity and high solubility in other liquids. For compounds containing the same alkyl groups the vapor pressures vary in the order $R_3P > (RO)_3PO > (RO)_2RPO > (RO)R_2PO > R_3PO$ if corrections are made for the change in molecular weight as the oxygen is eliminated. This progression, which is also seen in other physical properties such as viscosity, is directly related to the basicity of the compound (the electronegativity of the PO group in the case of the phosphine oxide derivatives)⁽⁸⁾⁽⁹⁾. This is supported by solubility and heats of solution as well as by infrared data for the P-O stretching vibration.

The solubility in water is an important property. In order to keep it low, of the order of 0.1% or less, it is usually sufficient to have the alkyl groups in the butyl-pentyl range or larger. To shift the viscosity and density to a more favorable range it is then often desirable to dilute with a non-polar organic solvent.

The density is perhaps the property least affected by the changing polarity. The following sequence illustrates the effect on the density at 25° C as oxygen is removed from the molecule:

Bu_3P , 0.812; Bu_2BuOP , 0.919; $(BuO)_3P$, 0.925;

$(BuO)_2BuPO$, 0.950; $(BuO)_3PO$, 0.973..

Complexing Reactions

Returning to the classification in Figure 1, there are five classes of compounds which, because of their chemical and thermal stability, have been studied in some detail with respect to complex formation with inorganic compounds. These are the phosphines, phosphine oxides, phosphinates, phosphonates and phosphates.

The trialkyl phosphines form additional compounds with many metal compounds, one of the best known examples being that of trimethyl phosphine with trimethyl aluminum, $\text{Me}_3\text{PAlMe}_3$ which is exceptionally stable.

The phosphines form addition compounds of the type $\text{MX}(\text{R}_3\text{P})$, $\text{MX}_2(\text{R}_3\text{P})$ and $\text{MX}_2(\text{R}_3\text{P})_2$. Mann and coworkers⁽¹⁰⁾ have characterized a number of these complexes where M is Au, Ag, Cu, Pd, Pt; X is a halogen; and R is Me, Et, Pr, Bu or phenyl.

Other complexes have been studied by Chatt and Shaw⁽¹¹⁾. They have prepared a number of compounds of the type $(\text{PR}_3)_2\text{NiR}'\text{X}$ where R is Et, Pr, phenyl, etc., and where R' may be $\text{C}\equiv\text{CH}$, $\text{C}\equiv\text{CMe}$, $\text{C}\equiv\text{C}-\text{Cl}$; etc. Some of these complexes can be sublimed without decomposition. Similar platinum complexes have also been described⁽¹²⁾.

The phosphines are all subject to oxidation to the phosphine oxide; however, the tetrahedral coordination of the phosphorus in the metal complexes leads to an enhanced stability. Very little information appears in the literature on the solubility of these complexes in organic liquids. They are, however, often prepared in benzene solution and are described as water insoluble.

One can consider the trialkyl phosphites $(\text{RO})_3\text{P}$ as trialkoxyphosphines. Although the phosphorus atom is less electronegative than in the alkylphosphines, it is found that similar complexes form, e.g., with CuCl , HgCl_2 , PdCl_2 , etc., which are of the type $(\text{RO})_3\text{PMX}_y$ or $[(\text{RO})_3\text{P}]_2\text{MX}_y$.⁽¹³⁾⁽²⁾⁽³⁾

The principal reactions of the phosphites besides the addition reaction are: oxidation to the phosphate, dealkylation by metal salts, and rearrangement to the phosphonate structure* - all of which can be easily promoted. Because of these reactions the phosphites have held little interest in solvent extraction studies.

Most attention has instead been focused on the esters of orthophosphoric, alkyl (or aryl) phosphonic and dialkyl phosphinic acids; and on the trialkyl (or aryl) phosphine oxides. These compounds are the most stable of the organo-phosphorus compounds discussed here. Their properties of interest in solvent extraction result from the basic oxygen of the phosphoryl group, and the complexes they form are generally similar in type. The range of complex strength, however, is very large - several orders of magnitude in terms of formation constants. This fact, together with the possibility of varying the solubility and other physical properties by modifying the organic groups is responsible for their widespread study in recent years.

Higgins, Baldwin and Ruth in 1952⁽¹⁴⁾ reported on the extraction properties of about a dozen trialkyl phosphates, several phosphonates, and one phosphinate.

The boiling points, densities, refractive indices, viscosities, solubilities and extraction properties of some 45 of these compounds were compared by Burger⁽⁸⁾⁽⁹⁾. Simultaneous work was carried out in the United Kingdom atomic energy program. Healy and Kennedy for example compared 15 organophosphorus compounds for the extraction of nitrates⁽¹⁵⁾

*The rearrangement is an important synthesis reaction (Michaelis) and is worthy of some comment. The overall result is exemplified by

Hydrolysis to form the "dialkyl phosphite" probably proceeds by the same mechanism thus producing the phosphonate

The phosphine oxides were examined in considerable detail by White⁽¹⁶⁾ and by Blake and Brown and coworkers⁽¹⁷⁾. White studied the extraction of over 40 elements from HCl, H₂SO₄, HClO₄ and HNO₃. Horner and Coleman⁽¹⁸⁾ and Siddall⁽¹⁹⁾ compared many phosphates and phosphonates which contained branched alkyl groups. More recently, the dialkyl phenylphosphonates as a class have been studied in our laboratories⁽²⁰⁾. Other workers have contributed additional compounds and Table II is a reasonably complete listing of the neutral monofunctional organophosphorus compounds that have been examined in solvent extraction studies. Tributyl phosphate (TBP) is of course the most widely known of these compounds.

It is of interest to briefly survey the types of compounds that have been found to extract from aqueous solutions using these phosphorus compounds. The common inorganic acids HNO₂, HI, HNO₃, HClO₄, HBr and HCl are easily extracted. Several metals also extract in the acid (i.e. anion) form, for example CrO₄⁼ and MnO₄⁻.

The metals that have been studied cover most of the periodic table, the nitrate and chloride salts having received the most attention. Data on the TBP system, studied up to 1954, were collected by Geary⁽²¹⁾. The HCl system was examined by Irving and Edgington⁽²²⁾ who discussed the extraction of HCl as well as zinc, indium, uranyl and several transition metals. The extraction of 50 elements from 1-12 M HCl solutions by TBP was, for example, recently summarized by Ishimari and coworkers⁽²³⁾. No attempt will be made here to cite the very extensive work in nitrate systems.

Perchlorates are generally quite soluble. Other interesting anions are the perchloro (and fluoro) acetates and the homologous propionates which form TBP-soluble salts in contrast to those of the parent analogs. Thiocyanates are often soluble, and at least one, NaSCN, has been studied in some detail⁽²⁴⁾.

It will be seen that there are occasional differences in extraction mechanism of metal salts as the anion is changed. It may also be noted here that metal salts of some organic acids such as TTA or dibutylphosphoric acid show appreciable solubility in non-polar organic solvents, often leading to very high extraction by neutral organo phosphorus solvents. This very interesting, so-called synergistic effect is the subject of other papers in this symposium⁽²⁵⁾⁽²⁶⁾.

The organophosphorus compounds were first examined as extraction agents for uranium and plutonium. The relation between solvent strength and phosphoryl electronegativity was clearly evident. Thus, as one would predict, the observed solvent strength increased in the order: phenyl phosphates < alkyl phosphates < phenyl phosphonates < alkyl phosphonates < phosphinates < phosphine oxides. This order of stability (which is due to the change in phosphoryl oxygen basicity) is readily correlated to the change in the P-O stretching frequency as shown in Figure I⁽⁸⁾. Also, it was confirmed that the substitution of electro-negative substituents on the alkyl group had the predicted effect. The appreciable stability of these addition complexes formed with uranyl nitrate is demonstrated by the complete elimination of water from the uranyl coordination sphere and by the formation of solid complexes of the type $UO_2X_2(RPO)_2$, where RPO represents the neutral organophosphorus molecule. Solid complexes of the metal halide-phosphine oxide type were prepared many years ago by Pickard and Kenyan⁽²⁷⁾. More recently Cotton and coworkers⁽²⁸⁾ have studied the structure of several triphenyl phosphine oxide complexes of Cu, Co, Zn and Ni salts. In addition to the usual disolvates, compounds of the type $(P_3)_4MX_n$, where X is a non-complexing anion, were formed.

The disolvate structure for the TBP extraction of uranyl nitrate was first proposed by Moore⁽²⁹⁾. In recent years the investigation of solvated species for many compounds has been carried out. In general, the species found by McKay and coworkers⁽³⁰⁾ by the solvent dilution method holds for other organophosphorus compounds. McKay has shown that it is necessary to respect the non-ideality of

these solutions in calculating the solvation number. Even so, there are disagreements on some of the structures.

TABLE III
STOICHIOMETRY OF TBP COMPLEXES (McKay)

<u>Type</u>	<u>M</u>
$MNO_3 \cdot TBP$	H
$MNO_3 \cdot 2TBP$	Li, UO_2 , NpO_2 , PuO_2
$MNO_3 \cdot 3TBP$	Na
$M(NO_3)_3 \cdot 3TBP$	Rare Earths
$M(NO_3)_4 \cdot 2TBP$	Zr, Th, Np, Pu

Most workers, for example, assign the trisolvate structure to the thorium nitrate complex. This is supported by the recent work of Madigan and Cattrall⁽³¹⁾. They studied the extraction of $Th(NO_3)_4$ by dibutyl butylphosphonate (DBBP) dissolved in nitrobenzene and in kerosene and found that over a wide range of concentrations the trisolvate was indicated.

It may be noted from the work of Bannister and Cotton⁽³²⁾ that the relative tendency of the anion to complex the metal may determine the solvation number, hence deviations from the structures in Table III may be observed for other anions.

The question of the amount of water accompanying the solute is also an important one. The free energy associated with hydration contributes to the total free energy of the extraction process and thus directly affects the extraction coefficient. It is also possible that water can be involved in bonding to the organic solvent molecules. Baldwin, Higgins and Soldano⁽³³⁾ have classified extraction behavior into Class I, where the salts retain primary hydration numbers, e.g., LiCl, and HCl, and Class II where there is strong competition between the salt and water for coordination with the organic solvent.

Nitric acid (at least at concentrations below about 6-7 M) and uranyl nitrate equilibrated with TBP are examples of the latter class. It should be recalled that these organophosphorus solvents as a class have very high coordinating ability and very low dielectric constants, so that in nearly all cases the organic phase is non-ionic. This is in contrast to many solvent systems.

The general reaction for the extraction process using a neutral organophosphorus solvent "RPO" can be written

In some cases the reaction must be written to include water in the complex. The equilibrium position is a function of many variables. In addition to the hydration energy of the aqueous phase, (mostly arising from the cation), the common ion effect in the aqueous phase and the strength of the neutral solvate complex, one must also consider the solvent properties of the organic phase, i.e., the work of hole formation in the organic phase and the van der Waal's forces involving the large complex. For most laboratory studies and nearly all process applications the solvent is diluted with a non-polar organic having suitable physical properties. It is probably erroneous however to describe these as "inert diluents" as is often done. Probably the only reason the diluent effect is not observed to be larger than it is, is because both the complex and the pure organophosphorus compound may frequently have similar activity coefficients which tend to compensate each other. With more polar diluents dipole-dipole forces are involved, and with diluents capable of hydrogen bond formation, e.g., $CHCl_3$, competition for the P-O bond is quite evident. The latter cases result in a marked decrease in extraction.

Considerations such as those have lead to many attempts to study the thermodynamics of the extraction process. In view of the many factors involved in the transfer process the value of separating the entropy and enthalpy factors is obvious.

Direct measurement of the activities of organophosphorus esters in diluent was first made by Healy⁽³⁴⁾. Negative deviations from Raoult's law were observed for TBP in CCl_4 and in benzene and zero deviation for the dibutyl-phenylphosphate solutions. The activity coefficients computed for TBP systems are not as low as solubility data would have predicted. The solubility of TBP in water from a number of diluents is seen in Figure 2⁽³⁵⁾. It is of interest to note the large difference between the two non-polar diluents dodecane and CCl_4 . Recently Siekierski⁽³⁶⁾ has studied the effects of many diluents on the solubility of TBP in water and on the extraction of europium and thorium nitrates. Qualitatively his results agree with those of Johnson and Dillon but the activity coefficients calculated do not agree closely. Rather extensive vapor pressure measurements on the systems tri-isobutylphosphate in hexane, CCl_4 and isopropyl ether have recently been reported by Schwabe and Wiesener⁽³⁷⁾. The hexane and diisopropyl ether solutions of tri-isobutylphosphate show positive deviations from Raoult's law. Measurements have not been made on systems of the more polar organophosphorus compounds.

Another thermodynamic approach is to consider the equilibrium extraction reaction. An equilibrium constant for the extraction reaction (1) can be written in several ways:

$$K_1 = \frac{C_{\text{org}} Y_{\text{org}}}{M^b X^a \gamma_{\pm(m)}^{a+b}} \quad \text{or} \quad (2)$$

$$K_2 = \frac{C_{\text{org}} Y_{\text{org}}}{M^b X^a \gamma_{\pm(m)}^{a+b} (RPO \cdot \gamma_{RPO})^n} \quad (3)$$

Where C is the concentration of the complex in the organic phase and the other symbols have their usual significance.

In the first, all changes in the organic solvent including its effective concentration are absorbed into the activity coefficient for the extracted metal. In the second, the solvent is included in the reaction. One has the further choice of defining (RPO) as either the total or the "free" organophosphorus solvent, and of including water in the reaction when pertinent. McKay and co-workers⁽³⁸⁾ and Rozen and Khorkhovina⁽³⁹⁾ have considered the thermodynamics of extraction of many metal salts by TBP. Such a study is of great value in the elucidation of the extraction mechanism which is the subject of a paper in this series by Fletcher⁽⁴⁰⁾. At Hanford such a study of the actinide nitrates using a phenylphosphonate is underway.

Of more concern in the present paper is the application to the comparison of different organophosphorus molecules by employing a fixed aqueous phase. The work of Siddall⁽⁴¹⁾ is perhaps the best example. Using an equilibrium constant of the type represented by equation (3) but neglecting the activity coefficients, his ΔH values for extraction of uranyl nitrate into various phosphate and phosphonate esters varied from about -5 to -8 kcal and ΔS values from about -12 to -16 e.u. Tri-ethallylphosphate, the only compound that showed a considerable deviation, gave $\Delta H = 3.1$ kcal and $\Delta S = -5.6$ e.u. It would appear that enthalpy and entropy contribute about equally to the overall process. Siddall's correlation of ΔH values with the electronegativities of the alkyl radicals was only partially successful. It should be noted that ΔH includes both the bond strength of the complex and the heat of solution of the complex in the organic phase in addition to the ΔH of the aqueous phase dehydration reaction. Independent data on bond strengths, heats of solution, deviations from ideality of the solvent-diluent system, etc. are needed for the most meaningful interpretation of extraction data. Katzin⁽⁴²⁾ has contributed some information on these points by measuring the heat of solution of various hydrated salts in a number

of organic solvents including TBP. The heats of solution of uranyl nitrate dihydrate and hexahydrate in a large excess of TBP were found to be -10.46 kcal and +0.80 kcal respectively.

Another factor which makes calculations difficult is the partial and variable transfer of species other than the one in question.. Water and the salting agent may be mentioned as two frequent offenders. For example, Siddall used nitric acid as a salting agent. The amount extracted was small but still enough to complex with 10-20% of the solvent, the amount being different for each solvent and for each temperature.

Although thermodynamics is the more elegant approach, to date perhaps the most significant information on effects of structure of the solvents has come from simple comparison of extraction coefficients for different metal salts. Brown and coworkers⁽⁴³⁾ found, for example, that of the various phosphate and phosphonate esters examined, the extraction of uranyl away from thorium in 4 M nitric acid increased in the order: $(\text{PentO})_2\text{PentPO}$, $(\text{HexO})_2\text{HexPO}$, TBP, $(\text{BuO})_2\text{BuPO}$, $(1\text{-BuO})_3\text{PO}$, $(2\text{-MeBuO})_3\text{PO}$, $(2\text{EHO})_3\text{PO}$, $(2\text{EHO})_2\text{EHPO}$, $(\text{Oct-2-O})_2\text{EHPO}$, $(1\text{-Pro})_2\text{EHPO}$, $(s\text{-BuO})_3\text{PO}$, $(\text{Oct-2-O})_3\text{PO}$.* The poorest separation was obtained with the n-alkyl esters.

Gresky and Mansfield⁽⁴⁴⁾ demonstrated increased separation of U from Th and fission products with branched chain compounds in the series $(s\text{-BuO})_2\text{EPO}$, $(\text{BuO})_2\text{EPO}$, $(\text{OctO})_3\text{PO}$, $(s\text{-BuO})_3\text{PO}$ and TBP. Horner and Coleman⁽¹⁸⁾ examined in some detail the extraction behavior of Pu from nitric acid solutions as a function of branching of the alkyl group. The separation of U(VI) from Pu(IV) and fission products is altered by a much smaller amount than from thorium. The data, however, show a significant gain in fission product separation in going from TBP to $(\text{BuO})_2\text{EPO}$ to $(s\text{-BuO})_2\text{EPO}$. The data of Petrov and coworkers⁽⁴⁵⁾ show a finite increase in U-Pu separation as branching increases.

*See footnote to Table II for abbreviations used.

Since branching would in general increase the basicity of the ester, any decreased extraction must be steric. It is reasonable then to expect changes in separation factors as the solvent structure is changed for those species which have different solvation numbers. This is the case for Th and U as pointed out by Siddall⁽¹⁹⁾.

One can perhaps generalize even more. Where water, solvent, and anion are in close competition for metal coordination, a considerable change in extraction - and hence selectivity - may occur if either the anion or the spacial configuration of the solvent is changed. The extensive studies of White on phosphine oxide extraction of metal salts have demonstrated many interesting anion effects. For example, it was shown that Cd is not extracted from HCl or HClO₄ by tris(2-ethylhexyl) phosphine oxide (TEHPO), but is extracted from H₂SO₄ solutions. Bi⁺³ can be extracted from HCl by trihexylphosphine oxide but not by TEHPO. These and other similar extractions are discussed in detail by White⁽¹⁶⁾ and Blake and coworkers⁽¹⁷⁾⁽⁴³⁾⁽⁴⁶⁾.

On the basis of these and other studies there seems to be some merit for the consideration of substitutes for TBP in large scale solvent extraction processes. The branched-chain phosphates and phosphonates and the dialkyl phenylphosphonates suggested by the Oak Ridge group are promising candidates.

Similar studies have been carried out at Hanford, especially with the aim of replacing TBP in the smaller operations such as the "Recuplex" facility for plutonium recovery. Dibutyl butylphosphorate was the first substitute considered, but the phenylphosphonates were found to offer more advantages.

Acid Extraction

The extraction of mineral acids by these compounds has received considerable attention, especially the extraction of HNO₃ and HCl by TBP. Among the first studies were those of the AERE group⁽⁴⁷⁾⁽⁴⁸⁾⁽⁴⁹⁾ and one of the more recent is that of Davis⁽⁵⁰⁾.

Qualitatively the distribution coefficients for acid extraction from dilute aqueous solutions are $\text{HNO}_2 > \text{HNO}_3 > \text{HI} > \text{HBr} > \text{HClO}_4 > \text{HCl} > \text{H}_2\text{SO}_4, \text{H}_3\text{PO}_4$ the exact arrangement depending on the concentrations. If the complexes are simple hydrogen bonded complexes to the phosphoryl group then one would expect a correlation with the P-O stretching frequency. We have found that the shift to lower frequency does not vary in the above order but rather, $\text{HNO}_3 > \text{HCl} > \text{HNO}_2 > \text{H}_2\text{O}^{(51)}$.

Actually, most of the acids extract as hydrates rather than as free molecules and it is evident from the controversial literature on the nature and the number of these hydrates that many of the equilibria are quite complicated. HNO_3 and HNO_2 do appear to extract in unhydrated form and replace water in the TPB phase - at least at low concentrations. In the case of HNO_3 , however, water is never completely eliminated and the equilibria involved are still in doubt. Perchloric acid - TBP systems have been examined by Hesford⁽⁵²⁾ and Kertes⁽⁵³⁾ and were included in our studies. The solutions appear to be ionized and as many as four water molecules accompany the HClO_4 molecule into the organic phase.

With the hydrated acids, coordination to the phosphoryl oxygen is probably through the shell of water, as suggested by Tuck and Diamond⁽⁵⁴⁾. This mechanism of the extraction of acids was also discussed by Baldwin.⁽³³⁾⁽⁵⁵⁾ As is the case of those metal salts which extract as hydrates, the role of water is very important. Considering the various equilibria involved and the differences between the acid hydrates, a simple correlation between P-O shift and extraction would not be expected.

As discussed earlier, there are many factors which affect the distribution between the two phases. In the case of the acids one of the most important variables is the degree of ionization in the aqueous phase. This accounts in part for the very high distribution of nitrous acid into organophosphorus solvents. However, compared to nitric acid at an equivalent concentration of unionized molecules the distribution coefficient is high by a factor of about two⁽⁵¹⁾⁽⁵⁶⁾. Fletcher⁽⁵⁶⁾ has shown that the TBP solution of HNO_2 has the ultra-violet absorption characteristic of molecular HNO_2 .

The infrared spectra of HNO_2 -TEP solutions indicates that water does not extract with the acid. In TEP-isooctane solutions the complex appears to be $\text{HNO}_2 \cdot \text{TEP}$ ⁽⁵¹⁾. Fletcher's results for hexane-TEP solutions are in agreement.

Nuclear magnetic resonance offers supplementary information on these systems. The chemical shift, δ , of the proton resonance with hydrogen bonding is well documented⁽⁵⁷⁾ and the variation in δ with dilution may often be employed to ascertain the species present⁽⁵⁸⁾⁽⁵⁹⁾.

The high resolution proton spectra of many organophosphorus compounds was presented by Shuler and Axtmann⁽⁶⁰⁾. Murray and Axtmann⁽⁶¹⁾ showed that the chemical shift of the water proton in TEP solutions varied linearly with the water content. At infinite dilution the shift upfield from pure water was about 2 ppm compared to about 4 ppm for the free water molecule. We have investigated the proton spectra of several organophosphorus compounds in different diluents and after equilibration with various acids and metal salts. The 60 mc TEP spectra is shown in Figure 3. The positions of the resonance absorptions of free water, dissolved water (saturated TEP solution) and dissolved anhydrous nitric acid (approximately 1:1 HNO_3 /TEP mole ratio) are shown. The water protons in a saturated solution in TEP are observed at a higher field, about 1.25 ppm from pure water, and the infinite dilution absorption is about 1.95 ppm upfield from pure water in good agreement with Murray's data. When TEP containing water is diluted with a non-polar diluent such as CCl_4 the shift is not linear but rises rapidly with dilution below about 20% TEP. This is typical of hydrogen bonded solutions and does not support the existence of a single hydrated TEP species. Figure 4 illustrates this behavior. Unfortunately the slope of the curve at infinite dilution cannot be determined with much certainty and hence offers little information on the species in equilibrium. Preliminary data for anhydrous HNO_3 in TEP showed a similar shift on dilution with CCl_4 ; however, the complete absence of water was not proved. Dilution of the "dry" HNO_3 -TEP solution with TEP showed a similar behavior. Shuler⁽⁶²⁾ examined the proton shift of HNO_3

in TBP. His δ values were smaller and changed with concentration much more than those observed in the present work. If the organic phase is prepared by equilibration with aqueous nitric acid the solution contains a variable amount of water as well as nitric acid. Rapid exchange of the protons produces a single sharp line but its position now also depends on the H_2O/HNO_3 ratio as well as the concentration of TBP in the diluent - if one is used, and the resulting shifts vary over a large range. The chemical shift for HNO_3 in TBP equilibrated with 0.15 M nitric acid gives a curve similar to that shown in Figure 5 for HCl. The δ values are, however, much larger and appear to go through a maximum. HCl, in contrast to HNO_3 , carries into the organic phase several molecules of water with each molecule of acid. It is interesting to note that the curve for perchloric acid which also extracts, carrying water, gives higher δ values, more like HNO_3 .

Nitrous acid is again an interesting example. The downfield shift of the HNO_2 proton in TBP is relatively small. Further, as the TBP- HNO_2 solution is diluted, with CCl_4 , the resonance absorption disappears even though IR and UV spectra, and chemical tests suggest that HNO_2 is still present.

When a strong complex is formed with the organophosphorus compound, such as that with uranyl nitrate, the resonance absorption due to the protons on the alpha carbon atom is shifted downfield appreciably. This may be of some interest in evaluating the strength of complexes formed. Of practical importance is the fact that the alpha protons in the parent alcohol show an absorption upfield from the alpha protons of the organophosphorus derivative thus making it easy to detect residual alcohol in the synthesized compounds.

Conclusion

This paper was intended as a brief survey of some of the interesting properties of the neutral organophosphorus compounds. No attempt has been made to examine all facets of work in this area and in particular those questions being discussed in other portions of this symposium, namely structural aspects from spectral studies, synergistic effects, TBP extraction mechanisms, and the polyfunctional compounds have been treated lightly or omitted entirely.

It is hoped that some of the problems that were discussed will serve to indicate that many interesting areas for investigation still remain.

TABLE II

NEUTRAL MONOFUNCTIONAL ORGANOPHOSPHORUS COMPOUNDS

EXAMINED FOR SOLVENT EXTRACTION

Symmetric Phosphates		Unsymmetric Phosphates			
R	Ref.	R ₁	R ₂	R ₃	Ref.
triEt (a)	(14) (b)	Et	Et	Bu	(8)
Pr	(14)	Et	Et	1-Bu	(8)
s-Pr	(14)	Et	Et	Pent	(8)
Bu	----	Et	Et	Dec	(8)
1-Bu	(14) (63) (19)	Bu	Bu	Me	(8)
s-Bu	(14)	Bu	Bu	Et	(8)
Pent	(14) (19)	Bu	Bu	Hex	(8)
1-Pent	(19) (63)	Bu	Bu	Oct	(8)
neo-Pent	(19)	Bu	Bu	Dec	(8)
c-Pent	(19)	Bu	Bu	EthoxyBu	(8)
Pent-3	(19)	1-Pent	1-Pent	Me	(65)
3-MeBu-2	(19)	Allyl	Allyl	Bu	(15)
Hex	(19)	⌀	⌀	Oct	(14)
c-Hex	(19)	Bu	Bu	Allyl	(15)
Oct	(66)	Bu	Bu	⌀	(15)
Oct-2	(63) (18)	⌀	⌀	Bu	(14) (8) (15)
2-EH	(17) (19)	Bu	Oct	⌀	(8)
Allyl	(15)				
Methallyl	(19)				
βchlorEt	(14) (8)				
⌀	(14) (15)				
ButoxyEt	(14) (8)				
Et-butoxyEt	(14)				

Phosphonates

RO	R	Ref.	RO	R	Ref.
diBu	H	(8) (15)	di2-EH	ChloroMe	(19)
Et	Me	(8)	Bu	Acetonyl	(45)
Bu	Me	(45)	Bu	Ethoxy Me	(45)
1-Pent	Me	(45)	Bu	Butoxy Et	(45)
Hex	Me	(45)	Bu	(c)	(45)
Hept	Me	(45)	Bu	(d)	(45)
			Bu	(e)	(64)
Oct	Me	(45)	Et	⌀	(8) (20)
Non	Me	(45)	Pr	⌀	(20)
Dec	Me	(45)	1-Pr	⌀	(20)
C-Hex	Me	(45)	Bu	⌀	(8) (14) (17) (18) (20)
⌀	Me	(45)	Bo-Bu	⌀	(20)
Bu, Hex	Me	(45)	S-Bu	⌀	(17) (63) (20) (18)
Bu, Hept	Me	(45)	t-Bu	⌀	(20)
diBu	Et	(8) (45)	Pent	⌀	(20)
1-Bu	Et	(45)	Hex	⌀	(20)
Bu	Pr	(45)	Hept	⌀	(20)

Phosphonates (Continued)

RO	R	Ref.	RO	R	Ref.
1-Pent	Pr	(45)	Oct	§	(20)
Et	Bu	(8) (66)	1-Oct	§	(8) (20)
Bu	Bu	(14) (8) (17) (63) (66) (45)	Oct-2	§	(17) (63) (18)
Eu, §	Bu	(19)	2-EH	§	(20)
diBu	Pent	(45)	β-chlorEt	§	(8)
1-Pent	1-Pent	(45)	Bu	toluyl	(45)
1-Pent	1-Pent	(45)	Oct	styrene	(8)
Pent	Pent	(19) (17) (63) (18)			
Et	Hex	(8)			
Bu	Hex	(8)			
Hex	Hex	(17) (63)			
Bu	c-Hex	(19) (63)			
Et	Oct	(8)			
1-Pent	Oct	(45)			
Bu	1-Oct	(8)			
1-Pr	2-EH	(63)			
Oct-2	2-EH	(63)			
2-EH	2-EH	(63)			
Bu	Dec	(8)			
Bu	Hexadec	(8)			
Et	TCM	(8)			

Phosphinates

RO	R	Ref.
Me	DiBu	(8)
Et	Bu	(8)
Bu	Bu	(8) (14) (17) (18)
Et	Hex	(8)
Bu	Hex	(17)
Et	chloro§	(8)

Phosphine Oxides

R	Ref.
triBu	(8) (14) (17) (15) (18) (45)
1-Bu	(45)
Hex	(16)
2EH	(16) (17) (18)
§	(8)
Dec	(45)
Dodec	(45)
diOct, H	(8)

Footnotes for Table II

- The usual organic abbreviations are used except:
EH = ethyl hexyl, c = cyclo
TCM = trichlormethyl
- References are not intended to be complete. Several are given for those compounds which have been extensively studied.
- CH(CH₃) CH₂ COO C₄H₉
- CH₂ CH₂ COO C₄H₉
- CH₂ COO C₄H₉

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FIGURE 1

VARIATION OF DISTRIBUTION COEFFICIENT
WITH PHOSPHORYL FREQUENCY

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5