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ORGANOPHOSPHORUS COMPOUNDS, OTHER THAN TBP, FOR
PROCESSING OF IRRADIATED FUELS AND BY-PRODUCTS*

by

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ABSTRACT

A brief general discussion is given of the nomenclature and types of organophosphorus compounds that could be useful for aqueous processing of irradiated fuels and by-product isotopes. Comments are made on the use of compounds that might give substantial process gains even though the compounds may not be readily available.

Application of alternative extractant-diluent systems is examined for: (a) simultaneous recovery of uranium and plutonium (Purex), (b) simultaneous recovery of uranium-233 and thorium (Thorex), and (c) recovery of uranium alone (enriched uranium or "25").

Recovery of by-product elements such as promethium, americium, and curium is discussed with particular emphasis on the possible use of bifunctional organophosphorus extractants.

A discussion is given of a number of specific types of compounds that are of interest to future investigations. These compounds are chosen on the bases of unusual structure, possible effects on synergistic relationships, interesting theoretical possibilities, and practical potential. A brief discussion is given of the powerful synthetic techniques developed over the last few years that make such a wide range of compounds potentially available for study.

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INTRODUCTION

The purpose of this paper is to set forth something of the broad range of organophosphorus compounds that could be useful as alternatives to tri-n-butyl phosphate for improving the processing of irradiated fuels, or that could be useful for the recovery of by-product isotopes. In a few cases there is experimental work to indicate the practicality of utilizing certain of these compounds to advantage. In other cases the discussion is frankly speculative. This paper is not intended to be a resumé of the past - there have been a number of reviews^(1,2,3) already - but it is intended to be a stimulus to future investigations. However, a certain amount of review is necessary to the discussion.

In general, the organophosphorus compounds that could be useful as extractants in aqueous fuel reprocessing are pentavalent compounds of phosphorus. Also, these compounds all contain the phosphoryl group and the remaining bonds from the phosphorus atom must be to carbon or oxygen atoms. These limitations come about because process extractants must be quite stable to hydrolytic cleavage and to oxidation. These requirements also eliminate those bidentate compounds with P-O-P or P-P bonds.

These requirements might be modified if a chloride or other non-oxidizing aqueous system were substituted for the nitrate systems now in use. Also, it is still not definitely proven whether or not compounds with a P-N bond such as the phosphoramides, $(RO-)_2 \overset{O}{\underset{\text{N}}{\text{P}}} \begin{matrix} \nearrow R \\ \searrow R \end{matrix}$

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are stable enough for process use. Finally, the rapid advances in the field of organophosphorus synthesis may broaden the types of acceptable compounds at any time.

The potentially useful types of compounds can be divided into two broad classes. These are the neutral compounds as exemplified by tri-n-butyl phosphate (TBP), and the acidic compounds as exemplified by di-2-ethylhexyl phosphoric acid. The neutral compounds are potentially useful in both the main line processing of irradiated fuels and for recovery of at least some by-product elements such as the lanthanides and trivalent actinides. The acidic compounds have only limited potential for main line processes, but have extensive potential in by-product processing. The applications of the neutral compounds are emphasized in this paper. The neutral compounds may also be divided into the monodentates and bidentates according to whether they contain a single phosphoryl group, a phosphoryl group plus a carbonyl group, or a phosphoryl group plus a second phosphoryl group.

The neutral monodentate compounds are still further divided into:

- (1) phosphates, $(RO-)_3 P=O$
- (2) phosphonates, $(RO-)_2 (R-) P=O$
- (3) phosphinates, $(RO-) (R-)_2 P=O$
- (4) phosphine oxides $(R-)_3 P=O$

Each of the first three of these is represented in the acidic class of compounds when one or two RO- groups is replaced by the acidic -OH group. This leads to:

- (1) dialkyl phosphoric, $(RO-)_2 \overset{O}{\underset{||}{P}}-OH$
alkyl phosphoric acids, $(RO-) \overset{O}{\underset{||}{P}} (-OH)_2$
- (2) alkyl alkylphosphonic acids, $(RO-) (R-) \overset{O}{\underset{||}{P}}-OH$
alkylphosphonic acids, $(R-) \overset{O}{\underset{||}{P}} (-OH)_2$
- (3) dialkyl phosphinic acid, $(R-)_2 \overset{O}{\underset{||}{P}}-OH$

Also, one, or even two of the alkyl groups may be replaced with an aryl group. Replacement of all three alkyl groups with aryl groups does give compounds that are useful at the present time.

To date, the potentially useful bidentate compounds are:

(1) tetraalkyl methylene diphosphonates, $(RO-)_2 \overset{O}{\underset{O}{\parallel}} P - CH_2 - \overset{O}{\underset{O}{\parallel}} P (-OR)_2$

(2) the dialkyl N,N-dialkylcarbamyldiphosphonates,

(3) the dialkyl N,N-dialkylcarbamyldimethylenephosphonates,

However, it is obvious that a number of substitutions can be made in these types of compounds, such as R- for RO-, to produce new types. Or other combinations with the functional groups may be combined with the phosphoryl group to give useful compounds. Finally, one or more RO- groups could be replaced by HO- groups to produce acidic compounds.

Even from this cursory outline it is evident that there is a great variety of potentially useful compounds; but there remains the question as to whether this potential can be realized in practice and is economically justified. The question of economics is discussed below in a general way. Later in the paper experimental and practical problems are described along with solutions to these difficulties.

The impetus to the investigation and application of new extractants is found in the very large capital and operating costs of aqueous reprocessing facilities. The capital costs of large facilities are in the range 1×10^7 to 1×10^8 dollars, while annual operating costs are in the range 1×10^6 to 1×10^7 dollars. The extractant inventory of such a facility is in the range of from 5×10^3 to 5×10^4 kilograms. It is possible to design a facility in which only a modest fraction of this inventory need be replaced each year.

It is evident from these numbers that a new extractant, if it is used to improve a process, or in a supplementary process for purposes of diversifying operations, can be very expensive and still be justified economically. Even if the improvement in productivity of the facility is raised by as little as 10%, a cost of from \$10 to \$100 per kilogram might be allowable for the extractant. Even the most unusual and least accessible compounds could very likely be produced at \$100 per kilogram, and a great variety could be made available at \$10 per kilogram. From this discussion it is evident that allowable prices for extractants may be in the range of those paid for fine chemicals rather than in the range of ordinary industrial chemicals.

Before beginning the main discussion, one important and unfortunate error in the testing of alternative extractants should be brought out. It is not unusual for investigators to compare alternative extractants with TBP at the same composition of the aqueous phase and at the same phase volume ratio. This can never be a valid comparison, capable of simple interpretation, except in the rare circumstance that the extraction of the elements to be recovered is exactly the same with the alternative compound as it is with TBP. Process flowsheets are designed with a view to obtaining certain acceptable levels of loss of the products. These calculated losses are obtained from the stage-by-stage extraction factors of the elements to be recovered. The extraction factors are set by stream concentrations and flows and the nature of the extractant. The same losses can be obtained for different extractants only by altering the compositions and the relative flows of the streams. If an extractant is weaker than TBP and the streams are left unaltered, an excellent separation from fission products may appear to have been obtained, but at the expense of losing the products to the waste stream. If the extractant is stronger than TBP, the losses may be so low that fission products also may be recovered to the detriment of decontamination of the products.

These considerations are a statement of fact and are not subject to any important qualification within the context. It is extremely unfortunate that results of experiments that did not allow for these considerations have been accepted at face value.

PUREX PROCESS

Once the Purex process with two cycles of solvent extraction was established, the main challenge to process chemists was to devise a successful Purex process with only one cycle of solvent extraction. Such an achievement could easily result in the saving of millions of dollars of capital expense in new facilities that might be constructed or in hundreds of thousands of dollars per year in operating expenses for old as well as new facilities. The possibility of achieving this end has already been demonstrated in pilot plant work and even with TBP as the extractant⁽¹⁰⁾. However, the realization of this possibility with TBP would depend on a very careful control of operating conditions and great attention to detail. It would be desirable to broaden the margin for error to achieve a safety factor against process upsets. Since TBP would perhaps allow a one-cycle process, it is evident that an alternative extractant with even only slightly improved qualities could provide a one-cycle process plus the desired safety factor. The major improvement required is in decontamination from ruthenium and from zirconium-niobium, and in separation of uranium from plutonium. In particular, an improvement in these respects would allow one-cycle operation at lower operating temperatures than would be required with TBP. The high operating temperatures required with TBP (up to 70°C) could possibly cause cumulative solvent damage over long periods of time, which in turn would adversely affect the very high order of separation required in one-cycle operation. An accumulation of solvent degradation products would need to be avoided at all costs, if separation of uranium and plutonium from fission products of the order of 1×10^6 were to be routinely obtained in a single cycle of solvent extraction.

In a one-cycle process it would also be necessary to minimize radiation damage to the organic phase, since degradation by radiation also produces materials that limit separation from fission products. This factor is apt to become even more important as fuels are irradiated to higher levels.

Finally, it is evident that diluents of very high quality will be required. It has long been known that the ordinary hydrocarbon fractions of commerce are either too unstable of themselves, or contain impurities that are too unstable, to be used when a very high degree of purity in the solvent phase must be maintained. To a certain extent the diluent problem is already settled. Extensive plant operation at the Savannah River Plant has shown that commercially available n-dodecane is very much superior to most, if not all, other aliphatic diluents. The cost of n-dodecane is still relatively high, about 90¢/lb. However, this cost will probably decrease substantially in the near future. Even if it does not, such costs are easily justified by the arguments already given for cost of extractants.

There remains the possibility that an aromatic diluent may be attractive because of the radiation protection it affords the organic phase. We doubt that the small gain in this respect (a factor of 2 or 3) justifies the losses in operating efficiency in ordinary contactors due to the increased density and viscosity of aromatic compounds. The increased susceptibility to nitration of aromatic diluents is apt to cause even higher densities and viscosities for the organic phase as the solvent is used. Still, there may be special situations where the gains offset the losses.

Although this paper is concerned with process chemistry, it is well to point out here that advances in the design of solvent extraction contactors might very profitably be joined with chemistry in making practical a one-cycle process or other difficult processes. Contactors with forced settling of the mixed phases⁽⁴⁾ can greatly reduce the exposure time of solvent to both radiation and unfavorable chemical environment.

The use of such contactors offers an elegant solution to the problem of processing highly irradiated fuels. Forced settling will also make it possible to operate with organic systems that have densities close to that of the aqueous phase. This could remove some, if not all, of the objections to the use of an aromatic diluent. It is possible that a combination of contactors with forced settling and an aromatic diluent will lead to the highest radiation tolerance of all aqueous processing systems.

There is only a limited amount of guidance for the choice of candidate extractants for improved separation from fission products. In fact, the only specific guide is that increased steric hindrance, up to a point, may actually improve the extraction of uranium, adversely affect the extraction of plutonium(IV) to only a minor extent, and substantially decrease the extraction of zirconium. This is illustrated in Table 1. These data were obtained in tracer experiments with simple batch equilibrations under rather idealized conditions.

There is much evidence that the limit on the separation of zirconium in the Purex process is due to abnormal chemical species of zirconium that do not behave reversibly in a rapid manner and do not correspond to the ordinary zirconium used in tracer experiments. It can be argued that the rate at which these abnormal species convert to ordinary species is the limiting chemical step in separation from zirconium.

This argument can be continued by the proposal that the abnormal species of zirconium are not formed in significant amounts from ordinary zirconium in the organic phase in the contactor. Further, either the abnormal zirconium must be present in the original aqueous feed, or it must be formed in the aqueous phase in the contactor; or, it possibly arises from both these sources. Then, granted that the abnormal zirconium has a very large extraction coefficient, the amount

of abnormal zirconium that enters the scrub section of the contactor will be independent of the choice of extractant. It would follow that the conversion of abnormal to ordinary zirconium is the sole factor that affects the ultimate separation from zirconium. If this proposal is carried even further, to the point that conversion of abnormal zirconium to ordinary zirconium also takes place only in the aqueous phase, then obviously the nature of the organic phase is largely irrelevant to the whole process of decontamination from zirconium.

We are not convinced of this proposal or of the extension of it. There is some evidence in favor and some against. In such a case the whole question is best settled by experiments - that is, by sustained countercurrent operation in a pilot plant with process feed and with alternative extractants that have a superior discrimination against ordinary zirconium. In any event, even if only a small part of the potential improvement that is indicated with tracer zirconium is realized in practice, it may be enough to give the extra margin of safety desired in actual plant operation.

Unfortunately, there are not even valid tracer experiments with ruthenium to test the proposal that hindered extractants will give better separation from ruthenium, but there is reason to hope that they will. It is generally accepted that the extractable form of ruthenium contains a nitro group, plus three nitrate groups, plus at least two extractant molecules in the coordination sphere of the ruthenium. In such a case the coordination sphere of ruthenium must be quite crowded. If it were further crowded by substituting bulky extractant molecules for TBP, the extractable ruthenium species should become less stable and therefore less prevalent than with TBP. All of these arguments are admittedly quite speculative; however, they must serve at present as the starting point for choosing alternative extractants.

Even though the factors that may lead to improved separation from fission products may not be clear, certain other requirements are quite definite. Consistent with other requirements, extractant molecules with the lowest molecular weight are the most desirable. Compounds of lower molecular weight will have lower viscosity. Also the degradation fragments from smaller molecules will be easier to wash out in the conventional solvent recovery operations. The initial preparation of pure extractant is also made easier since smaller molecules distill at lower temperatures. However, the extractant molecule must not be so small that it has a significant water solubility.

It is also highly desirable that the extractant not form two organic phases when diluted with the chosen diluent and then contacted with process solutions. When diluted with an aliphatic diluent, the formation of two liquid organic phases after aqueous contact, or the precipitation of a sparingly soluble adduct with uranyl nitrate can occur with a wide variety of organophosphorus compounds. Increased symmetry in the organic molecule and lower molecular weight both increase the tendency for the formation of insoluble solid adducts with uranyl nitrate. The branching of alkyl substituents that is required to produce the desired steric hindrance increases molecular symmetry and the tendency to form precipitates with uranyl nitrate. For example, di-2-butyl 2-butylphosphonate is unsatisfactory with an aliphatic diluent since the solid adduct with uranyl nitrate is only sparingly soluble. Di-2-butyl 2-amylphosphonate forms an adduct that is solid at room temperature, although it is quite soluble in n-dodecane.

At this time two compounds have been given the most extensive consideration as replacements for TBP in the Purex process. Di-2-amyl 2-butylphosphonate (DABP)⁽⁵⁾, diluted with n-dodecane, has been chosen for extensive study and testing at the Savannah River Laboratory. Di-2-butyl phenylphosphonate⁽⁶⁾, in an aromatic diluent, has been seriously considered at Oak Ridge National Laboratory. Even in these cases, no reports have been made of sustained countercurrent operations with feed solutions at full levels of activity. However, tests of DABP with full-level feed are planned for the miniature pilot plant at SRL in the near future.

"25" PROCESS

The process for the recovery of enriched uranium (the "25" process) presents, in one way, an easier problem than does Purex for the chemist who would investigate alternative extractants. Since only uranium is to be recovered, it is possible to concentrate on finding improved selectivity for uranium without regard for extraction of plutonium. Since the uranyl ion bears little resemblance to the chemical species of the fission products, one may hope to exploit to the fullest any unusual features of the chemistry of the uranyl ion. In particular, it should be possible to exploit the flexibility in allowed bond angles to ligands, and a coordination number of only four. These factors permit the accommodation of very bulky extractant molecules as ligands with relatively small sacrifice in extraction power.

The major problem in conducting a profitable search for an improved extractant for the "25" process is that a slight improvement is not sufficient to ensure a large economic gain. A decontamination factor (DF) of up to about $1 \times 10^{8(10)}$ may be required of the "25" process. Truly remarkable, even fantastic, performance must be obtained if this DF is to be obtained in a single cycle of solvent extraction. However, some decontamination can be achieved in the steps that follow the solvent extraction step, such as passage through a column of silica gel. In that case an improved extractant perhaps need be capable of a gain in DF of only 10 to 100 over that obtained with TBP to realize a one-cycle process. Even then, a contactor with forced settling would be a necessity to achieve the low exposure times needed if acidic degradation products analogous to dibutyl phosphate are to be kept to an acceptably low level. With the more radioactive feeds, it already may be the formation of dibutyl phosphate that limits the performance of TBP in the "25" process rather than limitations intrinsic to TBP itself.

The very challenging problem of finding an improved extractant for the "25" process has received very little attention. This author has done some work⁽⁹⁾ that suggests that certain N, N-disubstituted amides could serve this purpose. Since this work has not been carried beyond the preliminary stages and since this paper is meant to deal only with organophosphorus compounds, these compounds will not receive further discussion here.

An extrapolation of the data of Table 1 suggests a path to a "25" process extractant. It is seen that, as one proceeds from phosphate to phosphonate to phosphinate, substitution of secondary alkyl groups for n-alkyl groups causes a small decrease in the extraction of uranium. Data for tris-(2-ethylhexyl)-phosphine oxide⁽⁸⁾ show that even with an alkyl group branched at the carbon atom second removed from phosphorus, uranium extraction is depressed relative to that with tri-n-alkyl phosphine oxides. This suggests that with a tris(sec-alkyl)-phosphine oxide or even perhaps an n-alkyl bis-(sec-alkyl)-phosphine oxide uranium extraction would be depressed even further. At the same time extrapolation of the data in Table 1 to compounds of this type suggests that the extraction of other elements would be reduced to the vanishing point.

The "25" flowsheet with TBP given in the paper by Karraker⁽¹⁰⁾ can be used as an indication of just how far the extractant strength of trialkylphosphine oxides for uranium might be profitably depressed. With this flowsheet the solvent stream leaving the first contactor is at only about 30% of saturation by uranium (6% TBP = 0.22 M, 3 g/l of U = 0.037 M). The same flowsheet, with minor modifications, could be operated at about 80% of saturation given a solvent stream with an extractant one-third as concentrated as TBP but about 10-15 times as powerful an extractant for uranium. With unimportant changes in aqueous composition and/or flows, the loss of uranium to the waste stream would be the same in the modified flowsheet as in the original.

This alteration should have a beneficial effect on decontamination of uranium independent of the increased selectivity that would be built into the alternative extractant. First, the concentration of unused or free extractant is reduced by the ratio 7/2. This tends to force fission products out of the organic phase due to the lack of free extractant. Second, the lower concentration of extractant brings the solvent nearer the physical properties and some of the chemical properties of a pure diluent stream. If we add the hoped for improvement in selectivity against extraction of fission products, then a high degree of purification of uranium should be achieved in a single cycle of solvent extraction.

Until recently the methods were not available that are required to synthesize tris-(sec-alkyl)-phosphine oxides or possibly even n-alkyl bis-(sec-alkyl)-phosphine oxides. The customary reaction of the Grignard agent with phosphoryl chloride could be employed successfully only with n-alkyl and iso-alkyl compounds. Now there are several useful routes to the preparation of these compounds. Some involve the novel and very interesting reaction reported by Jungermann and McBride. Others involve some investigations which we now have underway. Especially in view of the small amount of extractant required for the "25" process, very expensive compounds could be justified on an economic basis.

THORIUM PROCESSING

Efficient decontamination of irradiated thorium (Thorex process) is a much more difficult task than that encountered in either the Purex or "25" processes. With TBP, extraction coefficients for thorium are only about one-fifth as large as they are for plutonium (IV) and only about one-eighth as large as they are for uranium (VI). For that reason thorium is intrinsically less separable from fission products in TBP systems. Due to the basically unfavorable chemistry of thorium there is no obvious way to greatly alter the relatively poor extraction of thorium by substituting an alternative extractant. However, it will be seen that by combining three modestly favorable possibilities, perhaps a significant over-all improvement can be obtained in the processing of thorium.

The difficulty with thorium chemistry lies in the fact that the important mechanism of thorium extraction involves the coordination of three extractant molecules to thorium as opposed to only two coordinated extractant molecules with uranium and plutonium. Since the coordination sphere is already crowded by these three molecules, any further increase in crowding by increased bulk in the extractant molecule results in a disastrous decrease in extraction⁽⁷⁾. In a manner of speaking the extraction chemistry of thorium is too much like that of fission products. For example, in spite of the difference in valence, the extraction chemistry of thorium resembles that of the rare earth elements in some respects.

It is this resemblance that suggests the first possibility for a modest gain. It is to be noted in Table 3 that phenylphosphonates are better extractants for lanthanides than are alkylphosphonates. This suggests that a phenylphosphonate may be a better extractant for thorium. Hopefully, the extraction of zirconium, niobium, and especially ruthenium would not increase in proportion. The separation from lanthanides probably would not be improved. Fortunately, although the extraction of lanthanides parallels that of thorium, it is at a much lower level and is rapidly and easily reversible.

The possibility of a modest gain in this respect receives encouragement from the work of Blake, et al.⁽⁶⁾. They performed some interesting experiments with two phenylphosphonates. Table 1 from their work is reproduced as Table 2. Some additional numbers calculated from their data have been added; these numbers are separation factors of thorium from other species.

The data in Table 2 show that with 2.4M HNO_3 and di-n-butyl phenylphosphonate there is an improvement over TBP for the separation of thorium from gross gamma activity, zirconium-niobium, and, by extrapolation, possibly also for ruthenium. As is to be expected, the selection against lanthanides, and consequently gross beta activity, remains essentially unchanged.

It is possible that further alteration in the extractant molecule will produce still further gains in separation. Lanthanide extraction is increased when ethyl esters are substituted for higher alkyl esters. The same effect should apply with thorium. However, in order that aqueous solubility of the ethyl ester be kept low and the formation of two organic phases be minimized, it would perhaps be necessary to substitute the phenyl group in the meta or para position. Substitution in the ortho position would be undesirable since it would tend to offset the decrease in steric hindrance gained by going to ethyl esters.

The second possibility for improved processing of thorium depends on either using an aromatic diluent, as suggested by Blake et al., or increasing the molecular weight of the extractant molecule over that of TBP by inclusion of larger hydrocarbon radicals. Both approaches are aimed at preventing the formation of a second organic phase when the organic phase is nearly saturated with thorium; TBP in an aliphatic diluent can be only partly saturated if a second organic phase is to be avoided. An excess of free extractant is undesirable since it increases the extraction of fission products.

The third possibility for improvement in thorium processing is to be found in increasing the permissible operating temperature. It is well known that decontamination from ruthenium can be greatly improved by raising the operating temperature of the Thorex process. Unfortunately, after short operating times, a very insoluble solid adduct of dibutyl phosphate forms with thorium. The accumulation of this adduct forces a shutdown of the runs. Although it is by no means certain, perhaps an extractant molecule could be devised that would either (a) be more stable against the formation of analogues of dibutyl phosphate and/or (b) form an analogue whose thorium adduct is soluble.

If all of these possibilities - (1) improved selectivity for thorium extraction; (2) high loading of the organic phase with thorium; and (3) higher permissible operating temperatures - could be combined, it is quite likely that an alternative extractant would lead to substantial improvement in the Thorex process. On the basis of present reasoning this extractant would have a structure something like:

BIFUNCTIONAL EXTRACTANTS

Rare earth elements are potential by-products of the processing of irradiated fuels. As irradiation periods are increased and as plutonium is used as a fuel, americium and curium are also produced in significant quantities. However, it will be necessary to process large volumes of aqueous waste to recover small amounts of these materials. It would be advantageous to reduce these volumes by a large factor in the first process step by as simple a means as possible. Precipitation as double sulfates can accomplish the volume reduction, but at the expense of introducing large amounts of sulfate into the aqueous wastes. Provided the salting strength of the waste stream is high and the acidity is low, an extraction step, even with TBP (100%) would be feasible. But if a high degree of concentration is to be obtained in the simplest manner possible from aqueous streams of various compositions, much more powerful extractants are required.

It does not appear that such a powerful extractant can be found among the monofunctional organophosphorus compounds. The results of some attempts to do so are given in Table 3. It is especially worth noting that passing from phosphates to phosphonates to phosphinates accomplishes little. This order is the order of increasing intrinsic extractant strength for rare earths even as it seems to be for all other species including nitric acid. Apparently it is the increasing affinity for nitric acid that prevents, by a mechanism of back-salting, the desired increase in the extraction of rare earths. Some improvement in extraction is obtained by introducing a phenyl group into the molecule and thereby reducing the base strength of the extractant, or by resorting to methyl or ethyl esters and thereby reducing steric hindrance. However, a great improvement is not obtained.

When a second functional group is introduced into the molecule in a position that permits chelation, a great increase in extractant strength is obtained⁽¹⁶⁾. This effect is shown in Figures 1, and 2. It is evident that provided suitable physical properties and chemical stability can be obtained, some of these compounds or related compounds can be utilized to extract rare earths and trivalent actinides under very adverse conditions.

Preliminary tests* indicate that the methylenediphosphonates are perhaps even slightly more stable than TBP against violent exothermic reactions with nitric acid. The carbamylphosphonates and carbamylmethylenephosphonates are somewhat less stable, but would probably still be safe, if precautions were taken to avoid introducing them into acid evaporators. These tests of stability were made by differential thermal analysis of small samples of extractant that had been equilibrated with 10M HNO_3 .

A limited amount of testing was also done, with favorable results, on a laboratory scale with actual-process type solutions. These tests confirmed expectations that rare earths, americium, and curium could be recovered in good yield (>80%) even with a single stage of extraction and with only one volume of extractant for 20 volumes of aqueous phase. The aqueous phase was stripped with 5 successive contacts with an equal volume of water. This strip solution can be concentrated to almost any desired degree by evaporation, since it contains only a very low concentration of salts.

Undiluted tetrabutyl methylenediphosphonate was used in this test. Since this compound is slightly more dense than water, phase separation from dilute acid or water is quite slow. Further, the extractant is the less dense phase in contact with feed solutions, but reverses and becomes the more dense phase during

* The author is indebted to Dr. G. S. Nichols of SRL for performing these tests.

stripping. This reversal of phases is not desirable in plant operation, especially if very simple equipment such as ordinary tanks instead of special contactors are to be used.

These difficulties have led to the choice of tetraamyl methylenediphosphonate (TAMDP) diluted with an equal volume of n-dodecane as a preferred solvent. This solvent phase always remains less dense than the aqueous phases and separates well after mixing. The amyl compound (TAMDP) was chosen in preference to the butyl compound (TBMDP) because the larger alkyl groups decrease the tendency of the solvent to form two organic phases. For example, with TAMDP only one organic phase is formed when the solvent is contacted with an aqueous phase containing up to 5M HNO_3 , while with TBMDP two phases are formed even with water as the aqueous phase. The tetrahexyl methylene compound would tolerate even higher concentrations of acid or salts in the aqueous phase, and would have a more favorable density. However, this compound is quite viscous, and is more difficult to purify by distillation because of its high boiling point. These compounds can be purified by molecular distillation at 1×10^{-4} mm of Hg and at about 145° , 170° , and 195°C for the butyl, amyl, and hexyl compounds, respectively. Decomposition is noticeable in the range $220\text{--}230^\circ\text{C}$, but probably commences at somewhat lower temperatures.

A flowsheet for the use of 50% TAMDP in n-dodecane is given in Table 4 along with anticipated performance. No tests with actual process feed have been made and this flowsheet should be regarded as typical rather than in any way unique. The actual choice of a flowsheet will depend on the detailed process conditions that are to be encountered as well as the processing equipment available. The flowsheet given in Table 4 is designed for maximum simplicity in operation with minimum equipment. An ordinary tank

with an agitator would be used for all mixing operations, while a single centrifugal separation might be used for phase separation. New facilities designed in advance to accommodate such by-product processing might include multistage, counter-current contactors and other refinements to permit more efficient operation.

It should be emphasized that neither TAMDP nor any of the other bifunctional compounds so far examined are capable of giving efficient separation from extractable fission products such as zirconium. It is to be expected that these will be recovered with the rare earth elements and the trivalent actinides. Also the separation of lanthanides from actinides or from each other is small. Radiochemical purification will depend on subsequent process steps. On the other hand TAMDP extracts sodium, aluminum and other solid constituents of waste only slightly in ordinary circumstances. The use of a compound such as TAMDP is then aimed only at separation from gross quantities of salts in a manner that permits large volume reduction. This step should greatly reduce the cost of subsequent radiochemical processing.

While TAMDP was selected for detailed study at the Savannah River Laboratory, other bifunctional compounds may be more suitable in different circumstances. For example, the dialkyl N,N-dialkyl-carbamylphosphonates, while more restricted in application, do have a special advantage. As shown in Figure 1, extraction by these compounds is strongly dependent on the concentration of nitric acid. This means that they can be stripped very efficiently with water. At the same time quite high concentrations of nitric acid are required for extraction. Also other nitrates such as sodium nitrate cannot be substituted in the place of nitric acid. It appears that the mechanism of extraction of lanthanide and actinide (III) nitrates must have something in common with adsorption of these elements by anion exchange resins.

At the moment the dialkyl N,N-dialkyl carbamylmethylenephosphonates appear to have no special advantages as compared to the other classes of bifunctional compounds. However, much investigation with all of these compounds remains to be done.

All of the bifunctional compounds have densities of almost one, which means that at least a slight dilution is desirable. Decahydronaphthalene* has one distinct advantage over n-dodecane as a diluent. With decahydronaphthalene the formation of a second organic phase is avoided over a wider range of extractant constitution and solution composition. For example, one-half-molar solutions of extractant give a single organic phase at 25°C with up to 12M HNO₃ in the aqueous phase for TAMDP, di-n-octyl N,N-diethylcarbamylphosphonate (DODECP), and di-n-hexyl N,N-di-n-butylcarbamylmethylenephosphonate (DHDBCMP). The first two of these give a single organic phase even with 15M nitric acid.

On dilution, as might be expected, these bifunctional compounds lose extraction power. Extraction of cerium (III) is about second-power-dependent on concentration of TAMDP, between second and third-power-dependent on concentration of DHDBCMP, and slightly greater than third-power-dependent on concentration of DODECP.

Still other classes of bifunctional compounds are rather easily prepared, while even more types could probably be synthesized after some investigation. J. J. Richards, et al.⁽¹⁷⁾ have prepared tetraalkylmethylenediphosphine oxides and have shown that these are extraordinarily powerful extractants. These authors appear to have a very active program on bifunctional extractants. Their very interesting work should be followed closely by those interested in extractant chemistry. However, as might be expected from the

* The potential usefulness of decahydronaphthalene for this sort of purpose was pointed out by workers at ORNL several years ago.

behavior of the corresponding monofunctional compounds, we found that tetra-n-hexylmethylenediphosphine oxide does not extract lanthanides and actinides from high concentrations of nitric acid nearly so well as do methylenediphosphonates.

Nevertheless, it would be surprising if the diphosphine oxides do not have some advantageous applications such as, perhaps, the extraction of strontium from highly salted neutral solutions.

Recent efforts in this Laboratory appear to have been successful in synthesizing both the dialkyl-N,N-dialkylcarbamyldiphosphine oxides and the dialkyl-N,N-dialkylcarbamyldiphosphonates. These compounds should be somewhat different as extractants when compared to the corresponding phosphonates. A preliminary indication that the phosphoryl groups are better electron donors is found in the lower infrared stretching frequencies of the phosphoryl group in these compounds.

Carbonyl- and carbonylmethylenephosphonates are also potentially valuable bifunctional compounds. Except for pivaloyl-

phosphonates $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\overset{\text{O}}{\parallel}\text{C}-\overset{\text{O}}{\parallel}\text{P}(-\text{OR})_2$ this author has never been able to

obtain pure samples of these compound types. Proton magnetic resonance spectrograms always show strong signals at low magnetic fields that cannot be assigned to the desired compounds. There have been many reports in the literature of the preparation of such compounds; however, few of these reports, if any, indicate that proton magnetic resonance spectra were obtained.

SOME UNUSUAL ORGANOPHOSPHORUS MOLECULES

The variety of organophosphorus molecules that is accessible by modern techniques is almost without limit. This author has chosen several compound types for discussion on the basis of unusual structural features. A much larger number of compounds might have been placed on the list.

All of the compounds given are esters or phosphine oxides. However, in each case one or more acidic derivatives could be obtained easily. These might be of great interest to the recovery of cesium or strontium, for separation of actinides (III) from lanthanides (though probably in a chloride system), or for separation of actinides from each other. Some of these acids might be interesting from a theoretical viewpoint in studies of extraction mechanisms and of synergism.

The list is arranged in the form:

Basic Structure (number of) compound	Structural modifications or comments on structures that are available
Reason for interest	Possible use
(1) tert $\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{P}}}(\text{OR}')_2$ Highly hindered.	R' secondary or primary For "25" Process. (Purex?)
(2) tert $\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{P}}}(\text{OR})_2$ Highly hindered.	R' secondary or primary For "25" Process
(3) (Sec-R) $\overset{\text{O}}{\underset{\text{O}}{\text{P}}}-\text{R}'$ Very highly hindered.	R' primary, secondary may not be accessible For "25" Process
(4) $\text{O}=\text{P}(\text{OR})-\text{CH}(\text{CH}_3)-\phi$	For ?
Unusual Structure	For ?

Low hindrance

Also R' in place of OR'

For Th, Lanthanides,
Actinides (III)

Lowest hindrance

Scheduled for investigation
at Oak Ridge National
Laboratory

Ring structure,
highly hindered

Also R in place of OR

For "25" Process

Ring structure,
multiple isomerism
(4 meso forms; 2 d, 1 pairs)

Also R in place of OR

For?

Ring structure, varying
hindrance, depends on R

A number of ring substituted
variations possible

For?

R' substituted for R'O

For lanthanides,
actinides (III)

R' substituted for R'O

For lanthanides,
actinides (III)

Intrinsically most
powerful extractant

For extraction of
strontium?

cis isomer probably
not accessible

Bifunctional groups
attached to a ring

For?

SOME NEW SYNTHETIC REACTIONS

Since the publication of Kosolapoff's book⁽¹¹⁾, the field of synthesis of organophosphorus compounds has grown enormously. A wide variety of preparative reactions are now available. Naturally there is no catalogue or review of this wide field written uniquely for the use of solvent extraction chemists. This paper is hardly sufficient to serve that purpose, but perhaps it will serve to focus interest on some of the possibilities that are now open for exploitation, since the publication of this book. The reactions discussed below are generally well known to specialists in the field. The Russian literature in particular, covers a tremendous range of studies of synthetic reactions in great detail.

The Reaction of E. K. Fields⁽¹²⁾

This remarkable preparation with three reactants proceeds easily to give very good yields:

where the various R's may be different.

Compounds of type (III) are potential chelating extractants although in one brief test this author did not find them to be especially effective for extraction of lanthanides and actinides (III). In addition, it is possible that they can be used to form a class of betaines -

Although it may be rather difficult to find a suitable solvent for these betaines, if such can be found these betaines could be very interesting extractants. The negative charge would actually be shared between the two singly attached oxygen atoms, but even so, the capacity to donate electrons to form bonds to metals should be extraordinary.

Kinnear and Perrin Reaction⁽¹³⁾

One of the most useful and versatile preparative reactions in organophosphorus chemistry is the reaction of Kinnear and Perrin.

Whenever the appropriate haloalkane is available, almost any desired secondary or tertiary alkylphosphonyl dichloride ($\text{R}\overset{\text{O}}{\text{P}} - \text{Cl}_2$) can be prepared in good yield by a simple reaction sequence. If the appropriate alkyl- or arylphosphonous dichloride (RPCl_2 or $\text{R} \langle \text{---} \rangle \text{PCl}_2$) is available the method can be extended to prepare phosphinyl chlorides ($(\text{R}-)_2 \overset{\text{O}}{\text{P}} \text{Cl}$ or $(\text{R} \langle \text{---} \rangle)_2 (\text{R}-) \overset{\text{O}}{\text{P}} \text{Cl}$). It is also quite likely that a wide variety of phosphine oxides could be prepared if the appropriate phosphinous chloride ($(\text{R}-)_2 \text{P Cl}$) were available. Furthermore, it is possible to use the reaction repeatedly in a series of steps. For example, in the first step the reaction is run and then followed by reduction to produce a phosphonous dichloride which is then employed in a second step to produce a phosphinyl chloride.

The phosphonyl dichlorides and phosphinyl chlorides are intermediates to produce a variety of final products. Esters are produced either by the action of an alcohol plus a tertiary amine or in difficult cases by action of the sodium alkoxide in an excess of the alcohol. The sodium alkoxide route is generally required when the R of R-P is tertiary. Organophosphorus acids are produced by simple hydrolysis of the chloride. Occasionally, reflux with dilute caustic is required for the hydrolysis, but pouring into water (cautiously) is usually sufficient.

The chief limitation on the reaction is that 1-alkylphosphonyl dichlorides and 1-alkylphosphinyl chlorides cannot be produced except for ethyl and methyl compounds. A 1-haloalkane always rearranges to a sec-alkyl phosphorus compound, except for 1-halo-2-alkylalkanes. These give tertiary-alkyl phosphorus compounds. In general, secondary and tertiary haloalkanes do not rearrange.

This pattern of rearrangement corresponds closely to that found with the Friedel-Crafts Reaction. Alkyl bromides seem to be as useful as alkyl chlorides in most cases. A possible exception is for vicinal dihalo compounds where dehydrobromination may occur but dehydrochlorination is less likely. This author has obtained good yields of 2-chlorocyclohexylphosphonyldichloride from trans-1, 2-dichlorocyclohexane, but the yield of the 2-bromocyclohexylphosphonyl compound was small from trans-1, 2-dibromocyclohexane. There does not appear to be much information on the utility of fluoroalkanes and iodoalkanes.

The Michaelis Reaction

The Michaelis Reaction is a venerable reaction and is discussed in detail by Kosolapoff and for that reason is discussed here only with respect to its use to prepare bifunctional organophosphorus compounds such as -

Two points of technique are extremely important if good yields are to be obtained. First, step (1) must be carried as near to completion as possible so that unreacted dialkyl phosphonate is kept to a minimum. Second, step (2) should not be carried out above room temperature. Even lower temperatures may be desirable. The author has obtained yields of tetraamyl methylenediphosphonate that varied from as low as about 10% to as high as 60% according to the care taken with these points of technique. The literature carries note of these points, but perhaps a restatement is worthwhile.

Dialkylphosphine oxides are also useful starting materials for the Michaelis Reaction. A preliminary search of the literature did not reveal any report of the use of the dialkylphosphine oxides, but such use is a straightforward extrapolation and was suggested by Kosolapoff.

This author believes he has been successful in preparing both dialkyl-N,N-dialkylcarbamyolphosphine oxides and dialkyl-N,N-dialkylcarbamylenephosphine oxides although some of the confirmatory chemical analyses have not yet been obtained. Unfortunately, the di-n-alkylphosphine oxides and their sodium salts are rather insoluble; at present dioxane appears to be the best solvent. The di-sec-alkylphosphine oxides and sodium salts are much more soluble and easier to handle.

The Reaction of Jungermann and McBride⁽¹⁴⁾
and the Reaction of McCormack⁽¹⁵⁾

The general utility of the reaction of Jungermann and McBride has not been established, but it is definitely quite successful in one very interesting preparation (1) and probably in at least one other (2):

Compound (I) is of great interest in the preparation of organophosphorus extractants because: (a) it represents one of very few cases (if not the only case) where there is an easy preparation of a compound with two tertiary carbon atoms linked directly to phosphorus and (b) it contains phosphorus in a four-membered ring with carbon. Compound (I) is easily esterified with a sodium alkoxide to form an ester or reacts with a Grignard reagent to form a phosphine oxide. Compound (I) is readily hydrolyzed to the corresponding acid. Evidently all three types of derivatives might have unusual and interesting characteristics as extractants.

The original authors and this author have made considerable efforts to extend the reaction to a more general reaction with other olefins. Unfortunately the reaction characteristically follows a very complicated course and gives a variety of unidentified products in small yields. Only with trans-4-methylpentene-2 have we been able to obtain a fairly clear-cut preparation (reaction (2) above). Even then the yields are variable (up to about 40%) and very sensitive to the conditions of purification of the product.

The isolation of compound (II) is probably complicated by the fact that isomers are possible. This is indicated by the fact that boiling takes place over a range of about 5°C and that part of the product is a solid at room temperature. However, this is of itself a challenge since it offers a chance to compare the behavior of different isomers as extractants.

This author has not as yet worked with the reaction of McCormack, but it offers the opportunity for preparing a wide variety of organophosphorus compounds that contain phosphorus in a five-member ring with carbon. This reaction has a much wider proven range of usefulness than that of Jungermann and McBride.

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FIG. 1. EXTRACTION OF CERIUM AT 30°C BY VARIOUS BIDENTATES AND BY DIBUTYL BUTYPHOSPHONATE

FIG. 2. EXTRACTION OF CERIUM, PROMETHIUM, AND AMERICIUM AT 30°C BY THREE BIDENTATE EXTRACTANTS

TABLE 1

Extraction of Tracer Uranium,
Plutonium (IV), Zirconium - 3.0M HNO₃ - 30°C

Compound*	Extraction Coefficient		
	Zr	U(IV)	Pu(IV)
Di-n-butyl n-butylphosphonate	0.27	35	24
Di-2-butyl 2-butylphosphonate	0.08	26	12
n-Butyl di-n-butylphosphinate	6.2	176	410
2-Butyl di-2-butylphosphinate	0.33	100	124

* 0.20 molar in n-dodecane

TABLE 2

Distribution Coefficients, D_a^0 : Batch Equilibration^(a)

Organic phase: 1 M reagent in indicated diluent

Aqueous phase: (1) 0.047 U(11 g/liter); 0.021 M Th(5 g/liter);
 1.03×10^7 β counts $\text{min}^{-1} \text{ml}^{-1}$; 1.84×10^7
 γ counts $\text{min}^{-1} \text{ml}^{-1}$; 4.2×10^6 Zr-Nb γ
 counts $\text{min}^{-1} \text{ml}^{-1}$; 6.3×10^5 Ru γ counts
 $\text{min}^{-1} \text{ml}^{-1}$; 8.3×10^6 TRE β counts min^{-1}
 ml^{-1} ; HNO_3 as indicated. (For all tests
 except those with plutonium)

(2) ~ 0.0006 M Pu(0.1-0.2 g/liter); HNO_3 as
 indicated. (For plutonium tests only)

Equal volumes of aqueous and organic phases; 10-min contact;
 motor-driven turbine mixers in open cylindrical separatory
 funnels; room temperature

Element or Activity	Equilibrium Aqueous HNO ₃ (M)	D _a ^o					
		TBP in Amsco 125-82	TBP in Xylene	DSBPP in Xylene	DBPP in Xylene		
U	2.4	21.0	31.5	38.0	52.7		
	0.65	6.2	10.0	16.5	19.4		
	0.18	2.9	4.2	7.5	11.1		
Th	2.4	1.75	1.43	0.16	4.40		
	0.65	0.46	0.36	0.06	0.93		
	0.18	0.13	0.10	0.03			
Gross β	2.4	0.013	0.007	<u>200</u> ^(c)	0.006	0.023	<u>190</u> ^(c)
	0.65	0.017	0.012		0.008	0.016	
	0.18	0.016	0.011		0.009	0.023	
Gross γ	2.4	0.018	0.010	<u>140</u> ^(c)	0.007	0.021	<u>210</u> ^(c)
	0.65	0.017	0.008		0.006	0.015	
	0.18	0.016	0.008		0.007	0.018	
Ru γ	2.4	0.043			0.027	0.034	<u>130</u> ^(c)
	0.65	0.185	0.198			0.060	
	0.18	0.163	0.276		0.250	0.320	
Zr-Nb γ	2.4	0.035	0.031	<u>46</u> ^(c)	0.032	0.053	<u>102</u> ^(c)
	0.65	0.006	0.009		0.006	0.014	
	0.18	0.007	0.012		0.008	0.007	
TRE ^(b) β	2.4	0.018	0.022	<u>65</u> ^(c)	0.045	0.065	<u>68</u> ^(c)
	0.65	0.011	0.037		0.021	0.052	
	0.18	0.007			0.050	0.028	
Pu(IV)	2.0	9.5	17		17	27	
	1.5	4.4	8.5		8.4	14	
	1.0	1.5	3.0		3.0	5	
	0.5	0.21	0.48		0.54	0.9	

(a) Reproduced from reference (6). Calculated separation factors added^(c).

(b) Total rare earths.

(c) Calculated separation factors.

TABLE 3

Extraction of Lanthanides from 12M HNO₃ at 30°C

Compound	Extraction Coefficient	
	Promethium	Cerium (III)
Tri-n-butyl phosphate	0.78	0.13
Tri-2-butyl phosphate	0.048	0.029
Di-n-butyl n-butylphosphonate	1.1	0.25
n-Butyl di-n-butylphosphinate	0.63	0.15
Dibutyl dichloromethylphosphonate	0.039	0.018
Diethyl phenylphosphonate	5.4	1.1
Di-n-butyl phenylphosphonate	2.3	-
Di-2-butyl phenylphosphonate	0.14	0.061
Diethyl benzylphosphonate	0.90	0.29
Dimethyl n-octylphosphonate	4.2	1.1
Diethyl n-octylphosphonate	1.9	--

TABLE 4

A Proposed Typical Flowsheet with
Tetraamyl Methylenediphosphonate (TAMDP)

Feed: 5 volumes of 3.5M HNO_3 , 0.8M $\text{Al}(\text{NO}_3)_3$, 1.5M NaNO_3
Solvent: 1 volume of 50 volume % TAMDP in n-dodecane
Scrub: 1/2 volume of 1.0M HNO_3
Strip: 1 volume of water, three times

Batch equilibrate feed with solvent. Batch scrub separated solvent once with scrub. Batch strip solvent with three separate lots of strip. Optional - replace third strip with 0.1M sodium carbonate. This would improve recovery slightly and wash degradation products out of solvent at same time.

Expected recovery of lanthanides and actinides (III) is 80-90%.