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ORGANO-PHOSPHORUS COMPOUNDS FOR SOLVENT EXTRACTION

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CHEMISTRY DIVISION

ORGANO-PHOSPHORUS COMPOUNDS FOR SOLVENT EXTRACTION

C. E. Higgins, W. H. Baldwin and J. M. Ruth

DATE ISSUED

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ORGANO-PHOSPHORUS COMPOUNDS FOR SOLVENT EXTRACTION

C. E. Higgins, W. H. Baldwin and J. M. Ruth

Summary:

The influence of the structure of phosphate esters on the distribution coefficient of uranium between solutions of these esters in carbon tetrachloride and aqueous nitrate solutions has been studied. Esters of secondary alcohols showed higher distribution coefficients than primary alcohols. Phenyl esters extracted less uranium than alkyl esters, and the presence of other negative groups also resulted in less extraction

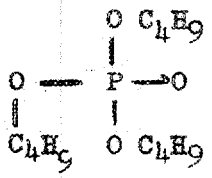
Compounds containing carbon to phosphorus bonds gave higher distribution coefficients than the corresponding esters, and the distribution coefficients increased with the number of such carbon to phosphorus bonds. Tributyl phosphine oxide (with three carbon to phosphorus bonds) showed high distribution coefficients with many salts, including uranyl nitrate, uranyl sulfate, uranyl chloride, thorium nitrate, plutonium (IV) nitrate and some of the fission products in nitrate solution. It is planned to study these and similar compounds further.

INTRODUCTION

Extraction with organic solvents has proven a valuable tool in the separation and purification of certain inorganic materials. The formation of coordination compounds between the solute and solvent requires that the solvent possess structural groups capable of coordination, such as oxygen containing groups. Some solvents known to possess this ability to coordinate are esters, ethers, alcohols, aldehydes, ketones, and those containing nitro groups. Additional requirements on physical and chemical properties, such as volatility, inflammability, viscosity, etc., may limit the usefulness of many organic compounds that have the necessary structural characteristics as far as extraction alone is concerned.

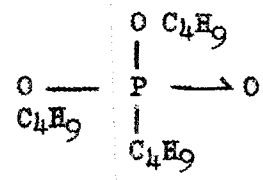
The earlier methods employed for the extraction of uranium from nitrate solutions required the use of salting agents to drive uranyl nitrate into the organic solvent phase. The use of nitric acid as a salting agent in such a process has significant advantages over metallic nitrates, but requires that the solvent be stable toward reaction with this acid. Tributyl phosphate is an organic ester of an inorganic acid that possesses high stability toward reaction with nitric acid and has a high affinity for uranium and other source and fissionable materials. Development work has been extensive with tributyl phosphate because it is commercially available, and it does have desirable properties. The present work was undertaken to study the behavior of tributyl phosphate and to seek other compounds that have more desirable properties. The phosphate molecule has been modified by preparing other esters that have different configurations in the organic chains and by connecting the organic chains directly to the phosphorus rather than through the ester linkage.

The tertiary butyl ester of ortho phosphoric acid has been assigned the structure

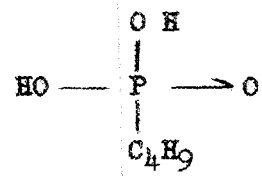


and is known either as tributyl phosphate or simply as butyl phosphate. Partial esters of phosphoric acid likewise are known. The monobutyl ester of ortho phosphoric acid in which there are two ionizable hydrogens is known either as monobutyl phosphoric acid or monobutyl phosphate. Similarly, the dibutyl ester is known either as dibutyl phosphoric acid or dibutyl phosphate.

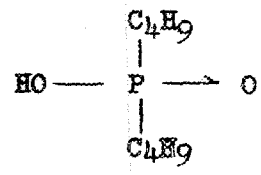
The ester in which one ester linkage has been replaced by a butyl group linked carbon to phosphorus is known as dibutyl butylphosphonate having the structure



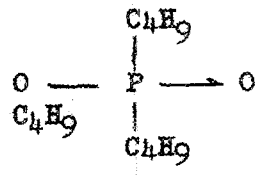
This is the dibutyl ester of butylphosphonic acid having the structure



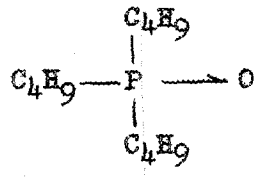
The acid in which two butyl groups are linked carbon to phosphorus is dibutylphosphinic acid with the formula



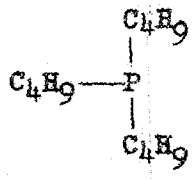
The butyl ester of this acid (butyl dibutylphosphinate) is represented



When all three linkages of the butyl groups are carbon to phosphorus, the resulting compound is tributyl phosphine oxide.



This compound can result from the oxidation of tributyl phosphine.



The trialkyl phosphines are basic compounds that form salts with acids in a manner similar to tertiary amines. However, the tertiary phosphine oxides show none of the basic reactions in aqueous solutions that are exhibited by the tertiary amine oxides.

EXPERIMENTAL

An organic phase (5 ml) consisting of 0.75 molar phosphorus compound dissolved in CCl_4 was equilibrated with 5 ml of an aqueous phase that contained 0.1 molar uranyl salt with or without a salting agent. The standard nitrate system containing 0.1 molar uranyl nitrate and 0.6 molar nitric acid was selected because tri-n-butyl phosphate extracted about 50% of the uranium from such an aqueous phase.

The two phases were equilibrated by tumbling end over end in a constant temperature bath (25 $\pm$ 0.2° C) for 30 minutes in glass stoppered centrifuge cones. The stoppers were greased with fluorocarbon lubricant. At the end of the tumbling period, the tubes were centrifuged immediately, aliquots were removed from each phase and submitted to the Analytical Chemistry Division where the analyses were usually completed within 24 hours.

RESULTS AND DISCUSSION

Extraction with Phosphates -- The trialkyl phosphates prepared from primary alcohols extracted about the same amount of uranium under the conditions of the test (see Table I). Phosphates of the normal alcohols (n-propyl, n-butyl, and n-amyl) and of isobutyl alcohol extracted 54 to 56% of the uranium. Triethyl phosphate extracted less uranium, but this is undoubtedly due to the greater solubility of the ethyl phosphate in water giving an effectively lower concentration in the organic phase. Phosphates of the secondary alcohols (secondary propyl and secondary butyl) extracted a significantly greater amount of uranium in the equilibration (68 and 72% respectively). Insufficient data are available to distinguish the contributions to be expected from steric effects and from electronic effects.

Phosphate esters containing electron attracting groups showed a decrease in the extraction of uranium. This is shown by the results obtained with dioctyl phenyl (11% extracted), octyl diphenyl (0.3%), butyl diphenyl (4%), and triphenyl phosphate (0.004%). Likewise the chlorine atom in trichloroethyl phosphate acts as an electron attracting group, and this solvent showed an extraction of only 5% of the uranium.

Tribenzyl phosphate, in which the phenyl group is farther from the phosphorus atom, gives better extraction than triphenyl phosphate (17.5% compared to 0.004%).

Tertiary esters that contained ether groups in the side chain, butoxyethyl phosphate and two ethyl butoxyethyl phosphate, extracted less uranium than did tributyl phosphate (23%, 33% and 54% respectively.)

Compounds containing carbon to phosphorus bonds in the molecule are listed in Table II and compared with tributyl phosphate in their ability to extract uranium. As the number of carbon to phosphorus bonds in the molecule was increased, the affinity for uranium likewise increased so that over 98% of the uranium was extracted from aqueous uranyl nitrate by the compounds that contained two (butyl dibutylphosphinate) or three (tributyl phosphine oxide) carbon to phosphorus linkages. As expected, the presence of nitric acid increased the extraction of uranium by the various compounds in this series. Some nitric acid was extracted along with the uranium.

The compound dibutyl phenylphosphonate extracted more uranium from 0.6 M HNO_3 than did tributyl phosphate (70% vice 56%). It is of particular interest to compare the behavior of this compound where the phenyl group is connected carbon to phosphorus with the phenyl esters reported in Table I. In general, however, either alkyl or aryl radicals enhance the extraction of uranium when joined directly to phosphorus, over those compounds where the linkage occurs through oxygen.

An approximation of the behavior of the compounds containing carbon to phosphorus bonds toward fission products was made using irradiated uranium that had been dissolved in nitric acid. The distribution of uranium (VI), plutonium (IV) and gross beta and gamma activities were measured after the equilibration of 0.75 molar solutions of phosphorus derivatives in CCl_4 with two sets of aqueous solutions containing respectively 0.1 molar uranyl nitrate alone and 0.1 molar uranyl nitrate plus 0.6 molar nitric acid. Increasing the number of carbon to phosphorus linkages caused increasing extraction of all components (see Table III).

The distribution of thorium nitrate between water and CCl_4 solutions of oxygenated phosphorus compounds has been summarized in Table IV. As the number of carbon to phosphorus bonds increased, the extraction of thorium increased. The phosphinate and phosphine oxide extracted much more thorium (74 and 98%) than did either tributyl phosphate or the phosphonate (3.5 and 18%).

The phosphinate and phosphine oxide extracted 16% and 95% uranyl sulfate from aqueous solution, while the phosphate and phosphonate extracted less than 0.1% (see Table V). The addition of sulfuric acid to the aqueous phase (2 molar) increased the amount of uranium extracted by the phosphinate to 48% and by the phosphine oxide to 96.8%. On shaking phosphine oxide in CCl_4 with an aqueous phase, 0.1 M in uranyl sulfate and 2 M in sulfuric acid, a third phase formed.

The facility with which the phosphinate and phosphine oxide extract uranium from sulfate solutions led to the suggestion that an estimate of the fission product extraction be made. D. E. Ferguson of the Chemical Technology Division compared the fission product extraction by the phosphinate from 0.5 molar aqueous sulfuric acid with the extraction by tributyl phosphate from 0.7 molar nitric acid solution (see Table VI). Under these two sets of conditions, about the same percentages of uranium are extracted. While the phosphinate did extract more fission products from sulfate medium than the phosphate did from nitrate medium (by about a factor of 8 for gross beta), the results are encouraging and warrant further study of the phosphinate in connection with sulfate media.

The phosphinate was found to extract 40% of the uranyl chloride from an aqueous UO_2Cl_2 solution; the phosphine oxide extracted 90% although sometimes a precipitate was formed. When the aqueous phase was made 1 molar in HCl the phosphonate extracted 26% of the uranium, the phosphinate extracted 92% of the uranium while the phosphine oxide caused all of the uranium to precipitate (see Table VII).

Solutions of three of the oxygenated phosphorus compounds in carbon tetrachloride were tested for the extraction of organic and inorganic acids. Tributyl phosphate has been shown to have a high affinity for organic acids that possess high water solubility and can be used to extract acetic, tartaric, and citric acids.(1) The phosphine

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(1) H. R. Pagel, K. D. Schwab, Anal. Chem. 22, 1207 (1950).

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oxide in carbon tetrachloride solution was found to extract not only the organic acids that were mentioned but also nitric and small amounts of phosphoric and hydrochloric acids. Again the phosphinate did not extract as much as the phosphine oxide but did extract some acetic, citric, tartaric and nitric acids (see Table VIII).

Acknowledgment The authors wish to express their appreciation to those members of the Analytical Chemistry Division for their cheerful cooperation in analyzing the samples that were submitted to them.

APPENDIX

SOURCE OF COMPOUNDS

Trialkyl phosphates are generally prepared by the reaction of 3 moles of alcohol with 1 mole phosphorus oxychloride in the presence of 3 moles of pyridine.[2] Phos-

(2) G. R Dutton and C. R. Noller, Organic Syntheses Collective Volume II, p. 109, John Wiley and Sons, New York (1943).

phates were thus prepared from n propyl, sec propyl, sec butyl, iso butyl, and n amyl alcohols.

Triethyl phosphate and tri-n-butyl phosphate were commercial samples that were purified by distillation in vacuo before use.

Tri (n-butoxy ethyl) phosphate, tri (2 ethyl butoxy ethyl) phosphate and tri (2 chloro ethyl) phosphate were obtained from the Carbide and Carbon Chemicals Division of the Union Carbide and Carbon Corporation.

Dibutyl phenylphosphonate was obtained from Victor Chemical Company.

Octyl diphenyl phosphate, di octyl phenyl phosphate, butyl octyl phenyl phosphate, butyl diphenyl phosphate and triphenyl phosphate were supplied by Monsanto Chemical Company.

Dibutyl phosphoric acid was prepared by the alkaline hydrolysis of dibutyl chlorophosphate.[3]

(3) W. H. Baldwin, C. E. Higgins and J. M. Ruth. To be published.

Tri benzyl phosphate was prepared by the reaction of benzyl chloride and silver phosphate.

Dibutyl butylphosphonate was obtained from the reaction of sodium dibutyl phosphite with butyl bromide.[4]

(4) G. M. Kosolapoff, JACS 67, 1180 (1945).

Butyl dibutylphosphinate resulted from the reaction between butyl dichlorophosphate and butyl magnesium bromide.[5]

(5) W. H. Baldwin and C. E. Higgins. To be published.

Tributyl phosphine oxide was prepared by the action of butyl magnesium bromide on phosphorus oxychloride.[6]

(6) W. C. Davies and W. J. Jones, J. Chem. Soc. 33 (1929).

MECHANISM OF EXTRACTION

It has been shown by Moore[7] that in the extraction of uranyl nitrate with

(7) R. L. Moore, HW 15230, Sept. 1949.

tributyl phosphate two molecules of the phosphate are associated with one molecule of uranyl nitrate. Furthermore, the phosphine oxides have been found to form addition compounds of the composition

$$2\ R_3PO \cdot M\ X_2$$

where R_3PO represents a tertiary phosphine oxide and M is a divalent cation.[8]

(8) R. H. Pickard and J. Kenyon, J. Chem. Soc. 89, 262 (1906).

The available evidence points toward the formation of coordination compounds between the phosphoryl group ($\equiv P \rightarrow O$) and a wide variety of salts and acids. The coordination compounds are stronger in those phosphoryl derivatives that have carbon to phosphorus bonds in the molecule and become stronger with more such bonds. The heat of mixing with chloroform has been used as a measure of the hydrogen bonding abilities of some organic phosphorus compounds.[9] Replacement of alkoxy groups by radicals that

(9) G. M. Kosolapoff and J. F. McCullough, JACS 73, 5392 (1951).

are directly bonded to the central atom raises the hydrogen bonding ability. This finding is in direct agreement with the extraction of uranium as reported in this paper.

Data are not yet sufficient to evaluate the relative influence of steric effects and the electronic effects. In the phosphate series, the electronic effects may be noticed in the greater extraction of phosphates of secondary alcohols over the primary alcohols. The steric effects are not known in this series. It is anticipated that the inclusion of other phosphate esters will add valuable evidence, and it is planned to obtain and test a few more phosphates.

A subject that has received little attention so far has been the steric relationships of these materials in solution and the effect of various diluents. These factors should receive additional attention.

TABLE I

Percentage Extractions of Uranyl Nitrate by Phosphate Esters

Organic Phase: 0.75 M Phosphate ester in CCl_4

Aqueous Phase: 0.1 M $UO_2(NO_3)_2$ and 0.6 M HNO_3

Ester	Uranium Extracted %
Tri ethyl	38
Tri n-propyl	54
Tri sec-propyl	68
Tri n-butyl	54
Tri iso-butyl	55
Tri sec-butyl	72
Tri n-amyl	56
Tri (n-butoxy ethyl)	23
Tri (2 ethyl butoxy ethyl)	33
n Butyl diphenyl	4
Tri phenyl	0.004
Di octyl phenyl	11
Octyl diphenyl	0.3
Tri chloroethyl	5
Tri benzyl	17.5
Di butyl phosphoric acid	98

TABLE II

Per Cent Extractions of Uranyl Nitrate by Organo-Phosphorus Compounds

Organic Phase: 0.75 M Compound in CCl_4

Aqueous Phase: 0.1 M $UO_2(NO_3)_2$

	Nitric Acid Concentration				
	0 M	0.6 M		3 M	
	Uranium Extracted (%)	Uranium Extracted (%)	Acid Extracted (%)	Uranium Extracted (%)	Acid Extracted (%)
Tributyl phosphate	11	56	4	96.5	8
Dibutyl butylphosphonate	55	97	6	99.4	11
Butyl dibutylphosphinate	98.5	99.9	15	99.9	14
Tributyl phosphine oxide	99.7	99.9	39	99.9	17
Dibutyl phenyl phosphonate		70			

TABLE III

Extraction of Uranium, Plutonium and Fission Products

Organic Phase: 0.75 M Compound in CCl_4

Aqueous Phase: 0.1 M $UO_2(NO_3)_2$ from dissolving irradiated U slugs in HNO_3 - 6 months cooling

	No Added HNO_3				0.6 M HNO_3			
	U(VI) %	Pu(IV) %	Gross β %	Gross γ %	U(VI) %	Pu(IV) %	Gross β %	Gross γ %
Tributyl phosphate	17.4	0.7	0.01	0.01	58	6.6	0.07	0.08
Dibutyl butylphosphonate	64	1.13	0.05	0.13	97	54	0.72	1.0
Butyl dibutylphosphinate	94	20	1.9	7.9	99.9	98	23	38
Tributyl phosphine oxide	99.9	97.3	37	64	99.9	99.8	72	77

TABLE IV

Per Cent Extractions of Thorium Nitrate by Organo-Phosphorus Compounds

Organic Phase 0.75 M Compound in CCl_4

Aqueous Phase 0.1 M Thorium Nitrate

	Thorium Extracted (%)
Tributyl phosphate	3.5
Dibutyl butylphosphonate	18
Butyl dibutylphospinate	74
Tributyl phosphine oxide	98.7

TABLE V

Per Cent Extractions of Uranyl Sulfate by Organo Phosphorus Compounds

Organic Phase: 0.75 M compound in CCl_4

Aqueous Phase: 0.1 M UO_2SO_4. Acid as indicated.

	Sulfuric Acid Concentration	
	0 M	2 M
	Extracted (%)	Extracted (%)
Tributyl phosphate	0.001% U	0.001% U
Dibutyl butylphosphonate	0.1 % U	0.03 % U
Butyl dibutylphosphinate	16 % U	48 % U
Tributyl phosphine oxide	95 % U	96.8 % U (1)

(1) Three phases were present, two of which were largely aqueous.

TABLE VI

Distribution of Fission Products

Organic Phase: 0.75 molar P compound in CCl_4

Aqueous phase as indicated

	Butyl Dibutylphosphinate	Tributyl Phosphate
	0.5 M H_2SO_4 F. P.*	0.7 M HNO_3 F. P.*
	% Extracted	% Extracted
Gross beta	0.06	0.008
Ru beta	0.3	0.1
Zr beta	0.6	0.001
Total Rare Earth beta	0.0001	0.006

*Fission products from H. E. W. irradiated uranium cooled 100 days.

Data kindly supplied by D. E. Ferguson of the Chemical Technology Division.

TABLE VII

Per Cent Extractions of Uranyl Chloride by Organo-Phosphorus Compounds

	Hydrochloric Acid Concentrations	
	0 M	1 M
	Uranium Extracted (%)	Uranium Extracted (%)
Tributyl phosphate	0.3	0.8
Dibutyl butylphosphonate	1	26
Butyl dibutylphosphinate	40	92
Tributyl phosphine oxide	90 Some precipitate formed	All precipitated

TABLE VIII

Extraction of Acids

Organic Phase: 0.75 M in CCl_4

Aqueous Phase: Approximately 1 normal acid

	Per Cent Acid Extracted						
	Acetic	Citric	Tartaric	HNO_3	H_2SO_4	H_3PO_4	HCl
Tributyl phosphate	25	0	0	7	0	0	0
Butyl dibutyl-phosphinate	49	20	20	27	2	3	0
Tributyl phosphine oxide	58	39	23	39	0	10	7