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M. Zangen[a]; Y. Marcus[a]; E. D. Bergmann[a]
[a] SOREQ NUCLEAR RESEARCH CENTER, ISRAEL ATOMIC ENERGY COMMISSION, YAVNE, ISRAEL AND THE HEBREW UNIVERSITY, JERUSALEM, ISRAEL

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Products of the Reaction between Alcohols and Phosphorus Pentoxide: I. Identity and Extractant Efficiency of the Various Products*

M. ZANGEN, Y. MARCUS, and E. D. BERGMANN
SOREQ NUCLEAR RESEARCH CENTER,
ISRAEL ATOMIC ENERGY COMMISSION,
YAVNE, ISRAEL
AND
THE HEBREW UNIVERSITY,
JERUSALEM, ISRAEL

Summary

The product of the reaction $P_4O_{10} + 4ROH$, where R is an alkyl radical, is known as a powerful and selective extraction agent. It was found to be a mixture of ortho-, pyro-, tri-, and trimetaphosphate esters, produced by alcoholysis of two-thirds of all the P—O—P bonds in phosphorus pentoxide.

The solvent-extraction properties with regard to U(IV) from phosphoric acid, of the various isolated compounds were found to be greatly inferior to those of the mixture, but in a few cases the combination of two compounds yielded distribution ratios comparable to those obtained with the total mixture. It may, therefore, be concluded that the powerful extractant properties of such mixtures is due to synergistic effects.

In the field of uranium production from low-grade sources, one of the hardest problems has certainly been its recovery from technical phosphoric acid. A solvent-extraction system was needed that could overcome the strong complexation of uranium in 4.5 *M* H_3PO_4. In addition, because of the low original concentration in uranium ($4 - 8 \times 10^{-4}$ *M*), the extraction step had to be at the same time a concentration step, i.e., a low organic/aqueous phase volume ratio had to be used. In other words, the process required an extractant of both exceptional efficiency and selectivity for uranium.

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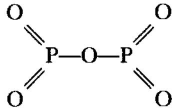
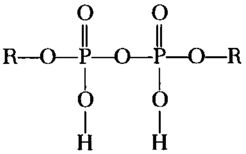
* Part of the Ph.D. thesis of M. Zangen, Hebrew University, Jerusalem, April 1965.

The first (and to date, best) answer to these requirements was provided by Ellis et al. (*1,2*); it was the product obtained by adding 1-octanol to a suspension of phosphorus pentoxide in kerosene, the stoichiometric proportion corresponding to the reaction $P_2O_5 + 2ROH$. The replacement of octanol by other alcohols containing between 8 and 14 C atoms yielded products of similar properties (*3,4*).

In the above publications, the formula P_2O_5 was considered as truly representing the structure of phosphorus pentoxide,



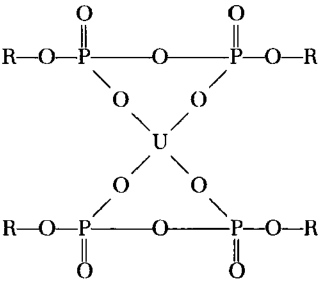
Therefore, the reaction with two molecules of alcohol was explained as the addition of the alcohol on two P=O bonds, yielding



$$\mathrm{R{-}O{-}P({=}O)(OH){-}O{-}P({=}O)(OH){-}O{-}R}$$

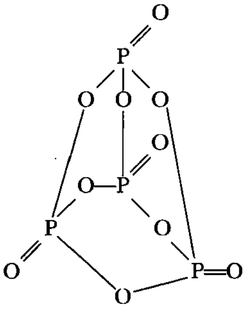
the symmetrical dialkyl pyrophosphate. Hence, in the case when R represents *n*-octyl, the product was called OPPA [(di)octyl pyro phosphoric acid], which has since found widespread use in radiochemical research whenever trace quantities of heavy elements must be extracted from concentrated solutions of Na or Li salts.

The formula of the extracted complex containing "OPPA" and U(IV) was taken as



and several authors (*5–7*) tried to obtain the equilibrium constants governing formation and extraction of this complex. In general, experimental points representing the distribution ratio *D* as a function of "dialkyl pyrosphosphate" concentration in the organic phase, or of phase volume ratio, were rather scattered, which prompted the conclusion that several complex species, of varying stoichiometric U:OPPA ratio, were extracted.

However, the real reason for seemingly conflicting experimental results, both in this case and in reactions of P_2O_5 with water, ethers, and ammonia, is the fact that the real formula of phosphorus pentoxide is P_4O_{10} and its structure is tetrahedral, containing six P—O—P bonds (*8,9*)



Its reaction with alcohols (or water, ethers, or ammonia) does not consist in addition to the P═O bonds, whose number remains unchanged throughout, but in alcoholysis (or hydrolysis, etc.) of P—O—P bonds (*10*). Since the stoichiometric ratio in our case now shows the reaction to be $P_4O_{10} + 4ROH$, this means two-thirds of all P—O—P bonds will be broken. The distribution of the remaining P—O—P bonds, however, remains undetermined.

In order to obtain only the symmetrical dialkyl pyrophosphate, as postulated in previous work (*1–7*), the following conditions would all have to be fulfilled:

1. Every P_4O_{10} molecule in the system should react with four ROH molecules (and not one part of the P_4O_{10} with more and another part with less), to leave two P—O—P bonds unbroken from each P_4O_{10} molecule,
2. Moreover, these two remaining P—O—P bonds should not be

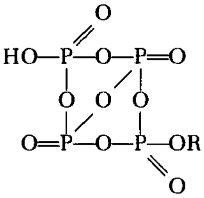
adjacent, or else one orthophosphate and one triphosphate will be obtained instead of two pyrophosphates,

3. In addition, alcoholysis of two out of three P—O—P bonds from each P atom should leave it carrying one —OH and one —OR group (and not two —OH or two —OR), or else the product could be a mixture of all possible pyrophosphate esters.

Unless all three conditions are fulfilled, a mixture of esters must be obtained, as was indeed found (*11*). In the absence of any other effects, the distribution of products in this mixture should depend only on statistical probability; this can be calculated to yield the following compounds (containing the following percentage of total phosphorus in the system):

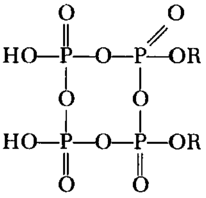
(1) unreacted P_4O_{10} 0.14

(2)



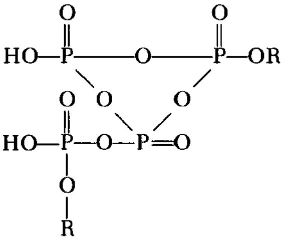
1.65

(3)



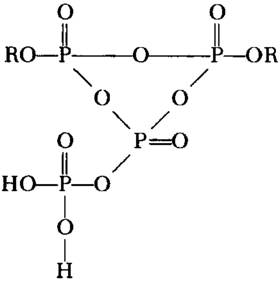
1.65

(4)



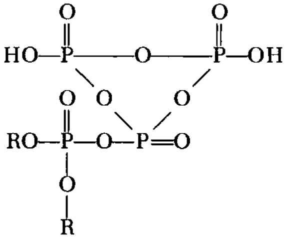
3.29

(5)

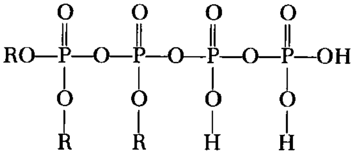


1.65

(6)

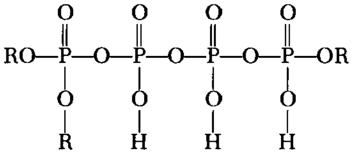


1.65

(7)  3.29

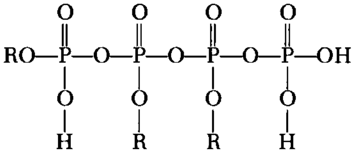
$$\mathrm{RO{-}P(=O)(OR){-}O{-}P(=O)(OR){-}O{-}P(=O)(OH){-}O{-}P(=O)(OH){-}OH}$$

1,1,2-trialkyl tetraphosphate

(8)  3.29

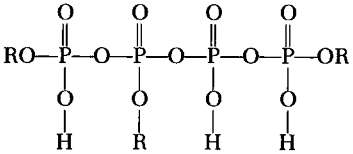
$$\mathrm{RO{-}P(=O)(OR){-}O{-}P(=O)(OH){-}O{-}P(=O)(OH){-}O{-}P(=O)(OH){-}OR}$$

1,1,4-trialkyl tetraphosphate

(9)  3.29

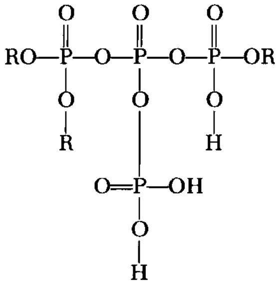
$$\mathrm{RO{-}P(=O)(OH){-}O{-}P(=O)(OR){-}O{-}P(=O)(OR){-}O{-}P(=O)(OH){-}OH}$$

1,2,3-trialkyl tetraphosphate

(10)  3.29

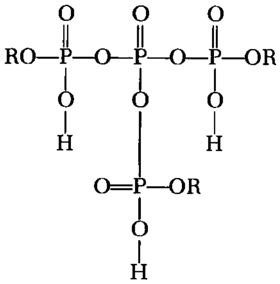
$$\mathrm{RO{-}P(=O)(OH){-}O{-}P(=O)(OR){-}O{-}P(=O)(OH){-}O{-}P(=O)(OH){-}OR}$$

1,2,4-trialkyl tetraphosphate

(11)  3.29

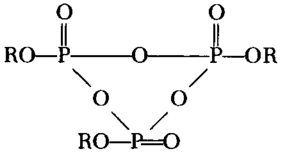
$$\mathrm{RO{-}P(=O)(OR){-}O{-}P(=O)[O{-}P(=O)(OH){-}OH]{-}O{-}P(=O)(OH){-}OR}$$

1,1,2-trialkyl isotetraphosphate

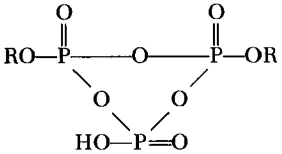
(12)  1.10

$$\mathrm{RO{-}P(=O)(OH){-}O{-}P(=O)[O{-}P(=O)(OH){-}OR]{-}O{-}P(=O)(OH){-}OR}$$

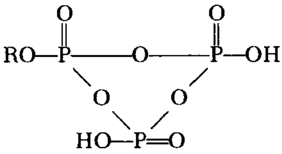
1,2,3-trialkyl isotetraphosphate

(13)  0.41

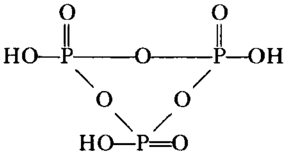
trialkyl trimetaphosphate

(14)  1.23

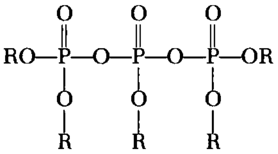
dialkyl trimetaphosphate

(15)  1.23

monoalkyl trimetaphosphate

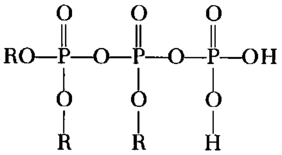
(16)  0.41

trimetaphosphoric acid

(17)  2.47

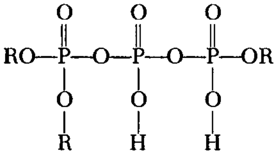
$RO-\underset{OR}{\overset{O}{P}}-O-\underset{OR}{\overset{O}{P}}-O-\underset{OR}{\overset{O}{P}}-OR$

1,1,2,3-tetralkyl triphosphate

(18)  2.47

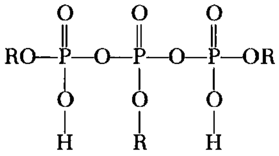
$RO-\underset{OR}{\overset{O}{P}}-O-\underset{OR}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-OH$

1,1,2-trialkyl triphosphate

(19)  2.47

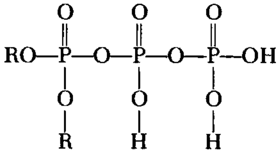
$RO-\underset{OR}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-OR$

1,1,3-trialkyl triphosphate

(20)  2.47

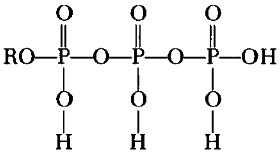
$RO-\underset{OH}{\overset{O}{P}}-O-\underset{OR}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-OR$

1,2,3-trialkyl triphosphate

(21)  2.47

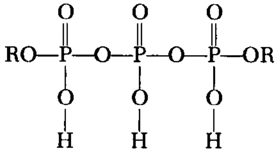
$RO-\underset{OR}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-OH$

1,1-dialkyl triphosphate

(22)  2.47

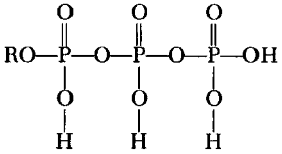
$RO-\underset{OH}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-OH$

1,2-dialkyl triphosphate

(23)  2.47

$RO-\underset{OH}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-OR$

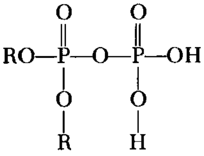
1,3-dialkyl triphosphate

(24)  2.47

$RO-\underset{OH}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-O-\underset{OH}{\overset{O}{P}}-OH$

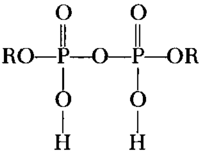
1-alkyl triphosphate

(25) tetraalkyl pyrophosphate 1.23 (26) trialkyl pyrophosphate 4.94

(27) 

$\mathrm{RO{-}P({=}O)(OR){-}O{-}P({=}O)(OH){-}OH}$ 2.47

1,1-dialkyl pyrophosphate

(28) 

$\mathrm{RO{-}P({=}O)(OH){-}O{-}P({=}O)(OH){-}OR}$ 4.94

1,2-dialkyl pyrophosphate

(29) monoalkyl pyrophosphate 4.94 (30) pyrophosphoric acid 1.23
(31) trialkyl phosphate 3.70 (32) dialkyl phosphate 11.11
(33) monoalkyl phosphate 11.11 (34) phosphoric acid 3.70

Steric effects, however, will tend to distribute the —OR groups in a more uniform way, decreasing the total number of products and increasing the proportion of pyrophosphates and of symmetrical compounds. The distribution of broken and unbroken P—O—P bonds and of —OH and —OR groups may be further complicated by induction effects.

The number of compounds formed in the reaction of phosphorus pentoxide with various alcohols (ranging from methanol to heptadecanol) was determined by paper-chromatographic techniques (*11,12*). Column chromatography (*12*), followed by infrared spectrophotometry (*13*) and comparison with organophosphates synthesized by other methods then allowed identification of the various compounds. Finally, in the case of R = *n*-octyl and R = 2,6,8-trimethyl-4-nonyl, the extractant properties of each individual component and of some binary mixtures was investigated.

EXPERIMENTAL

1. *Preparation of the ester mixture.* 100 ml of dry dearomatized kerosene (S.B.P. 80 to 100°) was introduced into a three-necked 250-ml flask and weighed on a balance. Approximately 14 g (~0.05 mole) P_4O_{10} was introduced by way of a broad funnel, held over the central opening of the flask and almost reaching the liquid surface (but not touching the flask); this way, only completely dry phosphorus pentoxide can be introduced. The flask was now weighed again, and a quantity of alcohol stoichiometrically equivalent (according to the reaction $P_4O_{10} + 4ROH$) to the exact quantity of

added P_4O_{10} was introduced in a separatory funnel, fitted to one lateral opening of the flask. The other openings were fitted with a mechanical stirrer and a thermometer, respectively. The alcohol, which had previously been distilled and dried on $CaCl_2$, was added dropwise to the P_4O_{10} suspension in kerosene, under constant stirring, the temperature being kept between 60 and 65°C. After addition of all the alcohol, stirring was continued for 1 hour. The reaction was considered completed on disappearance of both the odor of the alcohol and any remaining solid (unreacted P_4O_{10}).

With alcohols containing up to four carbon atoms, where the obtained mixture of phosphorus compounds was found to be insoluble in kerosene and formed a separate, viscous liquid phase, the second phase was dissolved in acetone or dioxane for further experiments.

2. *Column chromatography* was carried out as described in Part II of this series of reports (*12*).

3. *Extraction experiments* were carried out with the various fractions obtained by chromatographic separation, after the chromatographic solvent was distilled off under vacuum. The organic phase consisted of 0.05 *M* organophosphoric compound in dearomatized kerosene. In the case of binary mixtures, the mixture solution was 0.025 *M* in each organophosphorus compound, since synergistic effects are often most pronounced when the concentration of both extractants is of the same order of magnitude (*14,15*).

TABLE 1

Distribution Ratios

Extractant	*D*	Extractant	*D*
OPPA	89	TNPPA	340
O_1	0.12	TN_1	0.14
O_2	12.3	TN_2	14.0
O_3	0.91	TN_3	2.13
O_4	5.7	TN_4	5.4
O_5	2.8	TN_5	53
O_6	1.9	$TN_1 + TN_2$	19.2
O_7	21	$TN_1 + TN_3$	27.5
$O_1 + O_2$	16.7	$TN_1 + TN_4$	5.6
$O_1 + O_3$	21.8	$TN_1 + TN_5$	290
$O_1 + O_4$	5.4	$TN_2 + TN_3$	25.8
$O_1 + O_7$	83	$TN_2 + TN_5$	93
$O_2 + O_3$	15.2	$TN_3 + TN_5$	109
$O_2 + O_7$	26.6		
$O_3 + O_7$	33		

The mixture of all products from P_4O_{10} + 4ROH (OPPA or TNPPA) used for comparison had an "average" concentration of 0.05 *M*; i.e., this would have been its concentration had it consisted only of the "mean" product $R_2H_2P_2O_7$. The aqueous phase was 4.5 *M* in H_3PO_4 and 4.5×10^{-4} *M* in uranium. The latter was reduced to the tetravalent state by introduction of 0.5 g of iron powder per 100 ml of solution (*4*). The distribution ratio *D* was calculated by fluorometric determination of uranium concentration in both phases (*16*).

RESULTS

The various compounds (in order of separation in the chromatographic element) have been identified (*13*) as for the reaction of P_4O_{10}:

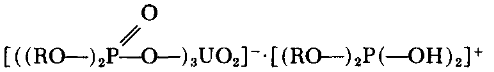
with *n*-octanol:
O_1: trioctyl phosphate
O_2: dioctyl phosphate
O_3: dioctyl pyrophosphate
O_4: monooctyl phosphate
O_5: dioctyl triphosphate
O_6: dioctyl trimetaphosphate
O_7: monooctyl trimetaphosphate

with 2,6,8-trimethyl-4-nonanol:
TN_1: tri(trimethylnonyl) phosphate
TN_2: di(trimethylnonyl) phosphate
TN_3: di(trimethylnonyl) pyrophosphate
TN_4: mono(trimethylnonyl) phosphate
TN_5: mono(trimethylnonyl) trimetaphosphate

The obtained distribution ratios *D* are given in Table 1.

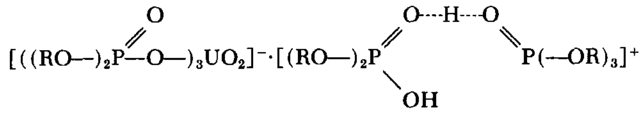
DISCUSSION

It can be seen from Table 1 that each component of the ester mixture is a much weaker extractant than the original mixture. Even the dialkyl trialkyl phosphate mixture, known for its synergistic properties (*17,18*) does not show a substantial increase in *D* as compared to the dialkylphosphate alone. This is not too surprising if we take into account that the synergistic effect of the dialkyl–trialkylphosphate mixture is mainly known in the extraction of hexavalent uranium (species containing UO_2^{2+}), and can be explained (*14*) by the existence of the ion pairs.



$$[((\mathrm{RO}-)_2\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{P}}}-\mathrm{O}-)_3\mathrm{UO_2}]^-\cdot[(\mathrm{RO}-)_2\mathrm{P}(-\mathrm{OH})_2]^+$$

and



$$[((\mathrm{RO}-)_2\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{P}}}-\mathrm{O}-)_3\mathrm{UO_2}]^-\cdot[(\mathrm{RO}-)_2\underset{\mathrm{OH}}{\mathrm{P}}{=}\mathrm{O}\cdots\mathrm{H}\cdots\mathrm{O}{=}\mathrm{P}(-\mathrm{OR})_3]^+$$

Tetravalent uranium, however, is not likely to participate in the negative part of an ion pair and thereby require stabilization of the hydrogen ion (in the positive part) by the trialkyl phosphate ester.

On the other hand, a synergistic effect is manifestly obtained by the addition of trialkyl phosphate to dialkyl pyrophosphate. This possibly may be explained by assuming that the dialkylpyrophosphate is normally highly associated through hydrogen bonds, whereas only the monomer or the dimer are strong extractants. The effect of the trialkyl phosphate should be, then, to break up the association polymers into smaller units, by analogy with one of the mechanisms proposed for the synergistic extraction of protactinium (*19*).

The only compound with extractant properties comparable to those of the original mixture is the monoalkyl trimetaphosphate. However, even this compound does not extract U(IV) quantitatively from phosphoric acid when the organic/aqueous phase volume ratio is 1:10, as in extraction with the OPPA mixture. A marked increase in D is obtained on addition of trialkyl phosphate to monoalkyl trimetaphosphate. Possibly this is again due to a decrease in association of the latter compound. Another possibility is that due to the ring structure of the trimetaphosphate, the oxygens of the P═O bonds are less available for coordination bonds with uranium, and only in a mixed complex also containing trialkyl phosphate does the uranium attain the coordination number 8, the most stable and, therefore, most extractable.

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