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Chemistry - Separation
Processes for Plutonium
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AEC RESEARCH AND DEVELOPMENT REPORT

THE HYDROLYSIS PRODUCTS OF TRIBUTYL PHOSPHATE AND THEIR EFFECT ON THE TRIBUTYL PHOSPHATE PROCESS FOR URANIUM RECOVERY

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By

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THE HYDROLYSIS PRODUCTS OF TRIBUTYL PHOSPHATE
AND THEIR EFFECT ON THE TRIBUTYL PHOSPHATE
PROCESS FOR URANIUM RECOVERY

INTRODUCTION

The use of tributyl phosphate as an extractant for uranium requires a knowledge of its stability and the chemistry of its decomposition products. Inasmuch as tributyl phosphate is an ester, its successive hydrolysis products will be the dibutyl and monobutyl phosphoric acids, orthophosphoric acid and butanol.

In the interest of efficiency and economy of uranium recovery, it is essential to know the effect of such decomposition products on the extraction behavior of uranium and also the possibility of removing such decomposition products from tributyl phosphate prior to recycling.

The tributyl phosphate process for uranium recovery involves the extraction of uranyl nitrate from a high nitrate-salted acid solution to an organic phase composed of normal tributyl orthophosphate diluted by an inert diluent such as high boiling aliphatic hydrocarbons⁽¹⁾ or carbon tetrachloride.

Uranium is recovered from the extractant by a simple water strip. The extraction and stripping operations are performed in countercurrent extraction columns commonly referred to as the RA and RC columns, respectively.

SUMMARY AND CONCLUSIONS

1. Tributyl phosphate hydrolyzes slowly in contact with 3 M nitric acid at 76 and 105° C. at rates of 0.045 and 0.23 % per day, respectively, which are satisfactorily low when extrapolated to column conditions of operation. Dibutyl and monobutyl phosphoric acids exhibit pseudo first-order hydrolysis rates at 76° C. in 3 M nitric acid with half lives of 8 and 18 days, respectively. At 25° C. the hydrolysis of monobutyl phosphoric acid in 3 M nitric acid showed a half life of 300 days which gives a calculated activation energy of ca. 11,400 cal/mole. All of the butyl phosphoric esters were stable in contact with sodium

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hydroxide at 76°C. Tributyl phosphate stability was unchanged by uranyl nitrate and light in the presence of nitric acid, but an approximately neutral uranyl nitrate solutions at room temperature and in the presence of light a slow photo reduction of U(VI) to U(IV) was observed accompanied by the decomposition of tributyl phosphate and the precipitation of uranium(IV) dibutyl phosphate.

2. The density and viscosity at 25°C. of monobutyl and dibutyl phosphoric acid are 1.2195 and 1.0648 and 4300 millipoises and 520 millipoises, respectively. X-ray diffraction powder patterns are tabulated for U(IV) and U(VI) dibutyl phosphate, U(VI) monobutyl phosphate, zirconyl dibutyl phosphate, aluminum dibutyl phosphate, thorium dibutyl phosphate and cerium dibutyl phosphate.

The solubility of dibutyl phosphoric acid was measured from 0-100°C. in water and 1 M, 3 M and 4 M nitric acid. The solubility of water in dibutyl phosphoric is 78 ± 1 g/l from 25-60°C.

The distribution of monobutyl and dibutyl phosphoric acids was measured between aqueous solutions and organic phases such as carbon tetrachloride and 15% TBP in Deo Base; the monobutyl ester is strongly water soluble while the dibutyl phosphoric acid is preferentially organic extracted. Studies of the distribution of U(VI) between 3 M nitric acid and the hydrocarbon, AMSCO 125-90 W, indicate that dibutyl phosphoric acid is a monomer in dilute organic solutions.

3. Monobutyl and dibutyl phosphoric acids form crystalline compounds with uranyl nitrate. The solubility of uranyl monobutyl phosphate at 25°C. in 15% TBP-85% Deo Base and in 1 M nitric acid is 0.08 and 3.3 g U/l, respectively.

The solubility of uranyl dibutyl phosphate at 25°C. in 15% TBP-85% Deo Base and in 1 M nitric acid is 12.1 and 0.16 g U/l, respectively.

A green, crystalline compound of U(IV) dibutyl phosphate, $U[(C_4H_9)_2PO_4]_4$, was prepared, and its solubility in both water and 15% TBP-85% Deo Base found to be very low.

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4. The extraction behavior of U(VI) under RC stripping column conditions was found to be strongly affected by small amounts of dibutyl phosphoric acid, the latter complexing the uranium nearly stoichiometrically into the organic phase.

5. Water or aqueous sodium hydroxide or sodium sulfate solutions proved adequate as scrubbing agents for the removal of 1 g/l quantities of monobutyl phosphoric acid from extractant, RAX. Dibutyl phosphoric acid was satisfactorily removed from RAX by sodium hydroxide or sodium carbonate solutions.

6. Nitration of a tributyl phosphate diluent high in olefin and aromatic content was found to occur in the presence of 3 M nitric acid and 0.01 M nitrite at 60°C.; tributyl phosphate alone was not affected. Nitration products could be readily removed from RAX by scrubbing with sodium carbonate or sodium hydroxide. AMSCO 125-90 W was also found to undergo marked nitration at 105°C. in the presence of 6 M nitric acid.

EXPERIMENTAL AND DISCUSSION

1. Preparation of Monobutyl Phosphoric (MBP) and Dibutyl Phosphoric (DBP) Acids

Tributyl phosphate (TBP) is manufactured by the reaction of n-butyl alcohol and either POCl_3 or P_2O_5 with subsequent treatment with caustic and distillation. Secondary products of this process are the mono (MBP) and dibutyl (DBP) esters of phosphoric acid. An industrial mixture had the following composition: 374 g/l MBP, 787 g/l DBP (cf. Graph I), and unknown small amounts of phosphoric acid and TBP. Two methods of separation and purification were used; the first is suitable for the preparation of small amounts and the second is suitable for large quantities.

Method I.

This method is a modification of the methods described by Crandall⁽²⁾ and Stewart and Hicks.⁽³⁾ One part of the industrial mixture is treated with one part of water and one part of dibutyl ether in a separatory funnel. Phosphoric acid and MBP extract into the aqueous layer while the TBP and DBP remain in the ether layer.

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GRAPH I

TITRATION OF COMMERCIAL MIXTURE
OF n-BUTYLPHOSPHATES (D_4^{25} 1.17)
MOLE RATIO DBP/MBP EQUALS 1.54

MBP is then extracted with ethyl ether and the aqueous layer containing the phosphoric acid is discarded. MBP is then de-etherized and dried by azeotropic distillation with benzene.

The dibutyl ether layer containing the TBP and DBP is washed with 10% sodium hydroxide and the dibutyl ether layer containing any TBP is discarded. The caustic aqueous layer containing the DBP is neutralized with 6 M HCl and the DBP which separates is then water washed. The DBP is then dried by azeotropic distillation with benzene. The recoveries from this mixture by method I were as follows:

Compound	Weight Recovered (Grams)	% Recovered	Molar Solution Obtained	Purity(%) [*]
MBP	150	40	7.86	99.5
DBP	354	45	5.03	99.4

* The impurity is the other butyl phosphoric acid.

Method II

Distribution coefficients (E_a^0) of MBP and DBP between water and carbon tetrachloride were found to be 0.016 and 2.60, respectively.

The above coefficients indicated that countercurrent extraction with the water-carbon tetrachloride system would separate the mixture into the two desired products. A six stage batch countercurrent extraction system was set up with separatory funnels, and the feed plate for the butyl phosphate mixture set at the fourth stage. The feed ratio of butyl phosphate mixture/ CCl_4 /water was 1/4/2. The system gave MBP of 95% purity, and DBP of 99.9% purity. The products of method II were agains dried by azeotropic distillation with benzene.

2. Physical Properties of MBP, DBP and TBP

The determination of the physical properties of butyl phosphoric acids was carried out with 99⁺% purity specimens in all cases and the results shown in Table I. The viscosities were determined with an Ostwald viscosimeter, while the refractive indices were determined with a Bausch and Lomb Abbe' type refractometer. Titration curves for MBP and DBP are given in Graph II.

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Table I

PHYSICAL PROPERTIES

Cmpd.	Color	Mol. Wt.	Density 25/4	Viscosity 25°C. (mp)	pK ₁	pK ₂	Ref. Ind. 20°C.	B. P. 760 mm.
TBP	None	266.3	0.976	33	***	***	1.4245	289
DBP	Pale Yellow	210.2	1.065	520	1.8	***	1.4260	**
MBP	None	154.1	1.220	4300	1.9	6.6	1.4199	**
H ₃ PO ₄	None	98.0	1.870	***	2.1	7.2	****	**

The apparent molar volume of the above series of compounds when plotted against the number of constituent butyl groups as shown in Graph III gives a linear relation which yields a molar volume of 74 ml/butyl group.

3. Chemical Properties of MBP

MBP precipitates a yellow crystalline compound $\text{UO}_2\text{C}_4\text{H}_9\text{PO}_4$ from aqueous uranyl nitrate solutions. This uranyl monobutyl phosphate analyzed as follows: Found: 55.1% U, 23.3% PO_4 ; Theory: 56.4% U, 22.5% PO_4 . The solubility of the uranyl compound at 25°C. is 0.07, 0.08 and 3.3 g/l in water, 15% TBP-85% Deobase and 1 M nitric acid respectively.

The distribution coefficient, E_a^0 , of MBP between an aqueous 1 g/l MBP solution and (1) 100% carbon tetrachloride and (2) 15% TBP-85% carbon tetrachloride is 0.016 and 0.014, respectively. It is concluded from these coefficients that monobutylphosphate resembles phosphoric acid in its solubility in water.

4. Kinetics of MBP Hydrolysis

The hydrolysis of MBP to butanol and phosphoric acid in 3 M nitric acid was followed by using the colorimetric determination of phosphate ion. Solutions were made up to 10 g/l MBP using 99% pure material. Data obtained from the hydrolysis studies at 25°C and 76°C. are given in Table II and Graph IV.

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GRAPH III

PLOT OF MOLAR VOLUME VERSUS
NUMBER OF CONSTITUENT BUTYL
GROUPS GIVES VALUE OF 74 ML
FOR VOLUME OF BUTYL GROUP

Table IIKINETICS OF MBP HYDROLYSIS IN 3 M HNO₃ AT 25 AND 76°C.

25°C.			76°C.		
Time (Days)	PO ₄ ⁻ (g/l)	Residual MBP (g/l)	Time (Days)	PO ₄ ⁻ (g/l)	Residual MBP (g/l)
0	0.05	9.92	0	0.05	9.92
2	0.09	9.85	2	0.43	9.23
7	0.13	9.78	4	0.86	8.54
9	0.17	9.71	5	1.09	8.17
12	0.22	9.64	6	1.31	7.87
23	0.35	9.41	-	-	-

The data of Table II when inserted in the rate expression for first-order reactions gives values for the rate constant, k , at 25°C. and 76°C. of 0.0023 day⁻¹ and 0.0385 day⁻¹, respectively. These two values of k when inserted into the Arrhenius equation give an energy of activation of hydrolysis of 11,400 cal/mole; this heat of activation is comparable to that for the hydrolysis of methyl acetate, i.e., 11,000 cal/mole. The pseudo-first-order half life for MBP at 25 and 76°C. is 300 and 18 days, respectively.

5. Chemical Properties of DBP

The solubility of DBP in water and dilute nitric acid was measured from 0-100°C. by the cloud-point method. The solubility in water was retrograde with temperature whereas the solubilities in nitric acid showed definite minimum values, the temperature corresponding to the minima decreasing with increasing acidity.

The solubility of water in DBP varies but slightly as a function of temperature, decreasing from 79 to 76 g/l as the temperature increases from 25 to 60°C. Data for these solubility measurements are given on Graphs V and VI.

Distribution of DBP in the organic-aqueous systems investigated indicated that DBP favors the organic phase. For example, aqueous 10 g/l DBP

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GRAPH VI

VARIATION OF SOLUBILITY OF WATER IN
DIBUTYLPHOSPHORIC ACID WITH TEMPERATURE

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contacted with 100% carbon tetrachloride and 15% TBP-85% Deobase gave E_a^0 values for DBP of 2.6 and 1.2, respectively. Addition of nitric acid to make the aqueous phase 3 M increased the E_a^0 value to 5.1 with 100% carbon tetrachloride.

A study was made of the effect of DBP on the distribution of uranium in systems simulating points in the RC column. An RAX (15% TBP-85% Deobase) solution containing 0.2 or 1 g/l DBP was equilibrated with equal volumes of aqueous 1 or 10 g/l UNH. The E_a^0 (UNH) values obtained are shown in Table III.

Table III

EFFECT OF DBP ON THE DISTRIBUTION OF UNH IN THE RC COLUMN (25°C.)

Initial Phase Compositions		Final g/l UNH		E_a^0 (UNH)
Aqueous, g/l UNH	Organic, RAX and g/l DBP	Aqueous	Organic	
1	0	1.00	0.002	0.002
1	0.2	0.77	0.32	0.41
1	1.0	0.05	1.02	21
10	0	9.83	0.19	0.02
10	0.2	9.17	0.67	0.07
10	1.0	8.23	1.80	0.22

DBP forms a yellow crystalline precipitate of uranyl dibutyl phosphate, $UO_2[(C_4H_9)_2PO_4]_2$, on addition to aqueous UNH solutions. Heating such a two-phase DBP-aqueous solution on a steam bath yielded a voluminous precipitate which, when filtered, washed, and dried, analyzed as follows: (Found: 33.9% U, 29.5% PO_4 ; Theory: 34.6% U, 27.6% PO_4 .)

Although uranyl dibutyl phosphate is only slightly soluble in water, it is readily soluble in carbon tetrachloride. This suggested its preparation by equilibrating a solution of DBP in carbon tetrachloride with solid UO_3 . This was done and the resulting solution contained 14.6 g/l U and 9.5 g/l PO_4 , equivalent to a PO_4/U ratio of 2:1 in reasonable agreement with the indicated formula. On evaporation the uranyl dibutyl phosphate solution in carbon tetrachloride formed a glass which, on standing, yielded crystals analyzing identically with the product of the first method.

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The solubilities of uranyl dibutyl phosphate in water, 1 M nitric acid, and RAX(15% TBP-85% Deobase) at 25°C. are 0.0026, 0.16 and 12.1 g/l, respectively.

The difference in viscosity between TBP and DBP, 33 versus 520 millipoises at 25°C., respectively, would lead one to suspect that DBP might possibly exist in solution as a dimer. Molecular weight determinations in benzene by freezing point depression give values of 250 (theory 210). If it should have been that DBP exists in solution as the dimer, it would be more difficult to remove by aqueous stripping operations.

A consideration of the equilibria in solution between uranyl nitrate and DBP indicates that in dilute solutions DBP exists nonetheless as a monomer. Aqueous 3 M nitric acid solutions which were also 5 g/l in UNH were equilibrated with AMSCO 125-90 W solutions containing 10, 15, 20 and 25 g/l DBP. If it be assumed that DBP is present as a monomer in AMSCO solutions, then the following expression will hold:

The equilibrium expression derived from this will have the following form:

$$K = \frac{[\text{UO}_2(\text{DBP})_2][\text{H}^+]^2}{[\text{UO}_2^{++}][\text{DBP}]^2} \quad \text{Inasmuch as } (\text{H}^+) = 3 \text{ M and remained essentially}$$

constant in these experiments, E_a^0 for U may be substituted resulting in the following expression:

$$E_a^0 = K(\text{DBP})^2$$

$$\log E_a^0 = 2 \log(\text{DBP}) + \log K$$

Thus, if a plot of $\log E_a^0$ versus $\log(\text{DBP})$, where (DBP) refers to free DBP, gives a straight line with a slope of 2, then the DBP in the organic phase is monomeric and the point where (DBP) = 1 gives the value of the equilibrium constant. Data from the experiment are shown in Table IV and on Graph VII.

Table IV

VARIATION OF $E_a^0(\text{UNH})$ WITH DBP CONCENTRATION

Original DBP in AMSCO (g/l)	Free DBP at Equilibrium (g/l)	$E_a^0(\text{UNH})$	$K (\text{L/M})^{2*}$
25	21	34.0	3351
20	16	17.1	2955
15	11	7.9	2867
10	6	2.5	3131
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* (L/M) = factor to correct grams per liter to moles per liter.

From the constancy of K we can conclude that DBP exists in dilute solutions of hydrocarbon as a monomer.

6. Kinetics of DBP Hydrolysis

To study the rate of hydrolysis of DBP to MBP in 3 M HNO_3 , titration of MBP to the second break has been used to determine MBP. The phosphoric acid formation was followed by colorimetric methods but the formation of phosphoric acid was negligible in comparison with the formation of MBP.

Data derived from the hydrolysis of DBP on a 10 ml. scale are presented in Table V.

Table V

KINETICS OF DBP HYDROLYSIS AT 76°C . IN 3 M HNO_3

Time (Days)	Free PO_4^- (g/l)	MBP (g/l)	DBP Decomp. (g/l)	DBP Remaining (g/l)	% DBP Rem.
0	0.00	0.00	0.00	10.00	100
4	0.038	2.25	3.06	6.94	69.4
7	0.180	3.17	4.34	5.66	56.6
9	0.35	3.86	5.28	4.72	47.2
11	0.37	4.40	6.00	4.00	40.0
14	0.39	4.87	6.65	3.35	33.5
16	0.46	5.35	7.29	2.71	27.1
21	0.56	5.97	8.15	1.85	18.5

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a plot of the above data showing the first-order hydrolysis of DBP and the build-up of phosphoric acid is shown on Graph VIII.

The data in Table V yields a first-order rate constant of 0.0805 day^{-1} , i. e., a half-life of 8.5 days. If an energy of activation comparable to that for the hydrolysis of MBP is assumed, i. e., ca. 11,400 cal/mole, a calculated rate constant of 0.0056 day^{-1} for the reaction at 25°C . is obtained equivalent to a half-life of 123 days.

The value of the rate constant for MBP determined by the previously described experiments may be checked by using the $\text{PO}_4^{=}$ data of Table V in the following manner. For two consecutive first-order reactions:

a moles of DBP hydrolyze to form x moles of MBP at a rate k_1 which then hydrolyze to y moles of phosphoric acid at rate k_2 . If the amount of starting material, a, is known then the amount y formed in time t may be calculated, assuming the rate constants to be known, by the following formula. ⁽⁴⁾

$$y = \frac{ak_2(1 - e^{-k_1t}) - ak_1(1 - e^{-k_2t})}{(k_2 - k_1)}$$

By inserting the values for a, k_1 , k_2 and t, which are 0.000476 moles, 0.0805 day^{-1} , 0.0385 day^{-1} and 21 days, respectively at 76°C ., one obtains 15×10^{-5} moles of phosphoric acid theoretically produced in 21 days; the actual experimental amount found was 6×10^{-5} moles of phosphoric acid. This discrepancy, while a factor of 2.5, shows the values of experimental rate constants to be reasonably compatible within the limits of experimental accuracy in the studies carried out.

7. Kinetics of Hydrolysis of Tributyl Phosphate

The hydrolysis of tributyl phosphate by 3 M nitric acid was studied in equivolume phase ratios of pure TBP and aqueous acid at 76°C . and 105°C . At 76°C . five ml of TBP and five ml of 3 M nitric acid were contacted for ca. 30 days with manual daily shaking. The decomposition of TBP to DBP was not followed; the MBP plus orthophosphate was followed titrimetrically with caustic and the

GRAPH VIII

FIRST ORDER KINETIC PLOT OF HYDROLYSIS OF
DIBUTYLPHOSPHORIC ACID TO MONOBUTYLPHOSPHORIC
ACID IN 3 M NITRIC ACID AT 76°C.

$k = 0.0805 \text{ days}^{-1}$ $t_{1/2} = 8.5 \text{ days}$

Per Cent of Initial DBP Remaining

Grams Per Liter Phosphate Produced

Reaction Time in Days

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orthophosphate alone was followed by phosphomolybdate colorimetric methods. Within the limits of experimental error the amount of dibasic titratable acid was found to be equivalent to the amount of free phosphoric acid determined colorimetrically; hence, the sum MBP plus orthophosphoric acid reduced to merely orthophosphoric acid. This indicated that the rate of formation of phosphoric acid was equal to the rate of decomposition of TBP and that the initial step of hydrolysis to DBP was the rate determining step in the series.

The 76°C. study showed an over-all 1% hydrolysis of TBP to phosphate in a 30 day period at a rate of 0.00045 fraction/day following an eight day induction period; the 105°C. case showed an over-all 2.2% hydrolysis of TBP to phosphate in 13 days at a rate of 0.0023 fraction/day following an induction period of 2 days.

A plot of the 76°C. and 105°C. hydrolysis of TBP by 3 M nitric acid is given on Graph IX and a comprehensive plot of the rates of hydrolysis for the entire series at 76°C. for a first order kinetic rate is given on Graph X.

To determine simultaneously the effect on the hydrolysis rate of variance of both acid concentration and phase volume ratio, pure tributyl phosphate and aqueous 3 M and 6 M nitric acid were refluxed at 105°C. for extended periods of time with phase volume ratios (org/aq) of 1:1 and 1:200. Data for these studies are given in Tables VI and VII.

Table VI

HYDROLYSIS OF TBP BY NITRIC ACID AT 105°C.
WITH EQUIVOLUME PHASE RATIO (100 ml:100 ml)

3 M NITRIC ACID RUN				6 M NITRIC ACID RUN			
Time (Days)	HNO ₃ (M)		TBP Fraction Remaining	Time (Days)	HNO ₃ (M)		TBP Fraction Remaining*
	Aqueous	Organic			Aqueous	Organic	
0	1.5	1.5	1.000	0	2.5	3.5	1.000
6	1.0	1.5	0.993	1	2.5	3.5	0.9996
8	0.9	1.5	0.987	2	2.5	3.0	0.9967
13	0.8	1.5	0.987	6	1.5	3.0	0.9775

* An apparent induction period of one day was observed

Per Cent Initial Tributyl Phosphate Remaining

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Table VII

HYDROLYSIS OF TBP BY NITRIC ACID AT 105°C.

WITH PHASE VOLUME RATIO ORGANIC/AQUEOUS 1:200 (1 ml:200 ml)

Time (Days)	Aqueous HNO ₃ (M)	TBP Fraction Remaining
0	3.0	1.0000
6	3.0	0.400
13	3.0	0.05

A graph of the data in Table VI gives a rate for the hydrolysis of TBP which is first order with respect to nitric acid concentration. If it is assumed that the rate has a first order dependence upon TBP concentration the following expression may be set up:

$$-\frac{d(\text{TBP})}{dt} = k(\text{TBP})(\text{H}^+)$$

Integrating:

$$\ln \frac{(\text{TBP})_t}{(\text{TBP})_i} = -kt(\text{H}^+)$$

where $(\text{TBP})_i$ and $(\text{TBP})_t$ represent the amounts of TBP initially present and remaining after time, t , respectively.

By expanding in a power series and neglecting terms of second order and higher the above expression can be written as follows:

$$(\text{TBP}) = kt(\text{TBP})_i (\text{H}^+)$$

wherein (TBP) now represents the approximate amount of TBP reacted in time t . This expression is general for either phase; giving rate constants for each phase k_a (aqueous) and k_o (organic).

The solubility of TBP in 3 M HNO₃ has been determined in this laboratory to be 0.2, 0.35 and 0.4 g/l at 25, 76 and 105°C., respectively. When this data at 105°C., the data for the 1:1 phase ratio 6 M HNO₃ run of Table VI and the 1:200 organic/aqueous phase ratio 3 M HNO₃ run of Table VII, are substituted into the above derived general equation, a set of six equations results as follows:

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Table VII Data

$$\begin{aligned}(\text{TBP})_1 &= k_a(13)(0.08)(3) \\(\text{TBP})_2 &= k_o(13)(0.97)(4) \\(\text{TBP})_1 + (\text{TBP})_2 &= 0.95\end{aligned}$$

Table VI Data

$$\begin{aligned}(\text{TBP})_3 &= k_a(5)(0.04)(2.5)** \\(\text{TBP})_4 &= k_o(5)(97)(3.5)** \\(\text{TBP})_3 + (\text{TBP})_4 &= 2.2\end{aligned}$$

* The nitric acid solubility in the organic phase is 4.0 M. The volume of the organic phase and thus the amount of TBP decreased from its initial value of course. This is the only such case in this series of experiments and the resulting uncertainty in this equation has little influence on the calculated reaction rate since the organic phase contribution to this rate is quite small in this instance.

** Time t in these equations is taken as 5 days to exclude a 1 day induction period.

Solving these equations for k_o and k_a , values of 0.0012 and 0.28 fraction/day/mole per liter acid, respectively, are obtained.

These foregoing values of the phase rate constants were reinserted in the set of six equations and the values of amounts of TBP decomposed in each phase calculated. These values are shown below in Table VIII and illustrate the effect of change in phase ratio upon location of the predominant amount of TBP hydrolysis.

Table VIII

COMPARISON OF AMOUNTS OF TBP HYDROLYZED
IN ORGANIC AND AQUEOUS PHASES AT 105°C.

<u>Phase Ratio</u>	<u>Organic Phase Decomposition (grams)</u>	<u>Aqueous Phase Decomposition (grams)</u>	<u>Time (Days)</u>
1 ml TBP:200 ml 3 M HNO_3	0.06	0.87	13
100 ml TBP:100 ml 6 M HNO_3	2.10	0.14	5

Data presented on Graph IX when inserted into the Arrhenius equation give a calculated value for the energy of activation of the hydrolysis of TBP in

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the presence of 3 M nitric acid of 14,700 cal/mole. This value is somewhat higher than that found for the hydrolysis of MBP, i.e., 11,400.

The above value for energy of activation for hydrolysis of TBP by 3 M HNO_3 when used to calculate the rate of hydrolysis of TBP in a similar equivolume phase system, at 25°C. yields a rate of 0.0012%/day. This rate would be effective only after an indeterminate induction period if the decrease observed in induction period in changing from 76°C. to 105°C. is significant.

Table IX

VARIATION OF HYDROLYSIS CONSTANTS WITH TEMPERATURE
(Units of k in fraction decomposed per day per M HNO_3)

<u>Temperature (°C)</u>	<u>k_a</u>	<u>k_o</u>
105	0.28	0.0012
76	0.06	0.0002
25	0.004	0.00002

It may be seen that the data in Table IX indicate the rate of hydrolysis in the aqueous phase to be greater than the rate of hydrolysis in the organic phase by a factor of ca. 230. This is off-set by the low solubility of TBP in water so that when the two phases are comparable in volume the "effective" hydrolysis takes place in the organic phase.

It is obvious from the data for the "over-all" hydrolysis of TBP shown on Graphs IX and X that the hydrolysis may be considered to be either zero or first order if one takes into account the short duration of hydrolysis here observed. However, if it is borne in mind that the organic phase serves as a reservoir to keep the aqueous phase constantly saturated with TBP, then the reaction may be reasonably considered to be pseudo-zero order. Further, the order will remain zero order until such time as the reaction has proceeded far enough that the volume of the organic phase remaining falls below the solubility of TBP in the aqueous phase present.

Data herein presented indicate that the "composite half-life" for the hydrolysis of TBP, if calculated on the basis of zero-order kinetics, by 3 M

nitric acid with an organic/aqueous phase volume ratio of 1:1, is 50-100 yrs., 3 years and 7 months at 25°C., 76°C. and 105°C. respectively.

It is to be pointed out that the conditions herein used for these studies are more rigorous than those to be expected in actual plant use of TBP with regard to high temperature, high acid concentration and use of pure extractant instead of extractant dissolved in diluent.

This study of the hydrolysis of TBP is not intended to be represented as an exhaustive one and the results are of low precision. However, the data can be used to determine TBP stability suitable for engineering calculations and to correlate with the previous studies on the butyl acid phosphates. Conversion of TBP stability from these data to a system in which a diluent is used is uncertain, but it is safe to say that a rate calculated from Table IX data would give the upper limit. In general at temperatures of the order of 25-50°C. neither TBP nor diluent should undergo any appreciably rapid decomposition by nitric acid.

8. Removal of MBP and DBP from Diluents by Scrubbing Agents

In order to study the ease of removal of MBP and DBP from extractant, RAX(15% vol. TBP in AMSCO 125-90 W) was spiked with either 1 g/l MBP or 1 g/l DBP. These two samples of spiked RAX were then washed with various aqueous solutions under equal phase volume conditions and the resulting RAX then tested for the spiked additive by measuring the E_a^0 (UNH) after an equilibration with an equal volume of 1 g/l UNH solution. Data for these experiments is given below in Table X.

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Table X

REMOVAL EFFICIENCY OF VARIOUS AQUEOUS SOLUTIONS
FOR SEPARATION OF MBP AND DBP FROM DILUENT

<u>Scrubbing Agent</u>	$E_a^O(\text{UNH at 1 g/l})$ after Scrubbing	
	<u>MBP Spiked</u>	<u>DBP Spiked</u>
10% NaOH	0.0006	0.0001
10% H_3PO_4	0.0170	4.5
10% Na_2SO_4	0.0020	0.28
10% Na_2CO_3	----	0.0008
H_2O	0.0030	0.55
No Spike	0.002	0.002
No Scrub	----	21

From the above tabulated data it may be concluded that water, sodium hydroxide and sodium sulfate are adequate scrubbing agents for MBP. After washing the MBP spiked sample with phosphoric acid a poor material balance resulted because of precipitate formation.

Adequate removal of DBP by scrubbing was obtained only with sodium hydroxide or sodium carbonate, reagents which neutralize the acid and make it organic insoluble and aqueous soluble. The scrubbing of DBP from diluent by various aqueous solutions was extended to the 10 g/l DBP range. Such test solutions were made up in RAX and washed with 10% sodium hydroxide and 10% sodium carbonate. After contacting the washed RAX with an equal volume of 1 g/l UNH solution, values of $E_a^O(\text{UNH})$ were obtained of 0.00005 and 0.00001, respectively. The washing was extended to a single solution which contained the components of uranyl dibutyl phosphate, viz. 10 g/l DBP and 24 g/l UNH; one contacting with 10% sodium carbonate removed the uranium and DBP to the extent that the $E_a^O(\text{UNH})$ between the residual solution and the wash solution was 0.00001.

9. Stability of Diluent

In a previous report (HW-19155)⁽⁵⁾ the nitration of RAX (15% TBP in

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AMSCO 149-92 Br) by 0.01 M HNO_2 and 3 M HNO_3 was described and compared to the "red oil" observed by the Chemical Development Section.⁽⁶⁾ Color formation was not noted with pure TBP. The extraction behavior of nitrated samples of pure AMSCO 149-92 Br and RAX before and after $\text{NaOH} - \text{Na}_2\text{CO}_3$ treatment have been measured under RC column conditions and the results are given in Table XI. The caustic-carbonate treatment gave a colorless product, but did not reduce the E_a^0 of UNH to the value of fresh RAX. Nevertheless, the value of E_a^0 is sufficiently low that adequate uranium recovery would be possible in the RC column.

Table XI

EXTRACTION BEHAVIOR OF NITRATED RAX AND AMSCO 149-92 Br
BEFORE AND AFTER CAUSTIC SCRUBBING

<u>Material</u>	<u>Oxidizing Reagents</u>	<u>Temp (°C.)</u>	<u>Time (Hrs.)</u>	<u>Scrubbing Reagents</u>	<u>Added to Make RAX</u>	<u>RC E_a^o Value</u>	<u>Remarks</u>
AMSCO 149-92 Br	3 M HNO ₃ 0.01 M NO ₂ ⁻	25	50	None	TBP	0.061	Amber color
AMSCO 149-92 Br	3 M HNO ₃ 0.01 M NO ₂ ⁻	25	50	10% Na ₂ CO ₃ 10% NaOH H ₂ O	TBP	0.017	Colorless*
AMSCO 149-92 Br	3 M HNO ₃ 0.01 M NO ₂ ⁻	60	5	None	TBP	0.09	Amber color
AMSCO 149-92 Br	3 M HNO ₃ 0.01 M NO ₂ ⁻	60	5	10% Na ₂ CO ₃ 10% NaOH H ₂ O	TBP	0.006	Colorless*
AMSCO 149-92 Br+ 15% TBP	None	25	--	--	--	0.001	
AMSCO 149-92 Br+ 15% TBP	3 M HNO ₃ 0.1 M NO ₂ ⁻	50	4	--	--	0.046	Amber color
AMSCO 149-92 Br+ 15% TBP	3 M HNO ₃ 0.1 M NO ₂ ⁻	50	4	10% Na ₂ CO ₃ 10% NaOH H ₂ O	--	0.017	Colorless*

* Amber color extracted by caustic which turned red.

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A two phase system (100 ml:100 ml) of RAX (15% TBP-85% AMSCO 125-90 W) and aqueous 3 M nitric acid was refluxed at 105°C. for a period of six days. Decomposition of the nitric acid started as soon as the boiling point was reached and proceeded rapidly until the nitric acid concentrations had changed after six days in the organic phase from 2.0 M to 0.07 M and in the aqueous phase from 1.5 M to 0.5 M.

A nitrogen balance was made on the two phase system and the data are given for this balance in Table XII below:

Table XII

NITROGEN BALANCE ON 3 M NITRIC ACID - RAX SYSTEM

% Original Nitrogen Combined with Organic	28.6
% Original Nitrogen Remaining as Nitric Acid	21.9
% Original Nitrogen Lost to atmosphere (by difference)	49.5

It is shown by Table XII that the AMSCO-125-90 W suffered heavy deterioration at 105°C. and as a result no data for TBP hydrolysis was derived from this experiment. The high per cent of nitrogen lost to the atmosphere is attributed to removal as oxides of nitrogen. The high per cent of nitrogen which combined the AMSCO 125-90 W was unexpected. Previous stability tests on diluents had indicated that only diluents which were high in both aromatic and olefin content would be expected to undergo oxidation by nitric acid at temperatures from 70 - 105°C.

10. Reaction Between Quadrivalent Uranium and DBP To Form

Uranium(IV) forms a green crystalline product with DBP which is insoluble in pure AMSCO 125-90 W, 15% TBP-85% AMSCO, and water. This compound has been produced in these laboratories in two ways, (1) by the reaction between aqueous UCl_4 and pure DBP and (2) the photo-reduction of UNH in pure TBP by fluorescent light.

The compound formed by photo-reduction seemed to have better crystalline properties than the product from direct synthesis, hence it was

chosen for gravimetric analysis. This was justified by the observation that the X-ray diffraction patterns for the two samples were practically identical as shown by data presented in Section 12 of this paper. The following analytical data was obtained for the compound: Found: 35.6% C., 6.81% H.; Theory: 35.75% C., 6.71% H. Uranium and phosphate analyses did not check well because of analytical method development difficulties.

Attempts to determine the variance of E_a^O U(IV) between RAX-DBP $\underline{M}$ and U(IV) $_{aq}$ with change in DBP concentration failed because of precipitate formation. However, data from such experiments are valuable as an estimate of the relative solubility of U(IV)DBP and the data are presented in Table XIII below:

Table XIII

EXTRACTION BEHAVIOR OF U(IV) BETWEEN
15% TBP-85% AMSCO 125-90 W AND WATER
IN THE PRESENCE OF DIBUTYL PHOSPHORIC ACID

<u>Initial Concentration*</u> (Molar)			<u>Final Concentration</u> (Molar)		<u>E_a^O U(IV)</u>
<u>U(IV)$_{aq}$</u>	<u>DBP$_{org}$</u>	<u>Observation</u>	<u>U(IV)$_{org}$</u>	<u>U(IV)$_{aq}$</u>	
0.012	0.00	clear	0.000003	0.011	0.00027
0.012	0.01	clear	0.00013	0.013	0.010
0.012	0.02	clear	0.00026	0.011	0.024
0.012	0.03	green ppt.	0.00088	0.004	0.22
0.012	0.04	green ppt.	0.0031	0.00074	4.19

* equivolume contacting

11. Evaluation of TBP Photodecomposition in the Presence of Uranyl Ion.

Equal volume quantities of 15% TBP-85% AMSCO 125-90 W and 3 $\underline{M}$ HNO_3 acid which was also 10 g/l UNH, were mixed in 25 ml. flasks. These mixtures were maintained either in the dark at 76°C. or under fluorescent light at 25°C. At various times the contents of the flasks were removed and placed

in a contactor where they were intimately mixed and allowed to separate into two phases. The organic phase remaining was contacted with an equal volume of water. These two operations simulated ordinary 1A and 1C operations and values for uranium distribution were obtained from the several phases treated and $E_a^O(\text{UNH})$ values calculated. The data so calculated is shown below in Table XIV.

Table XIV

URANIUM DISTRIBUTION FOR PHOTODECOMPOSITION STUDIES

Time(days)	Dark 76°C.		Light 25°C.	
	$E_a^O(\text{UNH})$ (1A)	$E_a^O(\text{UNH})$ (1C)	$E_a^O(\text{UNH})$ (1A)	$E_a^O(\text{UNH})$ (1C)
0	11.5	0.56	--	(2.0)*
3	> 10.0	1.74	19.0	0.64
8	> 10.0	2.12	--	0.94
13	> 10.0	3.19	--	0.80
17	--	(1.54)	6.7	0.60
21	--	2.81	8.1	0.98
25	> 10.0	5.00	--	(1.70)
28	> 10.0	6.70	15.7	0.74
31	> 10.0	7.61	76.0	0.87
36	> 10.0	9.10	6.52	0.85

The trend in the high temperature 1C column data above illustrates the effect of extractant decomposition while the low temperature 1C data shows no such effect.

In order to evaluate the distribution of UNH in the dilute (0.2 g/l UNH) region, carefully purified U^{233} as UNH was equilibrated between water and 15% TBP in Deobase. A linear relationship of $\log(\text{UNH})_{\text{org}}$ versus $\log(\text{UNH})_{\text{aq}}$ was observed over the range of 0.2-125 g/l in the aqueous phase. (7)

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During the course of these studies, it was observed by I. M. Rehn⁽⁷⁾ that the uranium content of the organic phase in the dilute region increased during prolonged contact and in the presence of fluorescent light. An aqueous solution containing 0.76 g/l UNH and 1.04 g/l HNO_3 in equilibrium with 15% TBP-Deobase gave an E_a^0 (UNH) which increased from 0.0048 to 0.0357 during four hours exposure to ca. 5-10 foot-candles fluorescent light. Similarly, an aqueous 10 g/l UNH solution was contacted with 15% TBP-85% AMSCO 125-90 W for 40 hours in the presence of fluorescent light with an observed increase in E_a^0 (UNH) from 0.0166 to 0.0615.

This photochemical effect was next studied with pure TBP in the absence of hydrocarbon diluent. TBP was contacted for 18 hrs. with an aqueous solution of 10 g/l UNH in the presence of fluorescent light and in a stream of oxygen. An intense deepening of the yellow color in the TBP phase occurred and the distribution of UNH increased toward the organic phase. Spectrophotometric examination of the yellow TBP indicated a modified UNH spectrum similar to uranyl dibutyl phosphate and, in addition, what appears to be a new unidentified organic species. Vacuum distillation yielded a volatile fraction with an ester-like odor and refractive index similar to butylbutyrate. Testing for butanol as reducing normality with dichromate gave negative results whereas the organic phase exhibited considerable reactivity to bromine. After seven days the yellow color in the organic phase changed to green, indicating predominance of U(IV). At eight days a precipitate occurred which when removed and dried consisted of green crystals which analyzed roughly as uranium(IV) dibutyl phosphate and gave an X-ray pattern corresponding to uranium(IV) dibutyl phosphate.

Experiments with TBP contacted with aqueous UNH under irradiation with fluorescent light but with nitrogen sparging gave somewhat different results. The U(VI) changed to U(IV) in ca. one-tenth the above time, but precipitation did not occur until after 30 days of contact.

It has been observed in this laboratory that recycled RAX after careful caustic washing and water scrub would turn from clear colorless liquids to light amber liquids in a few days during storage in clear glass bottles under laboratory

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light. These solutions were found to contain UNH of the order of 0.005 g/l, which might account for the results discussed here.

The significance of this reaction is in connection with the handling and treatment of analytical samples rather than with plant operation since photochemical reactions are unlikely to occur in plant equipment.

It is to be pointed out also that the above photochemical phenomena were observed in essentially neutral solutions; in the presence of 3 M HNO_3 , as shown by data in Tables XIV, the photolytic effect seems to be suppressed.

The stability of nitrite ion in a two phase system of RAX and modified IAF under conditions of dark and light is shown on Graph XI.

12. X-ray Diffraction Patterns for Various Compounds Encountered during this Investigation

The data in the following tables were obtained from Cu K(alpha) X-ray radiation in all cases. The intensity of the various lines is indicated by the following code letters: S, strong; M, medium; W, weak; VW, very weak.

GRAPH XI

DECOMPOSITION OF NITRITE IN TWO PHASE SYSTEM:

Aqueous: 3 M HNO_3 , 10 g/l UNH, 0.01 M HNO_2

Organic: 15% TBP-85% AMSCO (125-90 W) by volume
IN PRESENCE AND ABSENCE OF LIGHT AT 25°C.

A.	B.	C.	D.
Uranyl Acid Phosphate UO_2HPO_4	Uranyl Phosphate $(\text{UO}_2)_3(\text{PO}_4)_2$	Uranyl Dibutyl Phosphate $\text{UO}_2(\text{Bu}_2\text{PO}_4)_2$	Thorium Dibutyl Phosphate $\text{Th}(\text{Bu}_2\text{PO}_4)_4$
<u>d(Angstroms)</u>	<u>d(Angstroms)</u>	<u>d(Angstroms)</u>	<u>d(Angstroms)</u>
8.66 S	10.27 W	14.03 S	10.52 M
5.45 M	8.46 M	11.48 VW	9.07 M
4.92 M	6.12 VW	7.80 S	8.18 W
4.30 M	5.80 W	7.22 W	7.19 M
3.70 M	5.18 M	6.43 W	6.65 VW
3.50 M	4.82 W	5.25 W	5.46 M
3.25 M	4.27 M	4.80 W	4.82 VW
2.95 M	4.20 M	4.11 M	4.33 VW
2.73 VW	3.64 W	3.94 M	4.02 VW
2.69 W	3.53 M	3.77 M	3.69 VW
2.55 W	3.27 W	3.62 W	3.33 VW
2.50 VW	3.07 VW	3.50 M	3.17 VW
2.47 W	2.98 M	3.35 W	2.93 VW
2.37 W	2.93 VW	3.31 W	2.77 VW
2.25 VW	2.81 W	3.16 W	2.63 VW
2.21 W	2.72 VW	3.04 M	2.50 W
2.18 VW	2.61 VW	2.86 VW	2.30 VW
2.13 W	2.49 VW	2.83 M	2.22 VW
2.08 VW	2.43 W	2.70 VW	2.16 VW
2.06 W	2.25 W	2.64 W	2.08 VW
1.99 W	2.21 W		
1.89 W	2.19 W		
1.85 VW	2.12 W		
1.82 W	2.02 W		
1.79 VW	1.94 VW		
1.77 W	1.91 VW		
1.75 W	1.86 W		
1.71 W	1.82 VW		
1.66 VW	1.72 W		
1.65 W	1.64 VW		
1.62 W	1.58 VW		

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E.

Uranium(IV) Dibutyl Phosphate
 E_a (Direct Synthesis) E_b (Photolytic Product)

<u>d(Angstroms)</u>	<u>d(Angstroms)</u>
12.27 W	12.40 W
11.72 W	11.78 W
10.40 VW	10.60 VW
9.60 VW	-
8.11 M	8.12 M
7.25 M	7.17 M
5.47 M	5.48 M
4.90 W	4.86 W
4.31 M	4.33 W
-	3.96 W
3.69 W	3.62 W
3.39 W	3.33 VW
3.13 VW	-

F.

Zirconyl Dibutyl
Phosphate
 $ZrO(Bu_2PO_4)_2$

<u>d(Angstroms)</u>
14.17 M
7.34 W
4.07 W
3.18 W
2.75 M
2.62 S
2.43 W
2.24 M
2.03 W
1.50 VW
1.22 VW

G.

Cerium Dibutyl
Phosphate
 $Ce(Bu_2PO_4)_2$

<u>d(Angstroms)</u>
12.99 S
10.57 M
8.07 W
7.15 M
5.48 M
4.85 W
4.28 M
3.95 W
3.66 W
3.40 W
2.45 VW
2.40 VW
1.94 VW

H.

Aluminum Dibutyl
Phosphate
 $Al(Bu_2PO_4)_3$

<u>d(Angstroms)</u>
11.78 W
9.84 M
7.34 M
5.90 W
5.15 W
4.87 W
4.39 S
4.04 M
3.72 M
3.44 M
3.22 W
2.96 W
2.84 W
2.66 W
2.58 W
2.27 VW

I.

Uranyl Monobutyl
Phosphate
 UO_2BuPO_4

<u>d(Angstroms)</u>
9.11 VW
6.16 VW
4.44 W
3.86 W
3.27 W
1.13 VW
1.07 VW
0.87 VW

J.

Zirconyl Nitrate
 $ZrO(NO_3)_2$

<u>d(Angstroms)</u>
7.95 W
6.70 M
4.69 M
4.07 VW
3.59 VW
3.47 VW
3.23 W

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13. Solubility of Metallic-DBP Compounds in Various Solvents

The dibutyl phosphate of Th(IV), Ce(IV), Al⁺⁺⁺, ZrO⁺⁺ and U(VI) were prepared and their solubility in water, 3 M HNO₃, and carbon tetrachloride determined. The data so obtained is shown below.

Table XVI

SOLUBILITY OF HEAVY METAL DIBUTYL PHOSPHATES

	<u>Water (g/l)</u>	<u>3 M HNO₃ (g/l)</u>	<u>CCl₄ (g/l)</u>
Th(DBP) ₄	0.2	0.2	2.5
Ce(DBP) ₄	0.3	0.9	0.3
Al(DBP) ₃	0.4	2.2	6.4
ZrO(DBP) ₂	1.7	0.6	2.3
UO ₂ (DBP) ₂	0.1	1.9	6.4

The above data were obtained by analysis of the evaporative residue from 1 ml of saturated supernatant from a suspension of the compound in question in each solvent.

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