HW-40910

Chemistry - General

(M-3679, 17th Ed.)

THE CHEMISTRY OF TRIBUTYL PHOSPHATE

A REVIEW

By

L. L. Burger

Chemical Separations Unit
Chemical Research Sub-Section

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. W-31-109-Eng-52 between
the Atomic Energy Commission and General Electric Company

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Chemistry - General
(M-3679, 17th Ed.)

INTERNAL DISTRIBUTION

Copy Number

1	F. W. Albaugh
2	E. L. Burley
3	R. E. Burns
4	R. J. Brouns
5	J. P. Duckworth
6	K. M. Harmon
7	M. K. Harmon
8	O. F. Hill
9	H. H. Hopkins, Jr.
10	E. R. Irish
11	R. H. Moore
12	R. L. Moore
13	G. C. Oberg
14	H. M. Parker
15	A. M. Platt
16	W. H. Reas
17	R. B. Richards
18	R. J. Sloat
19	R. E. Smith
20	R. E. Tomlinson
21	E. E. Voiland
22	M. T. Walling, Jr.
23	J. B. Work
24	L. L. Burger
25	300 Files
26	300 Files - Extra
27	COD, HAPO - Patent Branch, Washington
28	COD, HAPO - Responsible Reviewer, HAPO - Declassification Branch, Oak Ridge
29 - 36	COD, HAPO - Declassification Branch, Oak Ridge

DECLASSIFIED

TABLE OF CONTENTS

TABLE OF CONTENTS (contd.)

LIST OF TABLES

LIST OF FIGURES

THE CHEMISTRY OF TRIBUTYL PHOSPHATE

A REVIEW

I. INTRODUCTION

The attractiveness of tributyl phosphate, TBP, as a process solvent in uranium technology is due to some extent to its chemical inertness. Neither oxidizing nor reducing agents have an appreciable effect at room temperature and its resistance to hydrolysis is extremely high. However, a more detailed study under process conditions, particularly in radiation fields or at high temperatures, indicates that chemical reactions and, in particular, hydrolysis reactions may occur at a rate fast enough to be of concern. Further, the reaction products are particularly objectionable.

The literature on organo-phosphorus chemistry is quite extensive but widely scattered. Wright[1] has made a literature survey of TBP as a uranium extractant and included some chemical properties. The reactions of phosphate esters reported in both unclassified and classified literature are to some extent in disagreement, particularly with respect to the kinetics. Thus it seemed desirable to review this work with the aim of determining and assembling the reliable information available and as a secondary aim to determine what further information is needed.

II. SUMMARY AND CONCLUSIONS

The preparation, purification and chemical properties of TBP have been reviewed with emphasis on the hydrolytic reactions. The latter is supplemented by data on other alkyl phosphates.

TBP is chemically a very stable compound as evidenced by its thermal stability and resistance to oxidation. The most important reactions are hydrolytic which cleave the butyl or butoxy group and normally produce butyl alcohol together with dibutyl and monobutyl phosphate (DBP and MBP, respectively), and eventually phosphoric acid.

(1) Wright, W. B., Critical Literature Survey of Tributyl Phosphate as a Uranium Extractant, Y-838, January 14, 1952.

Hydrolysis occurs in either the organic phase or the aqueous phase and is first order with respect to the ester. Although the rate in the aqueous phase is much faster than in the organic phase, the solubility is so low in aqueous solutions that the organic phase reactions become more important. Acid hydrolysis depends on both the nature of the acid and the concentration. The order with respect to acid concentration is close to one but often less than one. Hydrolysis is catalyzed by both acids and bases. In the latter case, the reaction occurs only in the aqueous phase and normally stops with the formation of dibutyl phosphate.

The hydrolysis rate increases greatly as the temperature is rasied and an activation energy of the order of 20 kcal is often found. The rates observed in the presence of 5 $\underline{M}$ acid at 60 to 70 C may be high enough to cause some concern in solvent extraction technology, since the product, dibutyl phosphate, has undesirable properties.

Impurities produced during manufacture or by thermal degradation during purification such as the pyrophosphates, if present, would yield the same objectionable products as TBP hydrolysis, but at a faster rate.

Included in the survey is a selected tabulation of physical properties of TBP.

Areas which need further investigation and clarification include (1) the relative hydrolysis rates of TBP, DBP and MBP in acid systems, (2) the effect on the hydrolysis of other components in solution, and (3) the mechanism of the hydrolytic reactions. Better analytical methods for DBP and MBP are also needed.

III. CHEMICAL PROPERTIES

A. Thermal Stability

TBP and other phosphate esters are quite stable thermally, but slow degradation does occur at temperatures somewhat above 100 C as evidenced by odor and color formation. Aside from the distillation

studies of Lane[2] discussed in Section VI C, the reaction has apparently not been studied. Decomposition temperatures of acid phosphates and of some condensed phosphates are listed by Adler and Woodstock[3], and are included in Table XVI.

B. Oxidation

Wagner found that TBP was stable toward 0.2 $\underline{M}$ dichromate in 1 $\underline{M}$ nitric acid[4], and dichromate has been found a useful reagent for determining butyl alcohol in TBP[5]. TBP is also relatively stable toward permanganate and treatment with potassium permanganate has been suggested as a purification method for alkyl phosphates[6]. Potassium permanganate in TBP will, however, slowly deposit manganese dioxide from solution after standing for a few days.[7]

The stability of TBP towards Ce(IV) is evidenced by its use by Warf as an extractant for cerium from nitric acid solutions[8]. Work at Harwell indicated no sustained reaction between 60 per cent nitric acid and TBP at 60 C, even when an initial decomposition was started with high energy electrons[9].

(2) Lane, E. S., TBP Purification by Distillation over Alkalies, AERE C/M-140, Feb. 1952.

(3) Adler, H., Woodstock, W. H., Chem. Ind., 51, 516 (1942)

(4) Albaugh, F. W., Monthly Report, Applied Research Sub-Section, October, 1949, Nov. 15, 1949. HW-15074.

(5) Rider, B. F., Selected Analytical Methods for Purex Process Control KAPL-890, April 30, 1953.

(6) Clemmenson, E., U. S. Patent, Chem. Abs. 27, 3944 (1933).

(7) HAPO - unpublished work.

(8) Warf, J. C., Extraction of Ce (IV) Nitrate by Tributyl Phosphate, AECD-2524, Aug. 7, 1947.

(9) Author unknown - Exothermic Reaction Between TBP and Nitric Acid Systems, NP-4900, Sept. 1953.

A vigorous reaction was considered possible only in the presence of a considerable amount of butyl alcohol.

Recent studies by R. H. Moore using nitric acid with added nitrous acid at 70 C also failed to show any sustained reactions with tributyl phosphate. Under the same conditions, the hydro-carbon diluent underwent nitration and oxidation[10]. This observation that the diluent is much more subject to chemical degradation than TBP has been noted by others[11],[12],[13],[14].

At much higher temperatures, TBP does react with nitrates, occasionally with explosive violence. Comprehensive laboratory tests carried out with TBP-uranyl nitrate and nitric acid mixtures were reported by Colvin, Nichols and Siddall[15] and showed:

(1) TBP-uranyl nitrate-nitric acid-water systems will react but not until the temperature has reached 135 C, the boiling point of 78 per cent uranyl nitrate hexahydrate.

(2) A high rate of temperature rise increases the chance of a reaction.

(3) Nitric acid-TBP-water will react violently if heated rapidly to greater than 150 C.

(4) TBP must be present to promote a noticeable exothermic reaction.

---

(10) Moore, R. H., Investigation of Solvent Degradation Products in Recycled Uranium Recovery Plant Solvent, HW-34502 Rev, April 28, 1955.

(11) Dawson, T. L., Lowe, A. R., Tri-n-butyl Phosphate as a Solvent, Parts 1 to 3, RDBW-8048, April, 1953.

(12) Solvent Degradation Meeting-ORNL, CF-52-8-8, Aug. 4, 1952.

(13) Technical Progress Letter-January, 1951, HW-19827.

(14) Quarterly Technical Progress Report-Savannah River Plant, January - March, 1954, DP-55 May, 1954.

(15) Colvin, T. J., Nichols, G. M., Siddall, T. H., TNX Evaporator Incident, January 12, 1953, Interim Technical Report - DP-25, May 15, 1953.

(5) Nitric acid aids the TBP-uranyl nitrate reaction.

(6) The reaction vigor increases as the ratio of TBP to uranyl nitrate increases.

(7) At high pressures, sustained reactions at lower concentrations are possible.

Subsequent work[16] indicated that temperatures for rapid reactions between TBP and nitric acid were 160 C for 22 per cent acid and 130 C for 68 per cent acid, and that the presence of glass wool lowered the temperature required by 30 to 40 C.

At atmospheric pressure, Wagner was able to produce explosive reactions in TBP-uranyl nitrate systems only at temperatures of incipient calcination of the uranyl salt[17].

No work has been reported on the air oxidation of TBP. The flash point (Tag closed cup) of 145 C[18] corresponds to a vapor pressure of about 8 mm mercury, a slightly higher vapor concentration than required for hydrocarbons of equal molecular weight.

Summarizing, TBP is very stable towards oxidation. No sustained reactions have been reported at temperatures of 70 C or below. TBP is stable towards nitrates at temperatures up to 135 C. At higher temperatures, violent decomposition may result probably as a result of nitration of the butyl groups.

C. Substitution Reactions

Lukovnikov[19] using several different esters including TBP

(16) Reference (14), see also Savannah River Laboratory, TNX Semi-works Bi-Weekly Reports, April-June, 1953.

(17) Bushey, A. H., Quarterly Progress Report, Chemistry Unit, January-February-March, 1953. HW-27727. April 30, 1953.

(18) Reactor Science and Technology, Vol. 3, No. 1, March 1953, TID-2008, p. 122.

(19) Lukovnikov, A. F., et al, Doklady Akad. Nauk USSR 70, 43 (1950), Chem. Abs. 44, 4315.

found no exchange with disodium phosphate after 20 to 30 hours
at 100 to 300 C. Dioxane was employed as a solvent. In
phosphoric acid, exchange does occur. Baldwin and Higgins[20]
found that phosphorus-32 initially in phosphoric acid exchanged
with TBP when heated at 170 C for a few hours. P-32 was found
in the TBP as well as in DBP and MBP fractions.

Exchange of alkyl groups between alcohols and alkyl phosphates
occurs readily inder certain conditions. This reaction is
discussed in Section VIB. The labile nature of the alkyl group
is illustrated by the reaction of TBP with benzene in the presence
of aluminum chloride to yield butyl benzene and DBP[21]. As
another example, triethyl phosphate was employed by Ropp[22]
to synthesize C^{14}-labelled ethyl acetate from sodium acetate.

D. Hydrolysis

1. General

As esters, a fundamental aqueous phase reaction of organic
phosphates should be cleavage of the P-O-C linkage, catalyzed
by either acids or bases to give alcohol and the partially
substituted phosphoric acid and eventually ortho-phosphoric
acid. The hydrolytic reactions are the most important
reactions which occur, and it is well to examine the general
nature of this process. The hydrolysis of esters of carboxylic
acids has been studied in detail by Lowry[23], Ingold[24] and
others. This reaction generally leads to fission of the acetyl
carbon bond (analogous to the P-O bond). Blumenthal and

(20) Baldwin, W. H., Higgins, C. E., Chem Div., Semi Annual Progress
Report, ORNL 1674, p. 53. Dec. 20, 1953.

(21) Behrman, Lowry, T., J. Am. Chem. Soc. 60, 2596 (1938).

(22) Ropp, G. A., J. Am. Chem. Soc. 72, 2299 (1950).

(23) Lowry, T., J. Chem. Soc., 1925, 127, 1380.

(24) Ingold, C. K., Structure and Mechanism in Organic Chemistry, Cornell
Univ. Press, Ithaca, N. Y., (1953).

Herbert[25], studying the acid hydrolysis of trimethyl phosphate, found instead that greater than 70 per cent of the decomposition was through the O-C bond rupture. They pointed out that the reaction could more truly be called de-alkylation rather than hydrolysis.

In this respect, the reaction resembles the cleavage of esters with dry halogen acids. Thus Gerrard, Green and Nutkins[26] obtained excellent yields of alkyl halide and dialkyl phosphate using dry hydrogen chloride, hydrogen bromide or hydrogen iodide on tertiary phosphates. This aspect of the reaction is of particular interest, since, as the size of the alkyl group increases, the solubility in water becomes very small and the reactions in the organic phase become more important. Alkaline hydrolysis, on the other hand, appears to occur by fission of the P-O bond as demonstrated by Blumenthal and Herbert[25].

Considerable information is available on the lower alkyl phosphates as a result of their biological interest. These include methyl and ethyl phosphates as well as glycerophosphates, alkoxyphosphates and substituted aryl phosphates. A discussion of this work appears in Section VI D. These compounds, largely aqueous soluble, can offer support in the prediction or interpretation of reactions of the similar molecule, TBP. Selected data are shown in Figure 1.

Pertinent conclusions from the survey of the lower esters include: (1) the hydrolysis is first order with respect to the ester, (2) the triester hydrolyzes 10 to 50 times faster than the diester, (3) in strong acid the hydrolysis rate is greatly

(25) Blumenthal, E., Herbert, J. B. M., Trans. Faraday Soc., 41,611 (1945).

(26) Gerrard, W., Green, W. T., Nutkins, R. A., J. Chem. Soc., 1952, 4076.
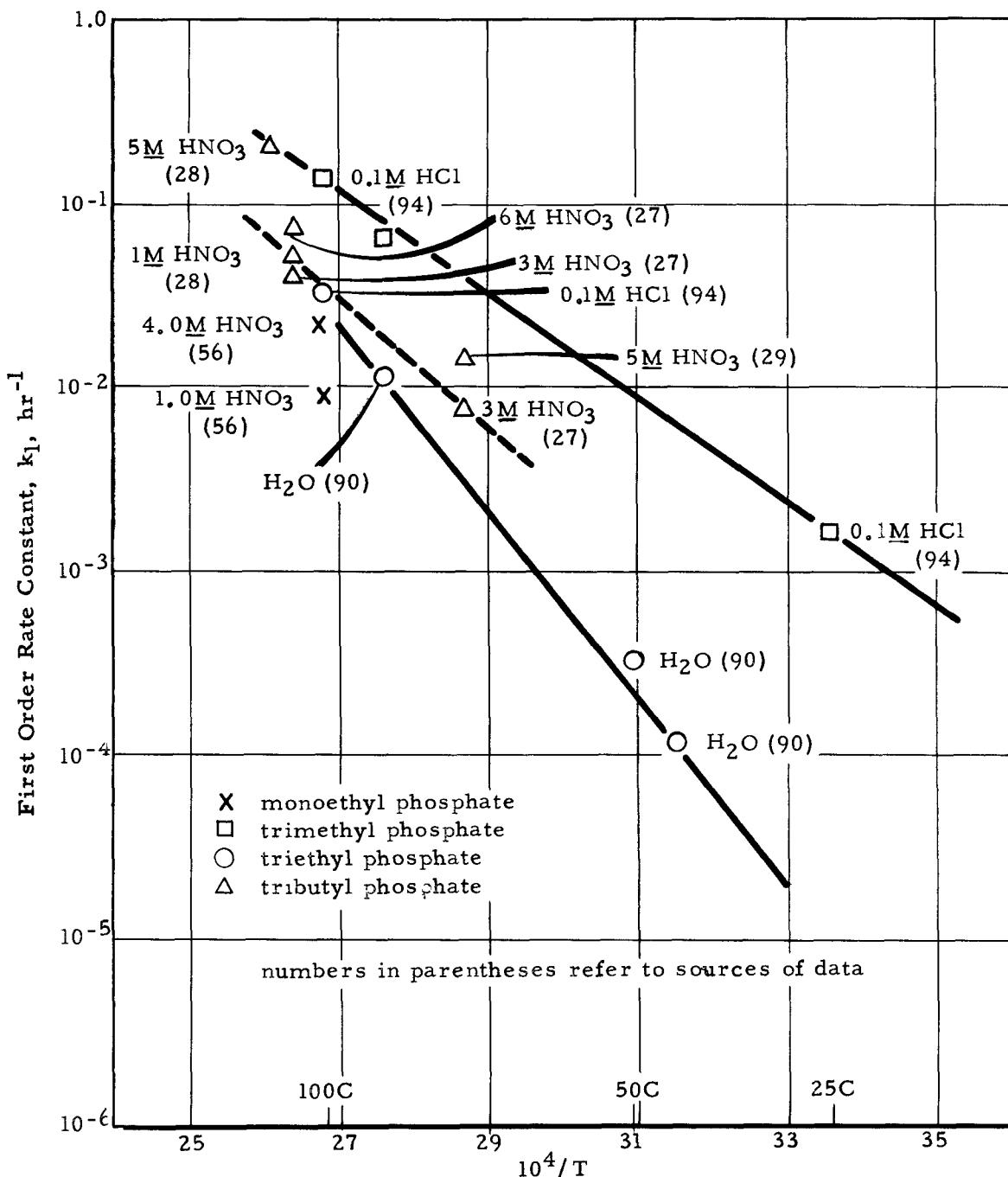
FIGURE 1

SELECTED AQUEOUS PHASE HYDROLYSIS RATES

increased, (4) in strong bases the hydrolysis usually stops at the diester, but occurs at roughly the same rate as acid hydrolysis, (5) in the "neutral" region the rate is very pH dependent, at least for the monoalkyl phosphates and probably for dialkyl phosphates.

The following points must be viewed with considerable uncertainty: (1) in acid solution the monoester hydrolyzes slightly faster than the diester, (2) the resistance to hydrolysis increases with the size of the alkyl group. Only the methyl and ethyl derivatives unambiguously support this often-stated generality. The hydrolysis of diisopropyl phosphate, for example, is somewhat faster than that of diethyl phosphate. (See Table XVII).

With the higher alkyl esters, the first and second hydrolysis products are much more water soluble than the parent ester. Thus aqueous phase reactions as well as those occuring in organic solutions are of interest, and it is of value to consider them separately.

2. Aqueous Phase Hydrolysis of TBP

The information on TBP hydrolysis comes completely from classified sources. The work on this problem has been plagued by the difficulties of working at the low concentrations defined by the solubilities, and the analytical problem of determining the individual hydrolysis products. The situation is made worse by the tendency to examine only that small facet of the problem that deals with a specific plant process, thus providing no comparative basis for the multitude of data.

The available information will be discussed as acid hydrolysis or alkaline hydrolysis.

a. Acid Hydrolysis

The earliest study of this system was that of Wagner[27]

---

(27) Wagner, R. M., The Hydrolysis Products of Tributyl Phosphate and Their Effects on the Tributyl Phosphate Process for Uranium Recovery, HW-19959, April 15, 1951.

who investigated the rate of hydrolysis of monobutyl phosphate (MBP) and dibutyl phosphate (DBP) in 3 $\underline{M}$ nitric acid at 76 C. Writing the reaction as

$$TBP \xrightarrow{k_1} DBP \xrightarrow{k_2} MBP \xrightarrow{k_3} H_3PO_4$$
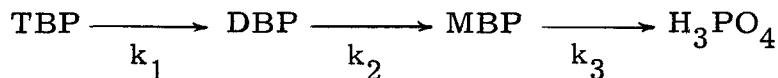
his experiment with MBP gave a first order rate constant, for k_3 of 1.6×10^{-3} hr^{-1}. The experiment with DBP gave a value for k_2 of 3.4×10^{-3} hr^{-1}. However, the data given for the DBP experiment do not confirm the previous value of k_3 but indicate that a value of about 2×10^{-4} hr^{-1} is needed. In view of the poor material balance indicated by the analytical data, one is inclined to disregard the experiment using DBP. His reported values for k_3 of 1.6×10^{-3} hr^{-1} at 76 C and 1.0×10^{-5} hr^{-1} at 25 C are more likely to be correct. The activation energy found for this reaction was 11.4 kcal.

The hydrolysis of TBP was also studied by Wagner [27]. He employed a two phase system with 3 $\underline{M}$ and 6 $\underline{M}$ nitric acid at 76 C and 105 C and phase volume ratios (aq/org) of 1 and 200 with results listed in the following table:

TABLE I

THE HYDROLYSIS OF TBP BY NITRIC ACID

Aqueous Phase: 3 or 6 $\underline{M}$ Nitric Acid

Organic Phase: 100% TBP

Temperature, ^{o}C	k_1 hr^{-1}, aqueous phase	k_1 hr^{-1}, organic phase
105	1.2×10^{-2} *	5.0×10^{-5} *
76	2.5×10^{-3}	8×10^{-6}
25	1.7×10^{-4}	8×10^{-7}

* Wagner's rate constants are expressed per mole of acid assuming first order acid dependence.

His calculation at 105 C involved expansion of an exponential which is invalid for the magnitude of the variables employed. However, more fundamental questions are raised by his assumption that the rate-determining step is the hydrolysis of TBP to DBP and by his conclusion that a determination of MBP and H_3PO_4 represented the TBP decomposed. DBP was never determined. His observation of an induction period further complicates the interpretation. (It seems probable then that the data in Table I do not actually represent step one in the hydrolysis of TBP.)

Lanham and Reilly[28] reported 10 per cent hydrolysis in the aqueous phase at the boiling point after 0.35, 0.55 and 1.9 hours with 8.6, 5.4 and 1.04 $\underline{M}$ nitric acid, respectively. Approximate k_1 values from their data are 0.28 hr^{-1}, 0.19 hr^{-1}, and 0.056 hr^{-1}, respectively. At 60 C in 5.4 $\underline{M}$ acid, a value of 2.9 per cent in 24 hours was found, or a value for k_1 of 1.2 x 10^{-3} hr^{-1}.

Baldwin and Higgins[29] in a single phase study with 5 $\underline{M}$ nitric acid found a value for k_1 of 0.014 hr^{-1} at 75 C. They also reported that the use of 5 $\underline{M}$ hydrochloric acid gave a hydrolysis rate four to five times faster than that with 5 $\underline{M}$ nitric acid. These data are summarized in Table V. Both of the studies at Oak Ridge employed P-32 as a tracer and the analytical results are probably better than the previously discussed work. These data indicate that the TBP decomposition is first order and do not show the induction period reported by Wagner.

b. Acid Hydrolysis with Uranium Present

Measurements of DBP in systems containing uranyl nitrate were

(28) Reilly, V. J., The Hydrolysis of Tributyl Phosphate and its Effect on the Purex Process, ORNL-1138, Dec. 13, 1951.

(29) Baldwin, W. H., Higgins, C. E., Chemistry Division Quarterly Progress Report for Period ending June, 1951. ORNL-1116. Feb. 14, 1952.

made by Brite.[30] TBP and DBP were added to 6 $\underline{M}$, 2 $\underline{M}$ and

0.2 $\underline{M}$ nitric acid solutions containing 0.11 $\underline{M}$ uranyl nitrate.

The following rate constants were computed for the reactions at

the reflux temperature.

TABLE II

HYDROLYSIS RATE CONSTANTS OF BUTYL PHOSPHATES

IN AQUEOUS SOLUTION

Temperature - Reflux, 0.11 $\underline{M}$ $UO_2(NO_3)_2$

Light not Excluded

HNO$_3$ Conc.	Rate Constants, hr^{-1}		
	k_1	k_2	k_3
$\underline{M}$			
6	0.61	0.20	0.14
2	0.112	0.043	0.030
0.2	---	0.014	---

As can be seen from Table II, these values are considerably higher

than those found by others for pure nitric acid solutions. The

reactions were not protected from the light and thus, as pointed

out by Brite, the known photochemical effect in uranium systems

may make the rates high in this experiment. Later work by

Brite has confirmed this.[31] Solutions containing 0.25 $\underline{M}$ uranyl

nitrate, 0.05 $\underline{M}$ nitric acid were shaken with 20 per cent TBP

in Shell Spray Base and the phases separated. The rates of

DBP buildup at 25 C were followed with (a) samples exposed to

laboratory light, (b) samples in amber colored bottles, and (c)

samples in the dark. In three to four days the DBP concentration

in (a) reached a maximum of 19 mg per liter, then dropped

rapidly. In (b) and (c) a very slow buildup of DBP was observed

over the ten day experiment. Assuming the solubility of TBP in a 20

(30) Bushey, A. H., Quarterly Progress Report, Jan., Feb., March, 1954,
     HW-31630, p. 61, May 1, 1954.
(31) Reas, W. H., Quarterly Progress Report, July - Sept., 1954,
     HW-33496, p. 31.

per cent TBP-hydrocarbon mixture to be 7.0×10^{-4} moles/1,[32], and a first order consecutive reaction, it is found that in the absence of light $k_1 = 1 \times 10^{-5}$ hr^{-1} (step two hydrolysis is negligible), and in the light, $k_1 = 5.0 \times 10^{-3}$ hr^{-1}, $k_2 = 2.8 \times 10^{-2}$ hr^{-1}. This calculation for the reaction in the light reveals two very interesting points. The first is that the rate is several hundred times faster than in the dark reaction, and the second is that the second step, the hydrolysis of DBP has changed from a slower step to one which is five times faster than the hydrolysis of TBP. An alternative explanation of the second point is that the aqueous solution was not initially saturated with TBP, since a lower initial concentration would raise the ratio of k_1 to k_2. If one assumes that $k_1 = 3 k_2$ or the apparent ratio from data obtained in the absence of uranium, then it is found that $k_1 = 2 \times 10^{-2}$ hr^{-1} and that the initial concentration of TBP corresponds to 22 per cent of saturation, a possible but unlikely situation. In any case, the observation of a greatly increased rate of hydrolysis in uranium solutions in the presence of light is still valid.

Swanson[33] working with a similar solution investigated the formation of DBP at 50 C. Starting with 0.15 g TBP/1 in a solution of 0.05 $\underline{M}$ nitric acid and 0.25 $\underline{M}$ uranyl nitrate, a series of 12 experiments at 48 C with light excluded showed a linear formation of DBP with time. In 70 hours, 2.2 mg/1 (1.05×10^{-5} moles/1) were formed. The amount of DBP formed represents only about 2 per cent of the initial TBP present. The data obtained are fitted by $k_1 = 3.0 \times 10^{-4}$ hr^{-1}. If the activation energy is assumed to be 14 kcal, (see Section VI D), then at 25 C $k_1 = 6 \times 10^{-5}$, which can be compared to 1×10^{-5} found from Brite's data. The factor of six here could possibly be explained by assuming that the initial TBP concentration in Brite's experiment was below saturation by that amount.

---

(32) Burger, L. L., Forsman, R. C., The Solubility of Tributyl Phosphate in Aqueous Solutions, HW-20936, April 2, 1951.

(33) Swanson, J. L., HAPO, unpublished work.

Data recently reported by Woodfield[34] make possible a further check of the above data. An "RCU" sample containing some entrained TBP was heated at 50 C and the DBP concentration followed for about 50 hours. The data are given in Table III.

TABLE III
Formation of DBP in RCU

RCU = 0.25 $\underline{M}$ $UO_2(NO_3)_2$, 0.05 $\underline{M}$ HNO_3 in H_2O

Temperature - 50 C

Time, hrs.	DBP Concentration	
	Parts per 10^6 parts U	$\underline{M}$ x 10^5
0	36	1.0
8	47	1.32
24	89	2.50
48	130	3.64
54	89	2.50

The DBP concentration in two other samples was followed after first removing the excess organic phase. No detectable difference from the first experiment was found. Since the aqueous phase was saturated, the initial TBP concentration should have been about 7.4 x 10^{-4} $\underline{M}$[32]. As in Swanson's work, less than 10 per cent of the dissolved TBP was destroyed during the time involved.* Thus as long as the excess organic phase volume was small enough, i.e., < 0.1 per cent, such that the organic phase reaction was not significant,** then no difference in the DBP formation should be expected in the three samples.

Values of k_1 = 9 x 10^{-4} hr^{-1}, k_2 = 4 x 10^{-4} fit the data with an uncertainty of about 20 per cent up to 48 hours. The 54 hour point must be questioned, for if k_1 > k_2 then the DBP concentration cannot drop as long as $[TBP] \cong [TBP]_{initial}$. This rate is three times higher than that found by Swanson and about 18 times that extrapolated from Brite's data. The initial TBP concentration appears firmly fixed in

---

(34) Woodfield, F. W., Progress Report, Chemical Development Unit, Sept. 1954, HW-33297, Sept. 30, 1954.

* 120 hours are required to destroy 10 per cent of the TBP if k_1 = 9 x 10^{-4} hr^{-1}.

** See 4-c, p. 32, this section.

Woodfield's experiment. The experimental control and analytical data are probably much better in Brite's and Swanson's work. One can only conclude that the rate constants for DBP formation and destruction in this solution cannot be fixed at present with any degree of certainty. It is suggested that Swanson's data be accepted at the present time. Typical data are shown in Figure 3.

In nitric acid solutions the agreement is a little better, as can be seen in Table V where the TBP data are summarized. There is doubt concerning the nitric acid dependence. The data indicate an order somewhat less than one over the concentration range of 1 to 6 $\underline{M}$ nitric acid.

c. Alkaline Hydrolysis

The alkaline hydrolysis of TBP has been studied only in a two phase system. Kennedy and Grimley[35] observed the rate of hydrolysis of TBP in 1.02 $\underline{M}$ sodium hydroxide from 30 C to 100 C. No difference was found when the organic phase volume was changed, and it was concluded that the reaction occurred only in the aqueous phase. Table IV gives the amount reacted per hour in 100 ml of aqueous phase. The solubility is estimated by the writer, from data given by Burger and Forsman[32] and Kennedy and Grimley,[36] as 0.16 g/l at 30 C from pure TBP and 0.10 g/l from 20 per cent TBP. The rather uncertain 10 to 20 per cent decrease in solubility as the temperature is raised with a minimum around 70 C is ignored for lack of precise data. With these data, the rate constants included in Table IV were computed. The data are plotted in Figure 2. An activation energy of about 18 kcal is indicated. The data for 100 per cent TBP give slightly higher rate constants but probably within the error of the estimated solubilities.

(35) Kennedy, J., Grimley, S. S., Radiometric Studies with Phosphorus-32 Labelled Tri-n-butyl Phosphate, AERE-CE-R-1284, Dec. 18, 1953.
(36) Kennedy, J., Grimley, S. S., Radiometric Studies with Phosphorus-32 Labelled Tri-n-butyl Phosphate, Part I, Solubility and Distribution Studies, AERE-CE-R-1283, Dec. 1, 1953.
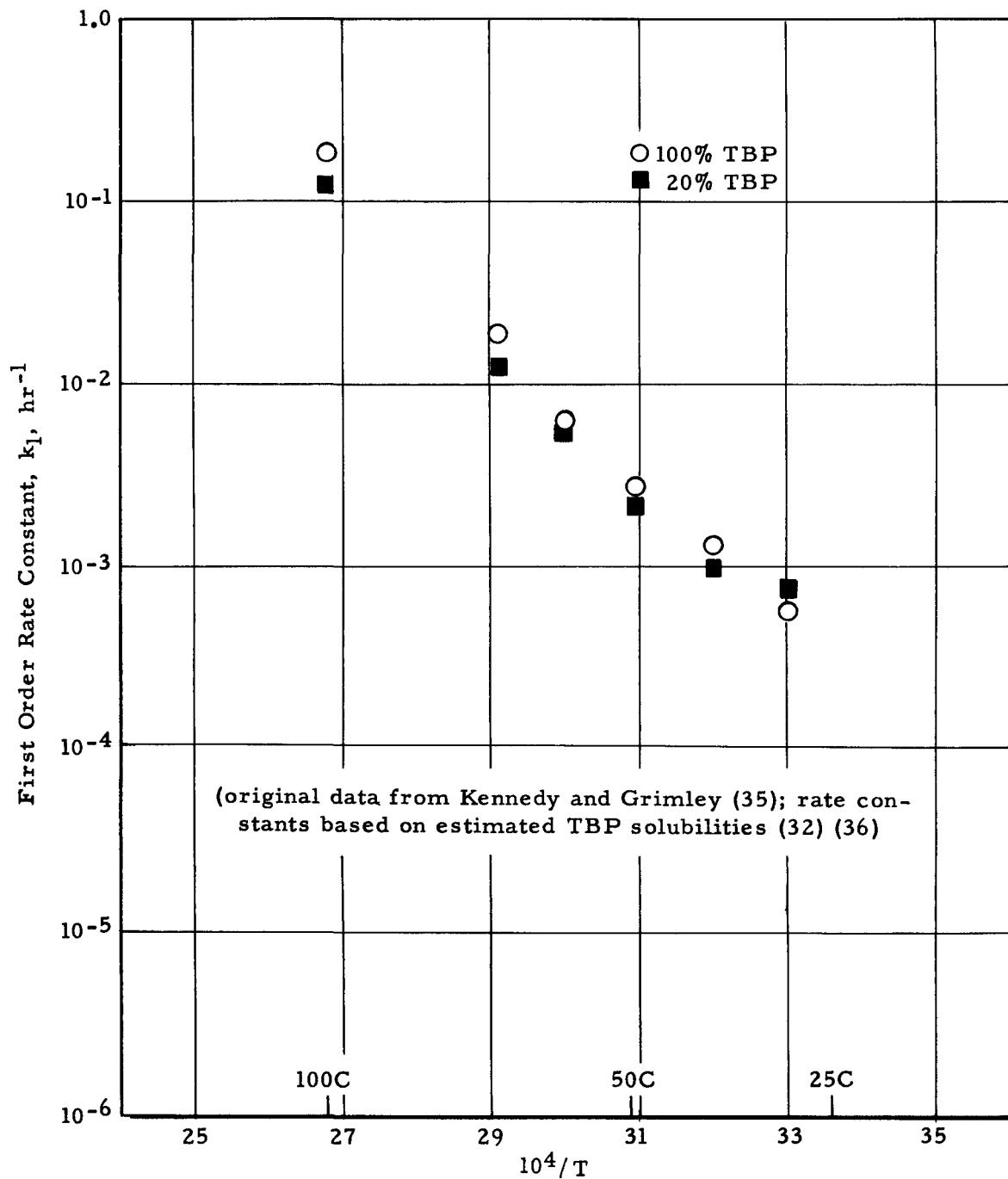
FIGURE 2

HYDROLYSIS OF TBP BY 1 <u>M</u> SODIUM HYDROXIDE

DECLASSIFIED
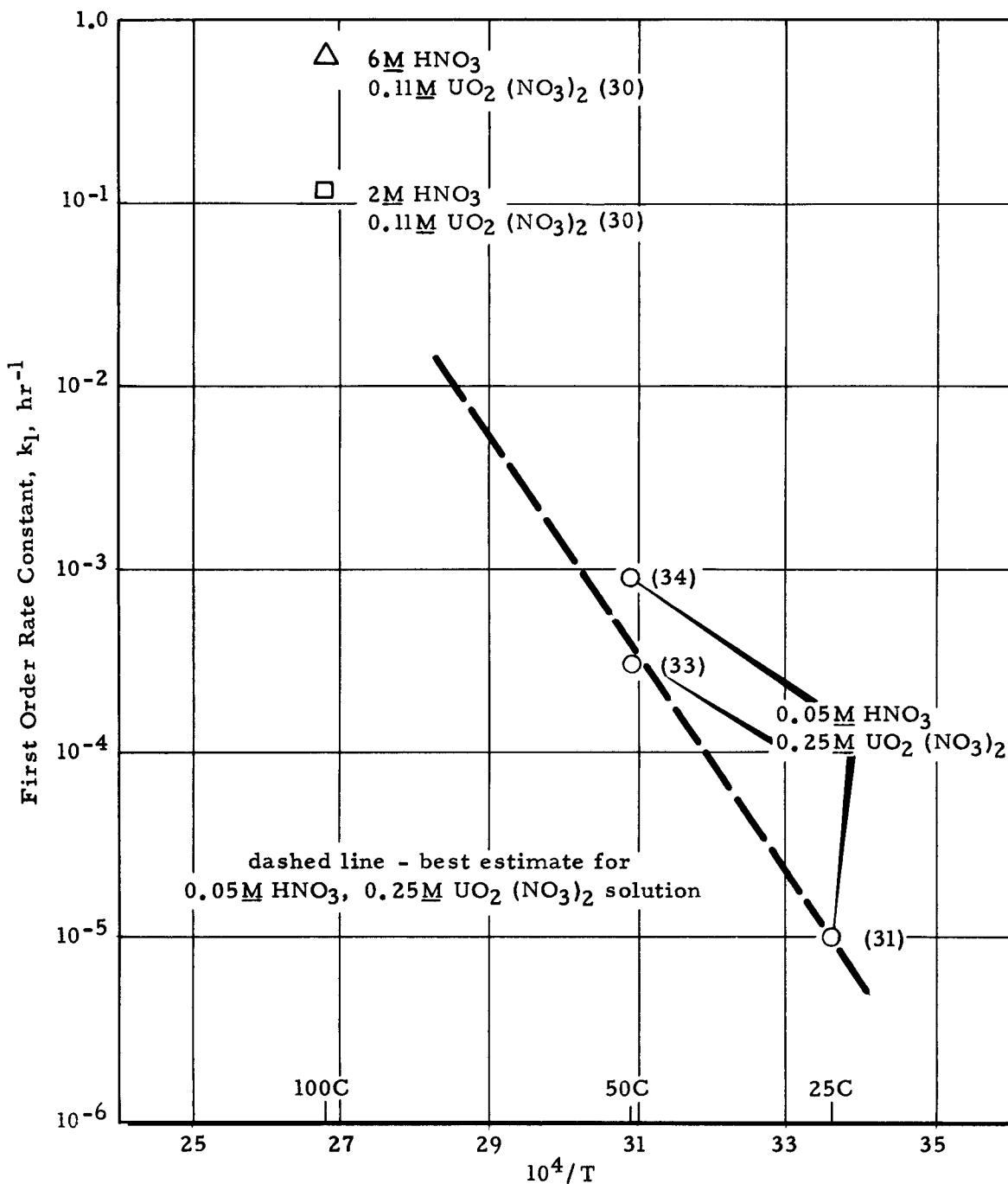
FIGURE 3

AQUEOUS HYDROLYSIS OF TBP (URANYL NITRATE SOLUTIONS)

AEC-GE RICHLAND, WASH.

Pollack[37] has reported results on the hydrolysis of 200 ml of TBP with 200 ml of 10 per cent sodium hydroxide at the boiling point. In four hours 0.148 moles of alcohol were produced.* Since the solubility of TBP at this high caustic concentration is even more uncertain than for the previous case, and since the experiment was complicated by the fact that the mixture was being continually distilled as the reaction progressed, a rate constant was not estimated. However, the observed rate, 419 g/hr TBP reacted per 100 ml of aqueous phase, is over 100 times faster than that observed by Kennedy and Grimley, Table IV.

3. Summary of Aqueous Phase Data for TBP

With the aid of the data on other alkyl phosphates reported in Section VI, the aqueous phase hydrolysis reactions of TBP can be summarized in the following manner:

a. Relative Rates of the Hydrolysis Steps

In the stepwise hydrolysis of the trialkyl phosphate esters, the first stage giving dialkyl phosphate is always more rapid than the second and third steps. In nitric acid solutions or uranyl nitrate solutions, the relative rates appear to be about 4:2:1 for the three steps ending in phosphoric acid. This is supported by the data for triethyl phosphate and trimethyl phosphate. In the region of pH = 2 to pH = 10, the ratio of the rates is unknown. The pronounced effect of pH on the third step showing a maximum rate at pH = 4.0 may be absent with trialkyl esters and may vary appreciably for dialkyl esters. Alkaline hydrolysis is probably more rapid than acid hydrolysis, but the reaction stops at the dialkyl phosphate.

---

(37) Pollack, H., Investigation of the Chemical and Physical Properties of Tributyl Phosphate, DPST-53-41-11, Aug. 19, 1953.

* Other work has indicated, Section VI-D, that alkaline hydrolysis stops the dialkyl phosphate; thus the alcohol produced is equivalent to the TBP reacted.

TABLE IV

HYDROLYSIS OF TBP IN 1 $\underline{M}$ NaOH SOLUTIONS

Source - Kennedy and Grimley[35]

Temp. C	Pure TBP		20% TBP in Kerosene	
	(a)	k_1 hr^{-1}	(a)	k_1 hr^{-1}
30	8.8×10^{-5}	5.5×10^{-3}	7.08×10^{-5}	7.0×10^{-3}
40	1.96×10^{-4}	1.2×10^{-2}	9.59×10^{-5}	9.6×10^{-3}
50	4.37×10^{-4}	2.7×10^{-2}	2.17×10^{-4}	2.2×10^{-2}
60	9.59×10^{-4}	6.0×10^{-2}	5.79×10^{-4}	5.8×10^{-2}
70	3.04×10^{-3}	0.19	1.22×10^{-3}	0.12
100	2.83×10^{-2}	1.78	1.20×10^{-2}	1.2

(a) grams reacted per 100 ml of solution per hour.

    b. <u>Acid Strength</u>

At concentrations between 1 $\underline{M}$ and 6 $\underline{M}$ nitric acid, the reactions are somewhat less than first order with respect to acid concentration, although there is not sufficient data to indicate whether the order is closer to 1/2 or to 1. The order probably increases at higher acid concentrations ($\underline{M} > 6$). This is supported by the data of Desjorbet on triethyl phosphate, Table XXI. As the acidity is lowered the rate, at least for the monoesters, passes through a minimum at about pH = 1, rises to a maximum at pH = 3 to 4 and then drops to an extremely low value at pH=8. The diester might be expected to be pH sensitive but no data are available.

    c. <u>Nature of the Acid</u>

It is reasonably certain that the hydrolysis rates in halogen acids are much higher than in nitric or sulfuric acid. The order for the third step at concentrations of 1 to 5 $\underline{M}$ acid is HI >HBr> HCl > HNO$_3$ $\geqslant$ H$_2$SO$_4$. For the first and second hydrolysis steps, there is no direct comparison; however, as will be seen in Section D-4, there is evidence for the same trend.

d. Uranium and Light

The reactions are accelerated by factors of several hundred if uranium is present and the if systems are exposed to light. Data suggest, but do not prove conclusively, that the rate of DBP destruction is greater than the rate of formation for these conditions.

The hydrolysis rate in 0.25 $\underline{M}$ $UO_2(NO_3)_2$, 0.05 $\underline{M}$ HNO_3 in the absence of light is uncertain, but probable values of k_1 are 4×10^{-5} hr^{-1} at 25° and 4×10^{-4} hr^{-1} at 50°, based largely on Swanson's measurements. These data are shown in Figure 3.

e. The Alkyl Group

The generalization of Kosolapoff[38] that increased radical size increases resistance to hydrolysis is not unequivocably supported. As will be seen later (see Section VI-D) the rule appears to be true in comparing the methyl and ethyl esters. Further, in mixed esters the smaller group is removed preferentially. However, the available data for the ethyl phosphates, propyl phosphates, butyl phosphates and octyl phosphates suggest that there is relatively little difference in stability. Substitution on the alkyl groups leading to greatly different electro-negativities may have much more effect on the stability.

f. Temperature

In acid solution, the activation energy for the first step in the hydrolysis of TBP is of the order of 12 to 14 kcal. This is supported by data on TMP and TEP and also by considerable work on phosphates of biochemical interest (Section VI-D). In strongly alkaline solution, the data of Kennedy and Grimley for TBP hydrolysis give an activation energy of 18 kcal. Since the mechanism may be different in different aqueous solutions, one

(38) Kosolapoff, G. M., Organophosphorus Compounds, New York: John Wiley and Sons, (1950), p. 232.

TABLE V

SUMMARIZED RATE CONSTANTS FOR THE AQUEOUS HYDROLYSIS OF TBP

System	Temp. C.	k_1 [1] hr^{-1}	k_2 hr^{-1}	k_3 hr^{-1}	Reference
8.6 M HNO_3	116	0.32	--	--	(28)
5.4 M HNO_3	108	0.20	--	--	(28)
1.04 M HNO_3	101	0.056	--	--	(28)
6 M HNO_3 0.11 M $UO_2(NO_3)_2$	100	0.61 [2]	0.20 [2]	0.14 [2]	(30)
2 M HNO_3 0.11 M $UO_2(NO_3)_2$	100	0.113 [2]	0.043 [2]	0.030 [2]	(30)
0.2 M HNO_3 0.11 M $UO_2(NO_3)_2$	100	--	0.014	--	(30)
6 M HNO_3	105	0.072	--	--	(27)
3 M HNO_3	105	0.04	--	--	(27)
	76	7.5×10^{-3}	3.4×10^{-3}	1.6×10^{-3}	
5 M HNO_3	75	0.014	--	--	(29)
0.05 M HNO_3 0.25 M $UO_2(NO_3)_2$	48	3.0×10^{-3}	--	--	(33)
0.05 M HNO_3 0.25 M $UO_2(NO_3)_2$	50	9.0×10^{-4}	--	--	(34)

TABLE V (Cont.)

System	Temp. C.	$k_1^{[1]}$ hr^{-1}	k_2 hr^{-1}	k_3 hr^{-1}	Reference
0.05 M HNO_3	25	1.0×10^{-5}	--	--	(31)
0.25 $\underline{M}$ $UO_2(NO_3)_2$		5.0×10^{-3} [2]	0.028	--	(31)
1 $\underline{M}$ NaOH	100	1.78	--	--	(35)
	50	0.027			
	30	5.5×10^{-3}			

(1) Rate constants k_1, k_2, k_3 refer to the first, second, and third steps of the TBP hydrolysis. They are computed as first order constants assuming that the acid concentration remains constant.

(2) Not protected from light.

would not necessarily expect a constant activation energy.
Typical aqueous phase data are shown in Figures 2 and 3.

4. Two-Phase Systems and the Organic-Phase "Hydrolysis"

Since alkaline hydrolysis occurs primarily in the aqueous phase,
for the organic phase only the acid or neutral hydrolysis need be
considered. TBP is only slightly soluble in water and the first
hydrolysis product DBP is nearly all distributed into the organic
phase in the presence of acid.[39] Thus with two-phase mixtures
the non-aqueous reactions may be the more significant.

a. Anhydrous Dealkylation

Reference has been made earlier to the dealkylation reactions
in anhydrous systems. The esters of the phosphorus acids
undergo carbon-oxygen cleavage with mineral acids, a reaction
which is useful in the synthesis of phosphonic and phosphinic
acids. Alkyl phosphates with hydrochloric acid yield alkyl
halides and the acid esters. Although the kinetics of these
reactions have not generally been studied, a typical view of
the rates is given by the work of Gerrard, et al.[26] These
authors employed hydrochloric acid and hydrobromic acid to
dealkylate TBP, triisobutyl phosphate, trisecondary butyl
phosphate and triisooctyl phosphate. Hydrogen chloride gas
passed into TBP and the solution stored for 12 hours at 17 C
yielded 0.43 moles of butyl chloride per mole TBP. However,
a period of three weeks was required, a portion of the time
at elevated temperatures, to obtain 2.75 moles of butyl chloride.

b. Water-Saturated TBP, Neutral Hydrolysis

Dawson and Lowe[11] have investigated the hydrolysis of pure
TBP and TBP diluted with kerosene after saturating with water.

---

(39) Burger, L. L., Partitition of Dibutyl Phosphate, HW-33682, Nov. 8, 1954.

The DBP was estimated by equilibrating with distilled water and measuring the pH of the aqueous phase. Any MBP or phosphoric acid present would be reported as DBP. For the undiluted TBP hydrate they found 0.001 per cent in ten days at room temperature and 0.01 per cent in 24 hours at 100 C. These correspond to rate constants of 2×10^{-7} hr^{-1} and 2×10^{-5} hr^{-1*}, respectively, and an activation energy of 14 kcal.

Dilution of the TBP with four volumes of kerosene reduced the rate to 0.0005 per cent in ten days at room temperature.

In another experiment a sample of the TBP hydrate was heated at 95 to 100 C for 110 hours and titrated with 0.1 $\underline{M}$ sodium hydroxide. MBP was indicated by the pH curve and phosphoric acid was found gravimetrically. The results given in the text of the report are 0.011 per cent DBP, 0.003 per cent MBP and 0.012 phosphoric acid*. These numbers give a rate constant for TBP decomposition of $k_1 = 1.1 \times 10^{-5}$ hr^{-1}. However, if one uses the data directly from the titration plot and assumes that the "5 ml of TBP hydrate" represents pure TBP and not the 20 per cent dilution, one obtains $k_1 = 2.2 \times 10^{-5}$ hr^{-1}, in good agreement with the pH method given above.

c. <u>Hydrolysis with Acid Present</u>

Since the successive hydrolysis products of any of the alkyl phosphates become more and more organic insoluble, and it is difficult to follow the reactions without the separation of a second phase, most of the work on the organic phase reactions of TBP has been in two phase systems.

Wagner's work included several two phase systems, some of which were discussed earlier in this section. The reaction

---

*Dawson and Lowe report percentages referred to 20 per cent TBP in kerosene. Hence, a factor of five must be included to convert to k values as given in the present report.

between TBP and 3 $\underline{M}$ nitric acid in equal volumes was observed
at 70 C and 105 C. No MBP was found. At 76 C he reported
one per cent hydrolysis in 30 days and at 105 C a 2. 2 per cent
hydrolysis in 13 days. In both cases an induction period of
several days was observed. His conclusion that the initial
step, TBP→DBP, was rate determining is not sound since
the DBP concentration was never determined. There are
insufficient data to permit calculation of individual rate con-
stants. His other experiments with 3 $\underline{M}$ nitric acid at 1:1 phase
ratios and 200:1 aqueous to organic ratios and with 6 $\underline{M}$ nitric
acid were mentioned in Part 2 of this section. Recalculation
of k_1 for the organic phase for these experiments places k_1
in the region $3. 4 \times 10^{-5}$ hr^{-1} $(mol\ HNO_3)^{-1}$ to $2. 5 \times 10^{-4}$ hr^{-1}
$(mol\ HNO_3)^{-1}$ at 105 C with a probable value of about 1×10^{-4}.
It is virtually impossible to evaluate rate constants from the
data at 76 C since only phosphoric acid was determined.

Among the best data available are those of Kennedy and
Grimley.[35] Phosphorus-32 was used to permit determination
of the products radiometrically. The hydrolysis of TBP as a
function of temperature, acid present, phase volume ratio and
dilution of the TBP was studied. The reaction times and
phase volume ratios were chosen such that the TBP concentration
could be considered constant and the aqueous concentration of
acid was not changed by extraction. Experiments with different
volume ratios indicated that the degradation was independent
of the volume of the aqueous phase. The contribution of the
aqueous phase was therefore negligible, and the fraction decom-
posed per unit time can be considered a rate constant for the
organic phase hydrolysis. Their data are reproduced in full
in Table VI. First order rate constants may be taken as these
values divided by 100.

TABLE VI

TBP HYDROLYSIS AS A FUNCTION OF TEMPERATURE

Kerosene Diluent
Per Cent TBP Reacted per Hour
Kennedy and Grimley[35]

Temp. C.	1 M HCl	1 M HNO$_3$		5 M HNO$_3$	
	Pure TBP	Pure TBP	20% TBP	Pure TBP	20% TBP
21	--	--	0.583	2.54	1.0
30	3.92	1.42	1.08	7.08	1.71
40	6.79	3.33	2.63	--	--
50	20.5	12.1	4.79	55.0	84.1
60	86.2	27.1	12.5	192.0	32.3
70	347.0	105.0	22.9	421.0	--
100	950.0	--	--	--	--

In addition, there is reported at room temperature, ($\sim 20\,C$) in contact with 8 $\underline{M}$ nitric acid a rate for pure TBP of 4.1×10^{-4} per cent hr^{-1} and for 20 per cent TBP, 1.3×10^{-4} per cent hr^{-1}. These workers state that at constant acidity at 30 C the difference in reaction rate, is roughly proportional to the product of TBP concentration (or solvent acidity) and the activity coefficient (~ 2.6) of TBP in 20 per cent TBP*.

The actual acid concentration in the organic phase varies with both the TBP concentration and the aqueous acid concentration. Table VII lists these concentrations (HAPO data). If the above rate constants at 30 C are divided by the actual nitric acid concentration in the organic phase, the data listed in the last column are obtained. It is seen that in the case of 1 $\underline{M}$ nitric acid, the activity coefficient correction is reasonable and in the

---

*The activity coefficient is based on the solubility of TBP in water from 20 per cent TBP referred to the solubility of pure TBP.

case of 5 $\underline{M}$ acid, it is not. An interesting result from this
latter comparison is the much higher rate, per unit acid con-
centration, in the case of hydrochloric acid. This supports
the aqueous phase data of Baldwin and Higgins.[29] Activation
energies calculated from the data have the following values:
100% TBP - HCl, 29 kcal; 100% TBP-HNO$_3$, 21 kcal; 20%
TBP-HNO$_3$, 14 kcal. From the smoothed curves, estimated
rate constants in 20 per cent TBP at 25 C for contact with 1 $\underline{M}$,
5 $\underline{M}$ and 8 $\underline{M}$ aqueous solutions of nitric acid can be given as
7.2×10^{-7}, 1.2×10^{-6}, and 2×10^{-6} hr^{-1*}, respectively. At
50 C corresponding values would be 5.6×10^{-6}, 1.0×10^{-5} and
1.4×10^{-5} hr^{-1}.

TABLE VII

ORGANIC RATE CONSTANTS BASED ON UNIT ACID CONCENTRATION

Temperature, 30 C

	Acid	Acid Conc. mol/l		k per mol acid hr^{-1}
		Aq.	Org.	
100% TBP	HCl	1	0.05	7.8×10^{-5}
	HNO$_3$	1	0.86	3.9×10^{-6}
	HNO$_3$	5	2.52	2.8×10^{-6}
20% TBP	HNO$_3$	1	0.14	7.7×10^{-6}
	HNO$_3$	5	0.67	2.8×10^{-6}

From Table V or Figure 1, the best value of k_1 for the
aqueous phase hydrolysis in 5 $\underline{M}$ nitric acid is 7×10^{-4} hr^{-1}
at 30 C. Thus it is seen that the ratio of the rate constants
for the aqueous phase and for the organic phase (pure TBP) is

---

*The value for 8 $\underline{M}$ is uncertain since the exact temperature was not specified.
A temperature change of 5 C is equivalent to a change of about 30 per cent
in k.

about 100, which when multiplied by the ratio of TBP concentra-
tions in the two phases $\frac{4.1 \times 10^{-4}}{3.50}$, gives 1.2×10^{-2}. Thus
for pure TBP in contact with an equal volume of aqueous 5 $\underline{M}$
HNO_3, 99 per cent of the reaction occurs in the organic phase.
With 1 $\underline{M}$ acid about 97 per cent would occur in the organic
phase. In acid hydrolysis in two phase systems, then, the
aqueous phase reaction can generally be ignored as stated
by Lanham and Reilly and by Kennedy and Grimley, and makes
possible evaluation of the miscellaneous rate measurements
reported for two phase systems. The reaction of equal volumes
of TBP and 8 $\underline{M}$ HNO_3, reported by Baldwin and Higgins, gave
0.28 per cent decomposed in 29 days. This is equivalent to
$k_1 = 3.9 \times 10^{-6}$ hr^{-1}. Kennedy's and Grimley's "room tempera-
ture" value of 4.1×10^{-6} hr^{-1}, also with 8 $\underline{M}$ HNO_3, is an
excellent check.

Lanham and Reilly[28] stored an equal volume of 30 per cent
TBP in Amsco 123-15 with 7.2 $\underline{M}$ nitric acid at 25 C. Two
separate experiments gave $k_1 = 2.2 \times 10^{-5}$ hr^{-1} and 1.6×10^{-5}
hr^{-1}. At 70 C, 30 per cent TBP in contact with 2.5 volumes
of 6.0 $\underline{M}$ nitric acid gave 0.4 per cent decomposition in 3 hours
or $k_1 = 1.3 \times 10^{-3}$ hr^{-1}. No measurement was made of the sub-
sequent hydrolysis steps but a study of the plutonium nitrate
distribution in the systems led to the conclusion that the major
component of the hydrolysis products was DBP. An activation
energy of the order of 19 kcal was indicated for the over-all
TBP destruction. As can be seen in Figure 4, their rates
are higher by a factor of about ten than the bulk of the data
from other sources indicates. Feber[40] has reported the rate
of formation of DBP in equal volumes of 100 per cent TBP and

(40) Feber, R. C., et al., Report for the Chemistry and Chemical Engineer-
ing Section, Aug. -Sept. -Oct., 1953, KAPL-1002, p. 73, January 11,
1954.
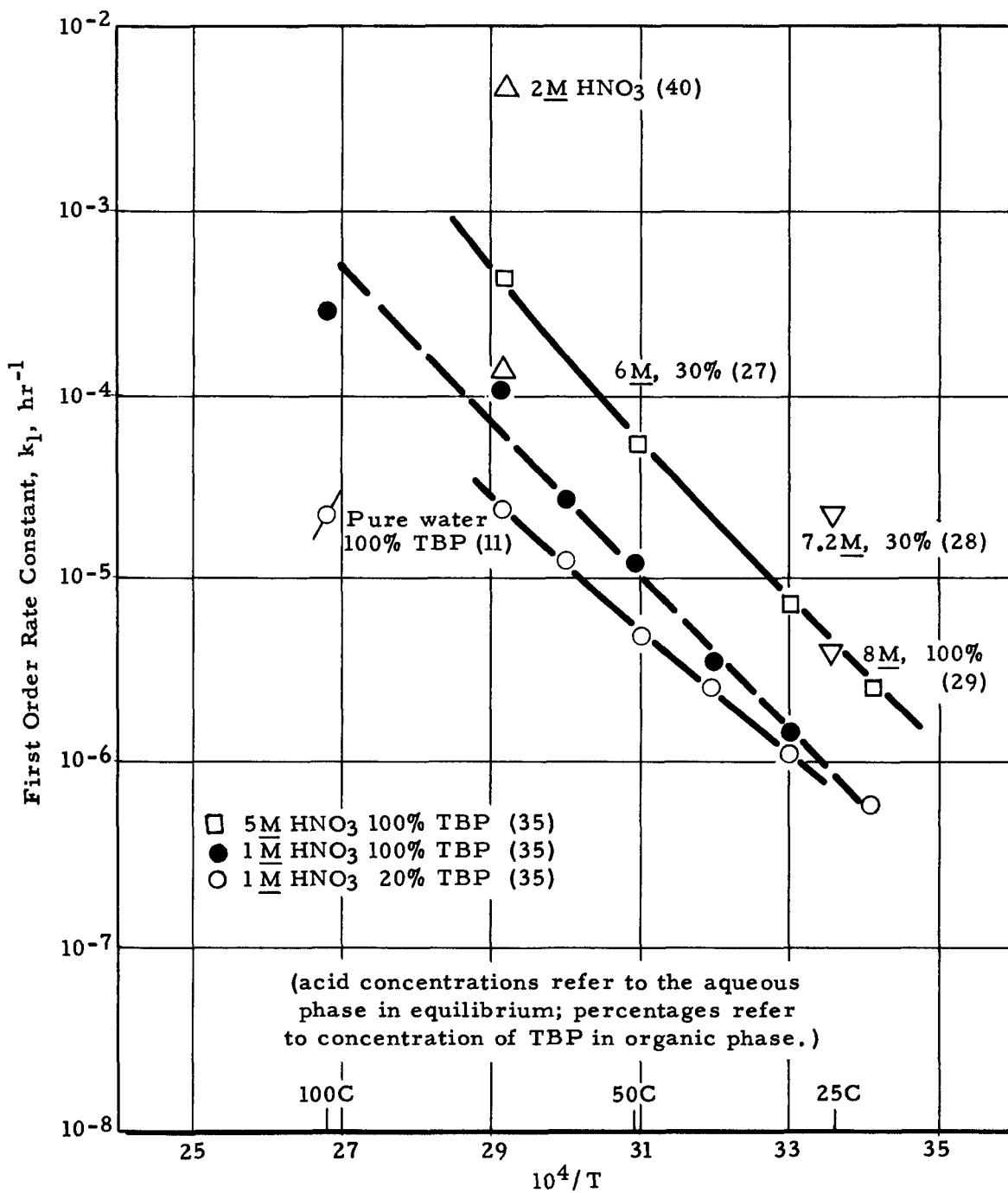
FIGURE 4

ORGANIC PHASE HYDROLYSIS OF TBP

2 $\underline{M}$ nitric acid at 70 C. From the observed rate of 0. 016 moles DBP per liter of TBP per hour, a rate constant $k_1 = 4.6 \times 10^{-3}$ hr^{-1} is calculated. This value is about ten times higher than that found by Kennedy and Grimley.

d. Hydrolysis with Acid and Uranium Present

The effect of uranium in the organic phase on the reaction rates is uncertain. Rodden[41] reports total DBP, MBP and phosphoric acid formed in a two phase reaction at 80 C. Four experiments were performed. (1) The first system was 30 per cent TBP in kerosene containing 10 g/l nitric acid and 100 g/l uranium as uranyl nitrate, with 10 volume per cent of water added. After the mixture was agitated for a week, 3. 48 per cent of the TBP was hydrolyzed. (2) The same solution but without uranium gave 1. 09 per cent. (3) A similar experiment to the first, with a one-half volume of 6 $\underline{M}$ nitric acid in place of the water, gave 1. 58 per cent, and (4) without uranium present, gave 2. 48 per cent. Rate constants for these reactions are 2×10^{-4}, 6×10^{-5}, 1×10^{-4}, and 1.5×10^{-4} hr^{-1}, respectively. Results from solutions without uranium present are in reasonable agreement with the data of Kennedy and Grimley. No mention is made as to whether light was exluded during the reactions. Assuming that light was not involved, one might deduce from the above experiments that adding uranium to the organic phase increases the rate by a factor of three, since the nitric acid in the organic phase is not greatly different (experiments 1 and 2). Experiments 3 and 4 are not necessarily in disagreement, since distribution calculations show that Experiment 4 has a higher nitric acid concentration in the

(41) Rodden, C. J., Progress Report for Period Ending June 30, 1951, NYO-2021, December 21, 1951.

organic phase, 0.8 $\underline{M}$ as compared to 0.1 $\underline{M}$ in Experiment 3.

Recent data of Swanson[42] can be compared here. Aqueous phases having the initial compositions indicated in Table VIII were equilibrated with an equal volume of 30 per cent TBP in Shell Spray Base and agitated in the absence of light at 50 C.

TABLE VIII

FORMATION OF DIBUTYL PHOSPHATE IN TBP

Equal Volumes of Aqueous Phase and 30 Per cent TBP-Spray Base

Source - Swanson[42]   Temperature - 50 C

Initial Aq. Solution	Final Org. Phase Composition*		Reaction Time- Hrs.	DBP g/l	Rate Constant Org. Phase hr⁻¹
	M U	M HNO₃			
0.092 $\underline{M}$ UO₂(NO₃)₂	0.08	0.75	26	0.11	
5.2 $\underline{M}$ HNO₃			54	0.21	2.7 x 10⁻⁵
0.02 $\underline{M}$ NaNO₂			145	0.44	
			118	0.50	
0.57 $\underline{M}$ UO₂(NO₃)₂	0.4	0.23	122	0.17	9 x 10⁻⁶
3.5 $\underline{M}$ HNO₃			197	0.44	
0.05 $\underline{M}$ NaNO₂					

* Most of the nitrite will be in the organic phase until destroyed. Line, for example, reports E_a^o = 20 for 0.01 $\underline{M}$ HNO₂.[43]

(42) Swanson, J. L., HAPO, unpublished work.

(43) Line, L. E., Jr., Progress Report, Purex Lab. Dev., Feb.-April, 1952, ORNL-1343, October 9, 1952.

As the buildup of DBP in this experiment appears to be linear with time, the second step was ignored and the rate constant k_1 was calculated directly from the data. The amount of TBP destroyed is negligible. For the first solution $k_1 = 2.7 \times 10^{-5}$ hr^{-1}. The data for the second experiment are more uncertain. An average of two points gives $k_1 = 9 \times 10^{-6}$ hr^{-1}.

As a comparison, for the case with no uranium present, the data of Kennedy and Grimley for 0.8 $\underline{M}$ HNO_3 in 20 per cent TBP gave $k_1 = 1.5 \times 10^{-5}$ hr^{-1} at 50 C. Their value, using 100 per cent TBP, was 3.5×10^{-5} hr^{-1} at 50 C.

Brite[44] measured the DBP formation rate in systems composed of equal volumes of 12 1/2 per cent TBP in Shell Spray Base and aqueous phases containing uranyl nitrate and nitric acid. The solutions were kept in brown bottles at 50 C and mixed once each day. The initial aqueous phases were as indicated in Table IX. The first order rate constants listed in the last column were calculated by the writer assuming that only the organic phase reaction is significant and that the second step in the hydrolysis is negligible. The latter assumption is valid for $k_2 t \ll 1$ or $t <$ 500 hours. The data are also included in Table XI along with estimated organic phase compositions. These rate constants are much higher than those of previous work. Further, the DBP concentration appears to be rising in the aqueous phase rapidly and at concentration levels much higher than one can reconcile with the distribution coefficient E_a^o of DBP, which is > 100 for these systems.

Table X summarizes the organic phase hydrolysis data for TBP. Some of the better data are reproduced in Figure 4.

---

(44) Brite, D. W., Observation of Hydrolysis Rate of Butyl Phosphates, HW-Undocumented, February 2, 1954.

TABLE IX

DBP FORMATION IN TBP DILUENT MIXTURES

Organic phase - 12 1/2 per cent TBP in Shell "Spray Base"
Temperature, 50 C   Source - Brite[44]

Aqueous Phase before Equilibrium	DBP Increase gl^{-1} Day^{-1}		Rate Constant Org.Phase hr^{-1*}
	Aq Phase	Org. Phase	
2.0 M UO$_2$(NO$_3$)$_2$ 6.0 M HNO$_3$	0.028	0.10	5.5×10^{-4}
" 2.0 "	0.0064	0.028	1.4×10^{-4}
" 0.2 "	0.0005	0.013	5.5×10^{-5}
0.11 M UO$_2$(NO$_3$)$_2$ 6.0 M HNO$_3$	0.017	0.11	5.5×10^{-5}
" 2.0 "	0.00036	0.023	9.8×10^{-5}
" 0.2 "	0.0005	0.011	5.1×10^{-5}

*Estimated organic phase compositions are given in Table X.

5. Summary of Organic-Phase Hydrolysis of TBP

   a. Acid Dependence

Alkaline hydrolysis does not occur in the organic phase. Neutral hydrolysis increases as the amount of water in the organic phase increases, and for pure-water-saturated TBP at 25 C, the first order rate constant is 2×10^{-7} hr^{-1}, and at 100 C is 2×10^{-5} hr^{-1}, indicating an activation energy of about 14 kcal. The rate constants for acid-catalyzed hydrolysis are much higher. At 30 C, the rate constant for pure TBP in contact with 5 M nitric acid is 7.1×10^{-6} hr^{-1} per mole of acid in solution. The acid dependence is approximately first order, although the dependence is very uncertain at low acid concentrations (less than 1 M). Halogen acids are more effective than nitric acid or sulfuric acid.

TABLE X

SUMMARIZED RATE CONSTANTS FOR THE ORGANIC PHASE HYDROLYSIS OF TBP

Aqueous Phase Composition	Organic Phase Composition during Reaction			Temp. $^\circ$C	First Order Rate Constant k_1	Ref.
	% TBP	$\underline{M}$ HNO$_3$	Other			
H$_2$O	100	--	--	100	2.2×10^{-5}	(11)
1 $\underline{M}$ HNO$_3$	100	0.86	--	70	2.8×10^{-4}	(35)
				50	2.7×10^{-5}	(35)
				30	3.3×10^{-6}	(35)
				21	1.4×10^{-6}	(35)
1 $\underline{M}$ HNO$_3$	20	0.14	--	70	2.3×10^{-5}	(35)
				50	4.8×10^{-6}	(35)
				30	1.1×10^{-6}	(35)
				21	5.8×10^{-7}	(35)
5 $\underline{M}$ HNO$_3$	100	2.5	--	70	4.2×10^{-4}	(35)
				50	5.5×10^{-5}	(35)
				30	7.1×10^{-6}	(35)
				21	2.5×10^{-6}	(35)
5 $\underline{M}$ HNO$_3$	20	0.67	--	50	8.4×10^{-6}	(35)
				30	1.7×10^{-6}	(35)
				21	1.0×10^{-6}	(35)
2 $\underline{M}$ HNO$_3$	100	0.4 (a)	--	70	4.6×10^{-3}	(40)
8 $\underline{M}$ HNO$_3$	100	3 (a)	--	"room"	4.1×10^{-6}	(35)
8 $\underline{M}$ HNO$_3$	100	3 (a)	--	25	3.9×10^{-6}	(29)
7.2 $\underline{M}$ HNO$_3$	30	1.2 (a)	--	25	1.9×10^{-5}	(28)
6.0 $\underline{M}$ HNO$_3$	30	1.1 (a)	--	70	1.3×10^{-3}	(28)
3-6 $\underline{M}$ HNO$_3$	100	1.5-3.5	--	105	5×10^{-5} (b)	(27)
			--	105	1×10^{-4} (b)(c)	(27)
			--	76	1×10^{-5}	(27)

(a) Estimated.

(b) Computed as k per mol of acid assuming first order acid dependence.

(c) Recalculated by the author.

TABLE X (contd.)

Aqueous Phase Composition	Organic Phase Composition during Reaction			Temp. °C.	First Order Rate Constant k_1	Ref.
	% TBP	M HNO₃	Other			
H₂O 10% by vol.	30	0.16	0.42 M UO₂(NO₃)₂(c)	80	2×10^{-4}	(41)
	30	0.16	0.0	80	6×10^{-5}	(41)
6 M HNO₃ 50% by vol.	30	0.16	0.42 M UO₂(NO₃)₂	80	1.0×10^{-4}	(41)
	30	0.16	0.0	80	1.5×10^{-4}	(41)
0.092 M U 5.2 M HNO₃	30	0.75	0.08 M UO₂(NO₃)₂ + some HNO₂	50	2.7×10^{-5}	(42)
0.57 M U 3.5 M HNO₃	30	0.23	0.4 M UO₂(NO₃)₂	50	9×10^{-6}	(42)
2.0 M U, 6.0 M HNO₃	12.5	0.1 (a)	0.23 (a)	50	5.5×10^{-4}	(44)
2.0 M U, 2.0 M HNO₃	12.5	0.1 (a)	0.23 (a)	50	1.4×10^{-4}	(44)
2.0 M U, 0.2 M HNO₃	12.5	0.1 (a)	0.23 (a)	50	5.5×10^{-5}	(44)
0.11 M U, 6 M HNO₃	12.5	0.2 (a)	0.1 (a)	50	5.5×10^{-4}	(44)
0.11 M U, 2 M HNO₃	12.5	0.1 (a)	0.1 (a)	50	5.5×10^{-4}	(44)
0.11 M U, 0.2 M HNO₃	12.5	0.1 (a)	0.02 (a)	50	5.1×10^{-5}	(44)
1 M HCl	100	--	0.05 M HCl	70	3.5×10^{-4}	(35)

(a) Estimated.

(c) Recalculated by the author.

b. <u>Uranium</u>

The effect of uranium is uncertain. Data exist which indicate both increased and decreased rates. It is probable that at a given nitric acid concentration, the addition of uranium in the absence of light does not change the rate by more than a factor of two. In the presence of light, uranium increases the hydrolysis rate.

c. <u>Temperature</u>

Activation energies reported range from about 14 kcal for water-saturated TBP to 29 kcal for TBP containing hydrochloric acid. For nitric acid-catalyzed hydrolysis the activation energy is 21 kcal and 14 kcal, respectively, for 100 per cent TBP and 20 per cent TBP in kerosene.

6. <u>Other Products of Hydrolysis</u>

The emphasis in Section III-E has been on the formation of DBP, MBP and phosphoric acid. In aqueous systems, the other product of reaction is butyl alcohol. The fate of the alcohol may be removal by distillation, by solvent partition in extraction cycles, or by chemical reaction. The last may involve either formation of butyl nitrate or oxidation. At high nitrate concentrations butyl nitrate may form as a primary reaction product, and evidence for its direct formation from the acid "hydrolysis" of TBP at temperatures above 100 C was presented by Nichols.[45] Subsequent work indicated that butyl nitrate was the major reaction product of TBP and nitric acid solutions at these temperatures. Nichols also observed that small amounts of nitric oxide were formed in the reaction, indicating that some oxidation was occurring. Butyl nitrate will, of course, hydrolyze to butyl alcohol. No data have been reported for the acid hydrolysis of butyl nitrate. The alkaline hydrolysis is extremely slow.[46]

---

(45) Nichols, G. M., Siddall, T. N., III, <u>Savannah River Laboratory TNX Semi-Works, Bi-Weekly Report</u>, April 28, 1953, May 14, 1953.

(46) Baker, J. W., Easty, D. M., <u>J. Chem. Soc.</u>, 1952, 1193.

If oxidation of the alcohol occurs, then aldehydes and carboxylic acids would be expected. Brite[47] has considered the possibility that butyraldehyde may form through the reaction of nitric acid and the hydrolysis products of TBP. In subsequent treatment of the solvent with alkaline wash solutions, he suggests that polymers could form by aldol condensation. It is important to remember that diluents commonly used with TBP may be a more likely source of these products.

7. Hydrolysis of TBP Derivatives

The reactions of TBP derivatives are significant both because of their possible presence in solutions of practical interest and because their behavior may aid in the interpretation of TBP reactions.

Inorganic pyrophosphates hydrolyze in water at a rate which is first order with respect to both pyrophosphate concentration and hydrogen ion concentration.[48]

The condensed phosphates may be considered as the anhydrides of dibutyl (or monobutyl) phosphoric acid. Thus, their hydrolysis yields DBP and/or MBP. Tetrabutyl pyrophosphate, TBPP, is the simplest of these structures and its behavior is probably typical.

Toy[49] has studied the tetraalkyl pyrophosphates as a class. The methyl, ethyl, propyl, isopropyl and butyl compounds were prepared and their hydrolysis in water studied. The resistance to hydrolysis increased with the size of the alkyl group; the isopropyl derivative

(47) Bushey, A. H., Quarterly Progress Report, Chem. Unit, Jan. -Mar. - 1954, HW-31630, p. 63, May 1, 1954.

(48) Sidgwick, N. V., Chemical Elements and Their Compounds, Oxford: Clarendon Press, London (1950) p. 744.

(49) Toy, A. D. F., J. Am. Chem. Soc. 70, 3882 (1948).

was exceptionally stable. In a stirred two phase system with water, the TBPP hydrolyzed to DBP at the rates shown in Table XI. A plot of the logarithm of the unreacted pyrophosphate against time shows an increasing rate with time, possibly due to the increasing acidity and/or increasing solubility.

TABLE XI

HYDROLYSIS OF TETRABUTYL PYROPHOSPHATE IN CONTACT WITH WATER

Temperature, 25 C

Time (Days)	Per cent Reacted
5	4
10	20
15	40
20	62
25	79
30	91

The initial rate corresponds to a half-life of about 30 days, $k \sim 10^{-3}$ hr^{-1}, while after 90 per cent had reacted the half-life was eight days. By comparison to the rates of hydrolysis of the lower pyrophosphates, it is probable that the reaction occurred largely in the aqueous phase. Lack of solubility data precludes calculation of individual rate constants. It may be noted, however, that the overall rate is roughly 100 times as fast as the hydrolysis of TBP. The alkaline hydrolysis of TBPP has not been studied but must be slow, since it is possible to synthesize the pyrophosphates from dialkyl chlorophosphates using sodium bicarbonate to remove the hydrochloric acid formed. This may not be true for all pyrophosphates, for Ketelaar and Blacksma[50] found a rapid hydrolysis of tetra-ethyl pyrophosphate in sodium hydroxide solutions. Their first order rate constant at 25 C was 0.093 hr^{-1}.

(50) Ketelaar, J. H. A., Blacksma, A. H., Rec. Trav. Chim., 67 665 (1948).

8. Mechanism of Hydrolysis

The organic phosphates that have been studied in most detail are those of biochemical interest, which often have reactive substituents. These functional groups may become directly involved in the hydrolysis reactions, or change the electron density about the phosphate nucleus such that these esters no longer serve to elucidate a general mechanism. The most comprehensive study of ester hydrolysis concerns the carboxylic acid esters, a study pioneered by Lowry[51] and co-workers. Ingold has contributed generously to this field and has recently summarized this work.[24] Here again the mechanism involving a R-C(O)-O-configuration is not necessarily representative of a R-O-P(O)-O-group, but enough similarities exist to permit classification in a like manner. Thus, we can consider alkaline, neutral or acid hydrolsis. Secondly, the reaction may be classified according to whether alkyl-oxygen fission or phosphorus-oxygen fission occurs, and finally whether the controlling step is monomolecular or bimolecular.

A consistent mechanism (or mechanisms) should account for the following observations of alkyl phosphate hydrolysis:

(1) Alkaline hydrolysis occurring only in the aqueous phase and stopping at the first hydrolysis product; e. g. , TBP terminates in DBP.

(2) A much greater rate of acid hydrolysis in aqueous solutions than in organic solutions.

(3) A dependence on acid concentration which is variable and slightly less than first order.

(4) The differing effect of various acids: $HI > HCI > HNO_3 \geqslant H_2SO_4$.

---

(51) See for example Waters, W. A. , *Physical Aspects of Organic Chemistry,* New York: Van Nostrand (1950) p. 327 ff.

In addition, one would hope to be able to predict:

(1) The relative rates of the three steps in the hydrolysis of TBP.

(2) The effect of complexing the TBP by other components.

(3) Catalysts that would hinder or accelerate one or more of the steps.

a.   <u>Alkaline Hydrolysis</u>

Two possible mechanisms of alkaline hydrolysis of TBP are:

$$HO^- + Bu\text{-}O\text{-}P(O)(OBu)_2 \longrightarrow BuOH + (BuO)_2\,P(O)\,O^- \quad (1)$$

or

$$\left.\begin{array}{l} HO^- + (BuO)_3\,P\,O \longrightarrow BuO^- + (BuO)_2\,P(O)\,OH \\ (BuO)_2\,P(O)\,OH + HO^- \longrightarrow H_2O + (BuO)_2\,P(O)\,O^- \\ BuO^- + H_2O \longrightarrow BuOH + HO^- \end{array}\right\} \quad (2)$$
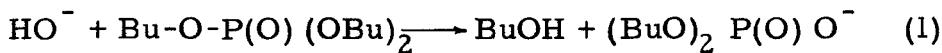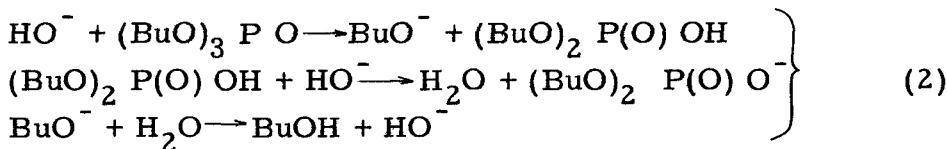
Mechanism (1) would be favored by very electropositive alkyl groups, and esters of strong acids. Neither condition fits TBP very closely.

Reaction (1) leads to an alkyl-oxygen split while reaction (2) leads to a phosphorus-oxygen split. Blumenthal and Herbert[25] using tracer oxygen observed that triethyl phosphate gave 100 per cent phosphorus oxygen cleavage with sodium hydroxide in aqueous solution, in support of mechanism (2). There is also considerable confirming evidence. Nucleophilic attack by the OH^- group requires an electroposition center, and the first step probably involves the attachment of the OH^- group to the phosphorus atom. Thus, it is not surprising that the reaction slows greatly after the first hydrolysis step, for in alkaline solution the hydrolysis product will exist as the ion which is further strengthened by resonance.
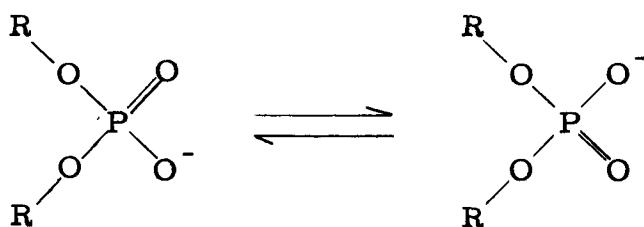
The phosphorus atom is less positive than in the parent compound TBP where the structure
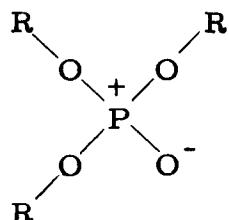
has an appreciable contribution.

However, a number of cases exist where the hydrolysis does not stop after the first alkyl group is removed. For example, diisooctyl phosphate according to Gerrard and his co-workers,[26] hydrolyzed rapidly with 1 $\underline{M}$ potassium hydroxide at the reflux temperature. Koshland[52] found that acetyl phosphate hydrolyzed at an increasingly rapid rate as the OH$^-$ concentration was increased above a pH of 10. In the latter case, the acetyl carbon may be involved.

The alkaline hydrolysis is an ionic one and requires a media having a high dielectric constant; e. g., aqueous solutions. The mechanism postulated is bimolecular, which is consistent with the first order dependence on both OH$^-$ and phosphate. (This second order kinetic law has been demonstrated for many phosphates although not specifically for TBP.)

(52) Koshland, D. E., Jr., J. Am. Chem. Soc. 74, 2286 (1952).

The increased stability toward alkaline hydrolysis of the phos-
phothioates, $(RO)_3PS$, over the phosphates[53] is consistent
with the mechanism since in the former case the phosphorus
is less positive.

Recently Amber and his co-workers[54] have examined with
the aid of tracer oxygen the alkaline hydrolysis of esters of a
variety of inorganic acids. In this rather complete study the
electropositive nature of the alkyl group, the acid strength
and the oxidation state of the central atom were all varied.
The majority of the esters retained the alkyl-oxygen bond on
hydrolysis. Of the esters which hydrolyzed by alkyl-oxygen
fission, all contained a tertiary carbon-oxygen bond. Several
other esters of strong acids including n-butyl nitrate hydrolyzed
partially by this mechanism. Esters of phosphoric acid were
not included in the study.

b. Acid Hydrolysis

The case for acid hydrolysis is more complex as reactions in
both aqueous and organic media must be considered. By analogy
to the carboxylic acid esters, a possible mechanism would be:

$$
H^+ + R-O-\underset{\underset{O}{\|}}{\overset{\overset{R}{|}}{\underset{|}{O}}}{\overset{}{P}}-O-R \longrightarrow R-\underset{\underset{O}{\|}}{\overset{\overset{R}{|}}{\underset{H}{O}}}{\overset{+}{\underset{|}{O}}}{\overset{}{P}}-O-R \qquad (3)
$$
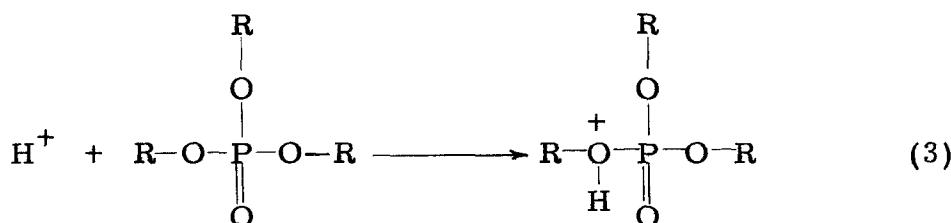
This product would then add a hydroxyl group (extremely
unlikely due to the low OH^- concentration) or a water molecule
to the central atom and the resulting unstable configuration would

(53) Ketelaar, J. H. A., et al., Rec. Trav. Chim. 71, 1253 (1952).
(54) Amber, M., et al., J. Chem. Soc., 1954, 3603.

cleave at the P-O bond, giving ROH. However, for TBP a more plausible reaction would involve adding a proton to the electronegative phosphoryl oxygen giving the structure

$$
H^+ + R-O-\overset{\overset{\overset{\displaystyle R}{\displaystyle |}}{\displaystyle O}}{\underset{\underset{\displaystyle O_-}{\displaystyle |}}{\overset{|}{P}}}\!\!\!\overset{+}{-}\!\!O-R \longrightarrow R-O-\overset{\overset{\overset{\displaystyle R}{\displaystyle |}}{\displaystyle O}}{\underset{\underset{\underset{\displaystyle H}{\displaystyle |}}{\displaystyle O}}{\overset{|}{P}}}\!\!\!\overset{+}{-}\!\!O-R \qquad (4a)
$$

followed by

$$
R-O-\overset{\overset{\overset{\displaystyle P}{\displaystyle |}}{\displaystyle O}}{\underset{\underset{\underset{\displaystyle H}{\displaystyle |}}{\displaystyle O}}{\overset{|}{P}}}\!\!\!\overset{+}{-}\!\!O-R \quad + \quad HOH \longrightarrow ROH + R-O-\overset{\overset{\overset{\displaystyle R}{\displaystyle |}}{\displaystyle O}}{\underset{\underset{\underset{\displaystyle H}{\displaystyle |}}{\displaystyle O}}{\overset{|}{P}}}\!\!\!=\!O \qquad (4b)
$$
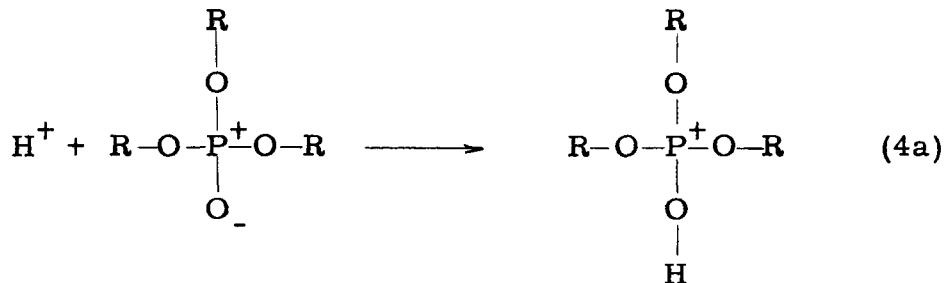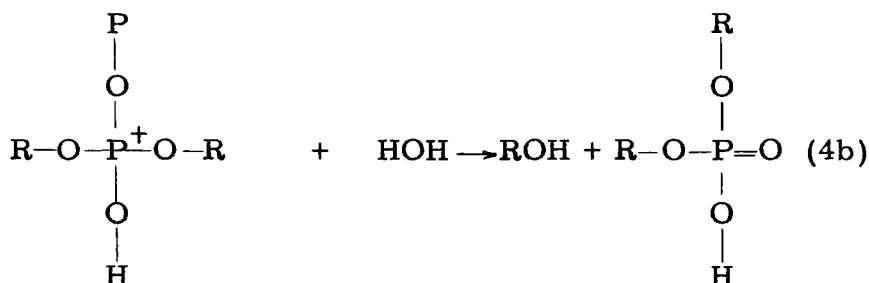
This mechanism was suggested by Blumenthal and Herbert to account for the 70 per cent cleavage of the alkyl oxygen bond which was observed for triethyl phosphate. In concentrated acids the second step could involve the acid anion instead of water, resulting in the ester RX in place of ROH. Since 30 per cent P-O bond fission was found by Blumenthal and Herbert, reactions (4a) and (4b) do not occur exclusively. Reaction (4b) could be replaced by nucleophilic attack by a water molecule. Since the acids, nitric, hydrochloric and hydrobromic which have roughly equivalent degrees of ionization show different catalytic effects, one may reason that the acid anion is involved in the second step.

In non-aqueous media the proton addition must be replaced by molecular addition of the acid; e. g. ,

$$HNO_3 + R-O-\overset{\overset{\overset{\displaystyle R}{|}}{\overset{\displaystyle O}{|}}}{\underset{\overset{\displaystyle O}{|}}{\underset{\displaystyle O^-}{}}}P^+O-R \; \rightleftharpoons \; R-O-\overset{\overset{\overset{\displaystyle R}{|}}{\overset{\displaystyle O}{|}}}{\underset{\overset{\displaystyle O}{|}}{\underset{\displaystyle O^-\text{-------}HNO_3}{}}}P^+OR \qquad (5)$$
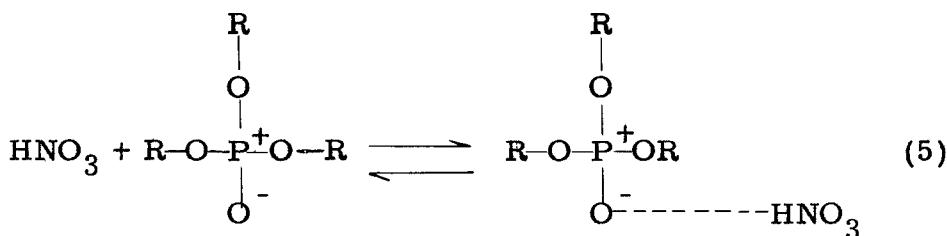
The second step would involve (a) splitting off of an alkyl nitrate molecule internally or a biomolecular reaction involving either (b) a water molecule or (c) another acid molecule. The second step depends on the relative rate constants k_a, k_b or k_c, respectively, and on the relative concentrations of ester, water and acid. Reaction (5) above reaches equilibrium rapidly. Thus (a), (b) or (c) is probably rate controlling. Both butyl alcohol and butyl nitrate have been found in hydrolysis reactions with nitric acid but the latter only in significant quantities at high temperatures, $> 100\,C$, and high acid concentrations.[45][55]

Since butyl nitrate is moderately stable toward hydrolysis,[46][54] the evidence for water-saturated solutions points to reaction (4b), although there is no reason to assume that only one reaction path is followed in such complex mixtures as water-saturated TBP-kerosene containing both uranyl nitrate and nitric acid. As the concentration of uranyl nitrate or acid is increased the water content is diminished, and at saturation (with salt) the solvent is nearly anhydrous. Under this condition, mechanism (b) would become unimportant. The fact that there is competition between the water and acid in the TBP solution and both are required for (4b) may explain the variable

(55) Nichols, G. M., Siddall, T. H., Savannah River Lab., TNX Semi-Works Bi-Weekly Reports, May 14, 1953, June 23, 1953.

and less than first order dependence on nitric acid.

The much lower extraction of hydrochloric acid than nitric acid by TBP was noted in connection with the work of Kennedy and Grimley.[35] Yet in view of the rapid hydrolysis with hydrochloric acid a strong complex must exist to be consistent with the postulated mechanism. One must conclude then that it is not the lack of complex strength that prevents hydrochloric acid extraction but rather the solubility characteristics of the complex and the strong complexing of the chloride ions in the aqueous phase.

In acid solutions the successive hydrolysis products of TBP are molecular DBP, MBP and finally phosphoric acid. Replacing a butyl group by hydrogen should make the phosphoryl oxygen less basic, although internal hydrogen bonds may complicate this. Thus the trend would be toward a slower reaction as alkyl groups are removed due both to this inductive effect and to the statistical effect; i. e. , fewer groups available in the molecule.

c. Neutral Hydrolysis

Neutral hydrolysis can only be considered as an independent case over the small range in pH where the reaction velocities involving either acid or hydroxyl ion are so slow, due to low concentration, that the direct addition of H_2O to the ester becomes a competitive first step. The very interesting work of Desjorbet on ethyl phosphates[56] and of Koshland[51] on acetyl phosphate (mentioned in Section VI-d) on the effect of pH on the hydrolysis can be considered an acid hydrolysis study and the rates can be related to the concentrations of the differently charged ester anions present. A transition from an alkaline to an acid hydrolysis mechanism must occur in

(56) Desjorbet, A., Bull. Chem. Soc., 1947, 809.

this region. With acetyl phosphate independent work by Bentley[57] indicated that the P-O bond splits at a pH of 4 to 6. This suggests that the acetyl carbon atom is involved in the hydrolysis of this compound.

It is clear that much work must be done before definite mechanism assignments can be made for TBP hydrolysis under the varied conditions of interest. In particular, studies in the organic phase and on the aqueous phase separately should be made so that the effect of acid and water as well as of inert diluent could be studied independently. It is surprising that the formation of a complex as strong as the one formed with uranyl nitrate has shown such little effect on the hydrolysis rates and casts doubt on the above mechanism.

Knowledge of the activation energies of these reactions would also be helpful and are noticeably lacking in most hydrolysis studies. Ketelaar's studies of the p-nitrophenyl phosphates are an exception, as is the work on TBP of Kennedy and Grimley. A curious observation of the latter workers is that the activation energy for hydrolysis of TBP in 1 $\underline{M}$ sodium hydroxide (approximately 18 kcal) was about the same as for nitric acid hydrolysis in the organic phase where a completely different mechanism is involved. Yet when the acid hydrolysis of 20 per cent TBP in kerosene was studied, an activation energy of only 14 kcal was found.

E. Radiolysis

No attempt will be made to survey this field here. A study of TBP decomposition by γ-radiation has recently been made and will soon be published.[58] In addition to hydrogen and small amounts of

---

(57) Bentley, R. J., Am. Chem. Soc. 71, 2765 (1949).

(58) McClanahan, E. D., Burger, L. L., Radiation Stability of Tributyl-phosphate-Diluent Systems, (to be published).

hydrocarbons, butyl alcohol, dibutyl ether, and acid phosphates are formed from TBP. The principal product is DBP. Thus, the net result of radiation damage is the same as that from the only important chemical degradation reaction. The DBP produced at a γ-dosage of 10^4, 10^6, and 10^8 r, respectively, has been found to be 0.016 g/l, 0.32 g/l, 32 g/l from pure TBP and 0.0058 g/l, 0.099 g/l and 12.2 g/l from 30 per cent TBP in an isoparaffin hydrocarbon. At high levels, $> 10^7$ r, there is also produced a small amount of unknown material which complexes uranium very strongly. By comparison to chemical damage, it can be seen that 10^4 r is roughly equivalent to contact with 5 $\underline{M}$ nitric acid for 20 hours at 25 C.

IV. PROCESS SIGNIFICANCE

In metal processing by solvent extraction, the difficulties introduced by the chemical reactions of TBP are those associated mainly with the formation of DBP and MBP. These may be present as impurities in the fresh solvent or be produced by hydrolytic reactions. Although DBP and MBP are not volatile and, therefore, are removed by distillation, the preparation and purification of TBP could conceivably leave small amounts of partially esterified phosphorus oxychloride or condensation products, such as dibutyl pyrophosphate or tetrabutyl pyrophosphate (see Section VI). These compounds hydrolyze at a rate several hundred times faster than TBP itself, and hence offer one possible path for the introduction DBP and MBP into TBP. The possibility of formation of metal complexes with the pyrophosphates should not be overlooked in considering TBP as an extractant.

Even if TBP which has had adequate purification is assumed to be obtainable, the problem of hydrolysis of TBP itself remains. This is a problem which one must live with and it is worthwhile to summarize again the rates of hydrolysis:

A. Water-saturated TBP

The rate constant of 2×10^{-7} hr^{-1} at 25 C corresponds to a rate of formation of DBP of about 1.4×10^{-4} g/l/hr. Thus a concentration of 0.1 g/l would be reached in about 700 hours. At 100 C, only 7 hours would be required. For a solution of 30 per cent TBP in an inert diluent, one calculates that the 0.1 g/l level would be reached in 2100 hours or 90 days at 25 C. However, Dawson and Lowe found a rate lower by about a factor of two if the TBP were diluted with kerosene. Presumably this reflects the lower water to TBP ratio of the diluted TBP, that is, the water content of 30 per cent TBP is much less than 20 per cent of that of pure TBP.[32] The hydrolysis rates of DBP to MBP and of MBP to phosphoric acid in these solutions are unknown, although it is certain that DBP is formed faster than it is destroyed.

B. TBP in Contact with Nitric Acid-Uranyl Nitrate Solutions

In this system the reaction in the organic phase is the important one. A solution of 30 per cent TBP in a hydrocarbon diluent in contact with 1 $\underline{M}$ nitric acid will produce about 1.5×10^{-4} g DBP/l/hr at 25 C and 1.2×10^{-3} g/l/hr at 50 C. With 5 $\underline{M}$ nitric acid the rates are about twice as high.

The effect of uranium on the rate of formation of DBP is uncertain. Although data exist which indicate rates 20 times higher for the same nitric acid concentration, it is probable that in the absence of light an increase by a factor of two or less is more likely. If a factor of two is assumed for the uranium effect, then 30 per cent TBP in uranium-containing systems with 5 $\underline{M}$ nitric acid present might produce DBP at the rate of 5×10^{-3} g/l/hr at 50 C. Increasing the temperature to 70 C would add another factor of four giving 2×10^{-2} g/l/hr. It must be emphasized that the latter values are really guesses rather than calculations.

C. Aqueous Acid Solutions

A separated aqueous phase will contain dissolved TBP in an amount varying inversely as the ionic strength of the solution. A solution of 0.25 $\underline{M}$ $UO_2(NO_3)_2$, 0.05 $\underline{M}$ HNO_3 which has been contacted with 20 per cent TBP will contain 7×10^{-4} mol of TBP per liter. The first order rate constant for TBP hydrolysis in this solution is about 1×10^{-5} hr^{-1} at 25 C and 3×10^{-4} hr^{-1} at 50 C with an uncertainty factor of about three. The second step, hydrolysis of DBP in aqueous solutions, is probably one-half to one-third as fast. At 50 C then, DBP would initially build up at a rate of 4×10^{-5} g/l/hr in the above solution, reaching a maximum of about 0.1 g/l in one month.

D. Alkaline Solutions

Alkaline hydrolysis is of much less concern, for the reaction occurs only in the aqueous phase. One liter of aqueous 1 $\underline{M}$ sodium hydroxide in contact with 20 per cent TBP will produce DBP at the rate of 7×10^{-4} g/hr at 30 C or 2×10^{-3} g/hr at 50 C. An important difference in alkaline hydrolysis is that the objectionable reaction products remain in the aqueous phase. The alkaline hydrolysis of DBP and of MBP is extremely slow.

V. SUGGESTED STUDIES

The organic phosphorus compounds offer an exciting field for mechanism studies in the field of theoretical organic chemistry. Particularly challenging are the rates of hydrolysis, or dealkylation, in non-aqueous media where little work has been done.

From a practical point of view, this may be the most important area also. For example, the important reactions, as far as mass contribution of degradation products is concerned, have been seen to occur in the organic phase. Yet there is no information on the rate of reactions of the

first or second hydrolysis products, DBP and MBP, in organic solutions. The major uncertainty in the acid hydrolysis of TBP itself is at low acid concentration, < 0.1 $\underline{M}$.

Whether or not uranium affects the hydrolysis rates, as the postulated mechanism would predict, is also uncertain. Swanson's work (Table VIII) indicated a rate higher by a factor of about two than Kennedy and Grimley found for organic phase reactions. The latter experiments (Tables VI, VII) were done in the absence of uranium.

Aqueous phase data also suggest a slightly higher rate.[30][31][33] It is suggestive that molybdate ion has a marked catalytic effect on the hydrolysis rate of many acid phosphates.[59][60] For the same reason, the apparent strong complexing of nitrous acid by TBP would lead one to question the effect of reducing agents in nitric acid systems on the hydrolysis of TBP. The aqueous phase data are more complete, but even here the rate constants in solutions of process interest are not known to better than ± 50 per cent. The ratio of k_2 to k_3 is particulary uncertain.

Finally, the writer feels that some consideration should be given to an elucidation of the mechanism of the hydrolytic reactions of TBP, DBP, and MBP in both phases. There is a definite possibility of controlling the initial destruction of TBP, or increasing the rates of hydrolysis of DBP and/or MBP through catalytic action, and a better understanding of the reaction steps would aid materially in predicting the nature of the required catalyst.

The inadequacy of the information on hydrolysis rates is due in a large part to the difficult analytical problem of determining small concentrations of the different acid esters in the presence of each other and in the presence of large amounts of nitric acid. More extensive use of tracer

(59) Lutwak, L., Sachs, T., J. Biol. Chem. 200,565 (1953).
(60) Weil-Malherbe, H., Green, R. H., Biochem. J. 49,286 (1951).

phosphorus will be of some aid. For separation of the acid esters, the ion-exchange studies of Baldwin and Higgins[20][61] and the addition products formed with S-benzylthiourea are possible approaches. The latter compound has been used for the characterization of acid phosphates by Lipkin[62] and by Kennedy and Grimley. [63]

Process experience has demonstrated that TBP has adequate chemical stability for use as a solvent in uranium or plutonium separations. This is substantiated by the rate constants for hydrolysis at 25 C listed in this review. However, the use of TBP in acid solution at temperatures higher than 50 C may become marginal insofar as buildup of hydrolysis products is concerned.

The physical properties of TBP, particularly the extraction coefficients for metals, are close to optimum for large scale operation. These factors combined with its availability will assure its continued use for some time to come. It seems reasonable, therefore, that a little more fundamental information on its hydrolytic reactions could be justified. The chemistry of some of the condensation products of TBP also warrants further examination.

VI. APPENDIX

A. Physical Properties

A summary of pertinent physical properties of TBP is given in Tables XII-XV. The data reported were selected on the basis of apparent purity of the TBP used, judged by density and refractive index and, where it was possible to evaluate, the degree of care employed in the experimental work. Many of the variations in data reported are probably due to small amounts of water which, for example, lower the refractive index and raise the density and

(61) Hill, O. F., Trip Report, Solvent Extraction Studies at ORNL and KAPL HW-19572, Nov. 27, 1950.
(62) Lipkin, D., The Isolation and Identification of Alkylated Phosphoric Acids, AECD-2234, August 23, 1948.
(63) Kennedy, J., Grimley, S. S., AERE CE/R-968.

TABLE XII

PHYSICAL PROPERTIES OF TBP

Property	Value	Temp $^{\circ}$C	Reference
Density	0.9727	25	(64)
	0.9730	25	(72)
	0.9596	40	(64)
Viscosity	33.2 millipoises	25	(72)
Boiling Point	289 C	--	See Table XIII
ΔH Vap.	14.68 kcal/mole	--	See Table XIII
Melting Point	-80 C approx.	--	
Solubility	0.4 g/1 in H_2O	25	See Table XIV
Refractive Index	$n_D = 1.4224$	25	(64)
	$n_D = 1.42256$	25	(73)
	$n_D = 1.4223$	25	(75)
	$n_D = 1.42496$	20	(65)
	$n_C = 1.4206$	25	(64)
	$n_F = 1.4274$	25	(64)
Dielectric Constant	8.05 $\pm$ 05	25	(75)
Surface Tension	27.79 dyne/cm	20	(65)
	28.15 " "	16.6	(65)
Interfacial Tension			
Against H_2O	7.4 dyne/cm	25	(74)
Against 5 $\underline{M}$ HNO_3	8.7 " "	25	(74)

TABLE XIII
VAPOR PRESSURE OF TBP[64]

Temp. $^{\circ}$C	Pressure, mm Hg
289	760
227	150
211	100
196	50
150	10

$$\log P \text{ mm} = 8.5861 - \frac{3206.5}{T}$$

$$\Delta H_v = 14680 \text{ cal.}$$

TABLE XIV

SOLUBILITY OF TBP IN AQUEOUS SOLUTIONS AT 25 C*

(References in parenthesis)*

Conc. TBP in Diluent vol. %	Solvent: Water	7$\underline{M}$ HNO$_3$	0.25 M UO$_2$(NO$_3$)$_2$	2 M UO$_2$(NO$_3$)$_2$
Kerosene diluent				
100	0.39 (32)	⎰0.16 (32) ⎱0.12 (36)	0.19 (36)	0.12 (36)
75	.33			
50	.29			
30	.25		0.19 (32)	
20	.23	0.080 (36)	0.19 (32)	0.01 (32)
10	.17			
5	.10			
CCl$_4$ diluent				
100	0.44 (71)			
75	.12			
50	.03			
30	.02			
20	.02			
10	.01			
5	.01			

* Data of Kennedy and Grimley (36) are at 17-19 C.

TABLE XV

SOLUBILITY OF WATER IN TBP AT 25 C

Vol. % TBP in Diluent	Water Content g/l	
	Kerosene Diluent[32]	CCl$_4$ Diluent[71]
100	63.7	--
75	37.1	28.7
50	19.2	11.7
25	5.8	3.7
15	2.4	1.65
5	0.54	0.1
0	0.06	--

viscosity. Other impurities are butyl alcohol and a variety of phosphorus compounds discussed in Sections III-D-7 and VI-B.

Of some interest in chemical reactions of TBP are the vapor pressure and water solubility. Vapor pressure data have been reported by many workers,[2][64-70] but only that of Evans[64] appears to represent more than an incidental boiling point measurement. All of the data except those of Lehmann and Flory, Furby and Ashworth and the one-mm point of Wagner are in fair agreement with those of Evans.

Solubilities reported by Kennedy and Grimley[36] are in substantial agreement with those of Burger and Forsman[32] and Baldwin and Higgins[29] and cover a wider selection of aqueous solutions. Craig[70] found much higher solubilities in aqueous solutions. The effect of different diluents on solubility in water was reported by Kennedy and Grimley and studied in more detail by Johnson and Dillon.[71]

(64) Evans, D. P., et al., "The Lower Trialkyl Orthosphosphates, Part I," J. Chem. Soc., 1930, 1310.
(65) Vogel, A. I., Cowan, D. M., J. Chem. Soc., 1943, 16.
(66) Noller, C. R., Dutton, G. R., J. Am. Chem. Soc. 55, 424 (1933).
(67) Furby, E., Ashworth, G. J., Estimation of Uranium in TBP Solutions, AERE-C/R-617, Dec. 1950.
(68) Wagner, R. M., Slansky, C. M., Evaporation of Process Streams in the Tributyl Phosphate Process for Uranium Recovery, HW-15172, Nov. 21, 1949, p. 8.
(69) Lehman, Flory, Durans, et al. (See Beilstein I, 2nd Suppl. p. 397).
(70) Craig, J., Quarterly Report for Period Ending Dec. 31, 1951, NYO-2024, p. 17.
(71) Johnson, W. F., Dillon, R. L., Physical Properties of Tributyl Phosphate-Diluent Solutions, HW-29086, Sept. 1, 1953.
(72) Burger, L. L., Slansky, C. M., Density and Viscosity of Solutions in the TBP Process for Uranium Recovery, HW-15233, Nov. 29, 1949.
(73) Burger, L. L., Analytical Applications of Refractive Index, HW-23228, Jan. 9, 1952.
(74) Bushey, A. H., Quarterly Progress Report, Chemistry Unit, Jan. - Mar. 1953, HW-27727, April 30, 1953, p. 46.
(75) Estok, G. K., Wendlandt, W. W., J. Am. Chem. Soc. 77, 4767 (1955).

Table XVI lists some physical properties of possible impurities or common reaction products of TBP.

B. Preparation of TBP and other Phosphates

1. Phosphorus Oxychloride Method

The most versatile and successful method of preparation of the tertiary esters utilizes phosphorus oxychloride, $POCl_3$, and alcohol with a base such as pyridine to remove the hydrochloric acid formed.[66][76]

This method is used on both laboratory and industrial scales and gives excellent yields. Presumably this is the method currently employed in industry for TBP manufacture. A modification employed by Murakami[77] used aluminum chloride, zinc chloride or magnesium chloride as a catalyst and an inert gas to remove the hydrochloric acid.

2. Phosphorus Pentoxide and Alcohol

Probably the cheapest method of manufactur of alkyl orthophosphates is by direct combination of alcohol and phosphorus pentoxide or syrupy phosphoric acid. The yield is largely mono- and diesters. Attempts to increase the yield of the triester by raising the temperature only result in degradation of the product. Kosolapoff[78] reviews this method and lists some 20 references. The mechanism is apparently the cleavage of the P-O-P chain by alkylation rather than a true esterification, thus accounting for a low yield of the triester.

3. Silver Phosphate Method

An excellent laboratory method is the reaction between silver phosphate and the alkyl halide.[79] An excess of the halide

(76) Karrer; Paul, Organic Chemistry (2nd Ed.), Elsevier Publishing Co., N. Y. (1946) p. 108.
(77) Murakami, K., Chemical High Polymers (Japan) 7, 188 (1950) Chem. Abs. 46, 419 i.
(78) Reference (37) p. 220-21.
(79) Reference (37) p. 225.

TABLE XVI

PROPERTIES OF SOME TBP IMPURITIES

Compound	Formula	Specific Gravity		Boiling Point $^{\circ}C$	Solubility in Water
Butyl alcohol	BuOH	0. 810	20/4	117	90 g/l
Butyl nitrate	$BuONO_2$	1. 048	0/4	136	insoluble
Butyl nitrite	BuONO	0. 9114	0/4	75-79	--
Dibutyl phosphate	$(BuO)_2 \overset{\overset{O}{\|}}{P} OH$	1. 065	25/4	dec. 175 C	18 g/l at 25 C
Monobutyl phosphate	$BuO \overset{\overset{O}{\|}}{P} (OH)_2$	1. 220	25/4	dec. 105-110 C	ca. 25 g/l
Tetrabutyl pyrophosphate	$(BuO)_4 P_2O_3$	1. 050	25/4	143-6 at . 01 mm	insoluble
Dibutyl pyrophosphate	$(BuO)_2P_2O_3(OH)_2$	1. 228	25/4	dec. 165-169 C	--
Dibutyl chlorophosphate	$(BuO)_2 \overset{\overset{O}{\|}}{P} Cl$	1. 074	25/25	103-106 at 1. 5 mm 132-5 at 15 mm	hydrolyzes
Butyl dichlorophosphate	$BuO \overset{\overset{O}{\|}}{P} Cl_2$	1. 2560	25/4	90 at 17 mm	hydrolyzes

*All compounds listed are miscible with most organic solvents.

is used. This method is very good for preparation of mixed esters or for preparation of labelled phosphates.[80] Other metal phosphates yield mostly primary esters.

4. Alkoxide Process

A process similar to the phosphorus oxychloride method discussed above employs sodium alkoxide[81] in place of the alcohol and thus avoids the hydrochloric acid problem. The use of aluminum alkoxide, $Al(OR)_3$, in place of sodium alkoxide is the basis of a patent by Bannister.[82]

5. Exchange Esterification

The esters of the acids of phosphorus are, in general, alkylating agents and thus are capable of exchanging alkyl groups with alcohols. The reaction

$$(RO)_3 PO + R' OH \longrightarrow (RO)_2 R' OPO + ROH$$
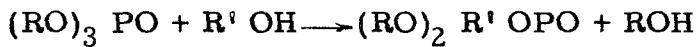
is favored if R' is larger than R. R' ONa will increase the rate of reaction[83] and the process can be utilized for the preparation of specific phosphate esters. Noller and Dutton[66] and Berman and Lowry[18] also studied the alkylation reactions.

6. Phosphorus Trichloride and Hydrocarbons

The direct formation of phosphates from phosphorus trichloride and hydrocarbons in the presence of oxygen was described by Clayton and Jensen.[84] Various products result, depending on concentrations and the temperature employed. The trialkyl

(80) Baldwin, W. H., Higgins, C. E., J. Am. Chem. Soc. 74, 2431 (1952).
(81) Evans, D. P., Davies, W. C., Jones, W. J., J. Chem. Soc., 1930, 1310.
(82) Bannister, W. J., U. S. Patent (1931), Chem. Abs. 25, 3014.
(83) Rueggeburg, Chernock, J. Am. Chem. Soc., 70, 1802 (1948).
(84) Clayton, Jensen, J. Am. Chem. Soc., 70, 3880 (1948).

phosphate yield is small. This preparation is essentially the oxidation of phosphites, $(RO)_3P$. A number of different oxidizing agents have been employed, including barium peroxide, vanadium pentoxide, arsenic pentoxide, nitrogen oxides, sulfur trioxide, sulfuric acid, and persulfuric acid. [85][86]

7. <u>Thermal Decomposition of Acid Phosphates</u>[87]

This reaction can be represented by

$$(RO)_2 NaOPO + 2(RO)_2 P(O)OH \xrightarrow{\quad 300\,C \quad} 2(RO)_3 PO + NaO(HO)_2 PO.$$
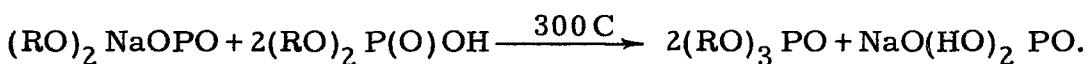
It is probably most applicable to preparation of low molecular weight esters.

For a detailed consideration of several of the above mentioned synthetic methods the reader should consult the extensive references listed by Kosolapoff. [38]

C. <u>Purification</u>

The method of large scale production of tributyl phosphate has not been ascertained but is presumed to be method 1. The crude product impurities would be butoxy phosphorus oxychloride, $BuOPOCl_2$; dibutoxy phosphorus oxychloride, $(BuO)_2 POCl$; dibutyl and monobutyl phosphates; butyl alcohol and "condensed" products such as the pyrophosphates,

$(BuO)_2 - \overset{O}{\underset{\|}{P}} - O - \overset{O}{\underset{\|}{P}} - (BuO)_2$; polyphosphates, $\left[(BuO)_2 \overset{O}{\underset{\|}{P}}O \right]_n \overset{O}{\underset{\|}{P}} - (OBu)_2$;
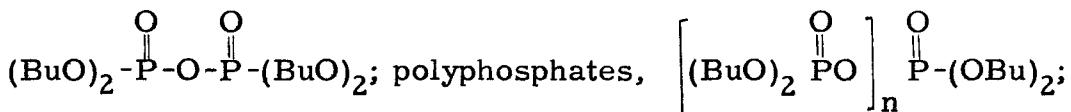
and the metapohosphates, $(BuOPO_2)_n$. It should be noted also that

(85) Chemisch Fabrick Von Heyden A. -G. British Patent, 398659, <u>Chem. Abs.</u> 28, 13625 (1934).

(86) Whitmore, F. C., <u>Organic Chemistry</u>, New York: D. Van Nostrand (1937) p. 173.

(87) Victor Chem. Co., U. S. Patent - 2,410,118 (1946).

the product tributylphosphate is not stable to many of the reagents employed in its synthesis. Thus phosphorus oxychloride, $POCl_3$, reacts with TBP to give intermediate esters; e. g., $BuOPOCl_2$.[88]

Similarly, a method of preparation involving P_2O_5 can give a high yield of the aforementioned condensed phosphates. These reactions go quite easily, and by controlling the ratio of P_2O_5 to TBP one can actually use this method to produce condensed phosphates of the stoichiometric structure.[3] A common property of the condensed phosphates is their ease of hydrolysis leading to butyl acid orthophosphates. The partially esterified $POCl_3$ hydrolyses even more easily. These reactions are considered in Section III-D.

Other compounds that have been reported present in commercial TBP include dibutyl butyl phosphonate, $(BuO)_2$-$\overset{O}{P}$-Bu.[63]

The hydrolysis products, and hence the condensed phosphates and partially reacted phosphorus oxychloride, can all be removed by water washing if sufficient time is taken. Sodium carbonate or sodium hydroxide solutions are much more effective than water. Distillation at reduced pressure following an aqueous wash should produce nearly pure TBP. However, if care is not taken, varying amounts of butyl alcohol and unhydrolyzed intermediates such as $(BuO)_2POCl$ might still remain. Traces of tetrabutyl pyrophosphate and most of the phosphonates, phosphinates or phosphine oxides, if present, could distill with the TBP. DBP and MBP are not volatile and therefore would be separated. (Traces of phosphonates, phosphinates and phosphine oxides are not objectionable from a solvent extraction point of view, although their hydrolysis products would be.)

Steam stripping from dilute caustic has been suggested for removing butyl alcohol.[11] A one hour treatment with steam and a five-fold

---

(88) Gerrard, W., *J. Chem. Soc.*, *1940*, 1464.

volume of 0.4 per cent sodium hydroxide removed all the alcohol and also reduced the acidity of crude TBP to a negligible value. Distillation of crude ester mixture over excess alkali is the basis of a patent assigned to the Food Machinery and Chemical Corporation.[89]

Distillation of TBP over solid sodium carbonate was studied by Lane[2] who concluded that such a distillation did not produce purer TBP than straight distillation but did eliminate "bumping," thus providing better control. Lane's other comments in regard to the distillation included: (1) distillation at 10-15 mm Hg pressure (~150 C) is satisfactory after the TBP has been washed, (2) distillation of crude TBP at greater than 100 C causes further decomposition, and (3) the acid decomposition products-DBP- for example, cause further TBP degradation. Decomposition during distillation is also discussed by Lanham and Reilly.[28] Another method of purification used by Lane consists of passing the TBP through a 12 in. x 1/2 in. column filled with calcium hydroxide. This dries the TBP and reduces the acidity to zero, and is claimed to be more effective than the anion exchange resin, "Amberlite IRA-400," which has also been used. The separation of the butyl acid phosphates by ion exchange was examined by Baldwin and Higgins.[20][61]

While distillation at reduced pressure is probably the most efficient method of purification of TBP and other tertiary esters, it should be noted that several of the reactions discussed in this section as well as pyrolysis may occur during the distillation step. The vapor pressures of some typical impurities are listed elsewhere in the Appendix.

D. Aqueous Phase Hydrolysis of Other Phosphate Esters

The following information is compiled from a comprehensive literature search on the hydrolysis reactions of other phosphate esters. It is

(89) U. S. Patent, Chem. Abs. 44, 3005.

included here to support the data for TBP.

One of the earliest studies of organic phosphate hydrolysis was made by Cavalier[90] who studied the "saponification" of PO_4R_3, PO_3R_2H and PO_4RH_2 where R was methyl (I) ethyl (II) and propenyl (III). These results are included in Table XXI and can be summarized briefly: (1) In H_2O at 88 C, the hydrolysis rates were III > I > II. (2) Hydrolysis rates of the triester were 10 to 20 times as rapid as those of the diester; hydrolysis rates of the monoesters were slightly faster than those of the diesters. (3) The hydrolysis rate of the triester was more rapid with a base than with water, whereas the di- and monoesters were stable to bases at 90 C. (4) The rates at 88 C were 100 times faster than at 44 C. Tennessee Eastman Corp. lists for triethyl phosphate 0.033 per cent per hour at 50 C.[91] Plimmer and Burch[92] studied the effect of 2 $\underline{N}$ sodium hydroxide and 2 $\underline{N}$ sulfuric acid on the hydrolysis rates of the ethyl and propyl esters. Their data are shown in Table XVII.

With caustic, only the triester hydrolyzed; the half life appears to be about six hours if first order kinetics are assumed. This corresponds to about twelve per cent per hour or ten times faster than with pure water at the same temperature (Cavalier at 88 C). Plimmer and Burch made no kinetic calculations. However, one may assume that the hydrolysis in 1 $\underline{M}$ sulfuric acid proceeds according to the equations

$$TEP \xrightarrow{k_1} DEP + ETOH \xrightarrow{k_2} MEP + ETOH \xrightarrow{k_3} H_3PO_4 + ETOH,$$

with each step first order with respect to the ester.*
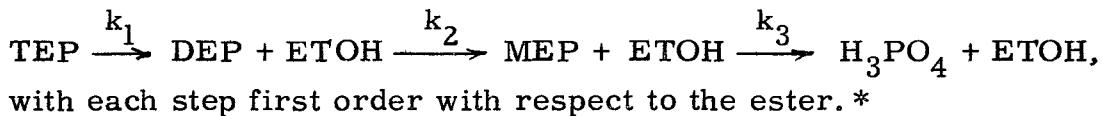
(90) Cavalier, J., Compt. Rend. 127, 114-5 (1898).
(91) Tennessee Eastman Corp., "Triethyl Phosphate" Industrial leaflet.
(92) Plimmer, R. H. A., Burch, W. J. N., J. Chem. Soc., 1929, 279, 292.

*Following the convention adopted with TBP and derivatives, the alkyl groups are represented by the first letter of the radical name, while mono- and di- are abbreviated M and D, respectively. P indicates orthophosphate.

TABLE XVII

REACTIONS OF PHOSPHATE ESTERS
WITH SODIUM HYDROXIDE AND WITH SULFURIC ACID

Concentration 5 g ester/l
Source - Plimmer and Burch[92]

Compound	Reflux Time at 90 C	Moles alcohol produced per mol ester
	2 M NaOH	
Ba diethyl phosphate	8 to 96 hrs.	No hydrolysis
Ba dipropyl phosphate	8 to 96 hrs.	No hydrolysis
Triethyl phosphate	15 hrs.	0.79
	30	0.92
	1 M H$_2$SO$_4$	
Ba diethyl phosphate	20	0.045
	48	0.086
	144	0.53
	216	0.82
	386	1.87
Ba dipropyl phosphate	48	0.275
	96	0.525
Triethyl phosphate	8	0.84
	48	1.12
	120	1.4
	240	1.8
	360	2.5

The total alcohol may then be shown equal to

$$EtOH_t = 3A_o - A_o \left[3 + 2 \frac{k_1}{k_2 - k_1} + \frac{k_1 k_2}{(k_1 - k_3)(k_1 - k_2)} \right] e^{-k_3 t},$$

$$+ A_o \left[2 \frac{k_1}{k_2 - k_1} - \frac{k_1 k_2}{(k_2 - k_3)(k_2 - k_1)} \right] e^{-k_2 t} - A_o \left[\frac{k_1 k_2}{(k_3 - k_1)(k_3 - k_2)} \right] e^{-k_3 t},$$

where A_o is the initial TEP concentration. A similar but simpler expression applies to the reaction which begins with diethyl phosphate (DEP). The data of Table XVII for the ethyl phosphates can be fitted by $k_1 = 0.15$ hr^{-1}, $k_2 = .003$ hr^{-1} with an uncertainty of about 30 per cent. All that can be said concerning k_3 is that it is greater than k_2 and much less than k_1. It is interesting that the rate constant for the first step, k_1, is about the same as that for the reaction in 2 M sodium hydroxide. The data for TBP, Table V, may be compared here. A faster rate for alkaline hydrolysis than for acid hydrolysis was indicated in the latter case.

Hochwalt[93] studied the stability of a five per cent solution of a mixture of DEP and monoethyl phosphate (MEP) in H_2O at 25 C. These data, presented in Table XIX, suggest that k_2 (DEP→MEP step) is about 3.5×10^{-4} hr^{-1}. Although k_3 cannot be evaluated with any certainty (since the data for MEP and H_3PO_4 are in some disagreement) a value of about 1.5×10^{-4} fits the MEP concentrations. Thus, Hochwalt's data show $k_2 > k_3$ in contrast to the previously mentioned results, and any reasonable value of the activation energy (e. g., 10-20 kcal) would yield rates at 50 C or 88 C much higher

(93) Hochwalt, C. A., et al., Ind. Eng. Chem., 34, 20 (1942).

than the previous data show. As will be seen later, comparison of rates in water solution is difficult because of the change of pH as hydrolysis progresses. Hochwalt's five per cent solution is actually quite acid.

Drushel[94] studied the primary hydrolysis of several simple and mixed phosphate esters. In 0.1 $\underline{M}$ hydrochloric acid a trimethyl phosphate solution gave rate constants $k_1 = 1.6 \times 10^{-3}$ hr^{-1} at 25 C and 3.2×10^{-2} hr^{-1} at 100 C, corresponding to an activation energy of 12.7 kcal. The methyl phosphate hydrolyzed four times faster than the ethyl ester.

In the region between the strong acid hydrolysis and alkaline hydrolysis the picture has been clarified by the work of Desjorbet.[56] A study of the hydrolysis rate of monoethyl phosphate in water at 100 C as a function of pH revealed that a minimum rate occurred at pH = 1. As the pH was raised to 4, the rate increased. At about pH = 5, the rate decreased, and became negligible at pH = 8. At higher acidities than pH = 1, the rate increased very rapidly in 2 $\underline{M}$ hydrochloric acid was about eight times faster than in 0.1 $\underline{M}$ hydrochloric acid, and in 7.5 $\underline{M}$ hydrochloric acid about 120 times faster. His data show a first order rate constant, k_3, of 6.5×10^{-3} hr^{-1} in 0.1 $\underline{M}$ hydrochloric acid and 0.046 hr^{-1} in 2 $\underline{M}$ hydrochloric acid. The reactions were followed nearly to completion and the work appears to be carefully done. Desjorbet pointed out that the maximum rate occurred at the point of neutralization of the first hydrogen (pH = 4 to 5) and the negligible rate at the neutralization of the second hydrogen (pH = 8). On the high acid side, the nature of the acid was important. Data taken from Desjorbet's curves are listed in Table XIX.

(94) Drushel, W. H., Am. J. Sci. 190, 643 (1951).

TABLE XVIII

HYDROLYSIS OF ETHYL PHOSPHATES

5% water solution, 25 C
Source - Hochwalt[93]

Time, days	Per cent P present as:		
	Diethyl-	Monoethyl-	Phosphoric Acid
0	40.3	50.0	9.7
4	39.7	48.0	12.3
11	36.1	50.0	13.9
18	34.3	50.0	15.7
26	31.4	53.3	15.3
32	31.2	53.4	15.4
39	29.2	54.7	16.1

TABLE XIX

HYDROLYSIS OF MONOETHYL PHOSPHATE

0.1 $\underline{M}$ solution, 100 C, source Desjorbet[56]
(% Hydrolyzed in 6 hours)

Acid	Acid Conc.: 1 $\underline{M}$	2 $\underline{M}$	4 $\underline{M}$
HI	17	27	100
HBr	13	23	84
HCl	10	16	38
HNO_3	6	7	17
H_2SO_4	5	6	7

Desjorbet's work shows that the rates, while generally increasing with acid concentration, are not proportional to it except over small ranges.

Considerable work has also been done on the hydrolysis of methoxy-ethyl phosphates and glycerophosphates, $(AO)_2P(O)OCH(CH_2OH)_2$ where A is a hydrogen atom or an alkyl group[95-99] as well as acetyl phosphate[52] and other phosphates of biochemical interest.[100] These studies, in common with those on alkyl esters, show that, (a) the methyl group is more easily removed than a larger one,[95] (b) there is a marked pH effect on alkaline hydrolysis,[52][100] and (c) alkaline hydrolysis usually stops at the diester.[94][95] An apparent anomaly is that organic acids are reported to have a greater catalytic action than strong acids. For example, 1 $\underline{M}$ acetic acid produces hydrolysis of glycero dihydrogen phosphate and methyl dihydrogen phosphate at a rate 3 to 4 times more rapid than does 1 $\underline{M}$ sulfuric acid.[97][98] In addition to hydrolysis, these compounds containing complex ester groups frequently undergo reactions directly involving those groups.

Ketelaar[101] examined the rates of hydrolysis of the methyl and ethyl p-nitrophenyl phosphates in neutral solution and in alkaline solutions. His study was carried out in 50 per cent acetone solution to increase the solubility, and was concerned with the first stage, the hydrolysis of the tertiary ester. Only the nitro-phenyl cleavage was determined. His results indicated a faster reaction as more nitrophenyl (NO_2ph-) groups were added; e. g. , the hydrolysis rates for $(ETO)_2(NO_2phO)PO$, $(ETO)(NO_2phO)_2PO$,

(95) Bailly, O. , Gaume, J., Bull. Soc. Chem. 2, 354 (1935); 3, 1396 (1936).
(96) Malengreau, F. , Prugent, F., Z. Physiol. Chem. 75, 68 (1911).
(97) Fluery, P. , Courtois, J. , Bull. Soc. Chim. 9, 570 (1942).
(98) Verkade, P. E. , Stoppelenburg, J. C. , Cohen, W. D. , Rec. Trav. Chim. 59, 886 (1940).
(99) Darmon, M. , Bull. Soc. Chim. 1947 262.
(100) Fluery, P. , Compt. Rend. 221, 416 (1945).
(101) Ketelaar, J. A. , Gersman, H. R. , Koopmans, K. , Rec. Trav. Chim. 71, 1253 (1953).

and $(NO_2phO)_3$ PO were in the order 0.4, 31.5, 2060 1 mol^{-1} at 25 C in dilute caustic. * The significance of this may be questioned since the ethyl group may hydrolyze easier than the ph-NO_2 group, and in this case he would actually be measuring the rates for the compounds (NO_2phO)-$P(O)(OH)_2$, $(NO_2phO)_2P(O)(OH)$, and $(NO_2phO)_3$ PO, a quite different situation. ** The work is interesting from the mechanism standpoint and is mentioned in that section. The activation energy varied from about 12 to 14 kcal for the hydrolysis reactions of the ethyl derivatives and was about 4 kcal for trinitrophenyl phosphate.

Gerrard, Green, and Nutkins[26] refluxed various isooctyl esters of phosphoric acid with potassium hydroxide solution and determined the alcohol produced. The data together with pertinent calculations are shown in Table XX.

Thus, even though an excess of organic may be present, these reactions can probably be treated as aqueous phase reactions. The aqueous phase is saturated at all times; however, as the solubility is not known, a rate constant cannot be calculated. The apparently greater rate for the diisooctyl acid phosphate is perhaps a reflection of the much larger solubility of this compound. However, the minor effect produced by solubilizing the triester with ethyl alcohol does not suggest this. Data on this hydrolysis of diisooctyl phsphate are in disagreement with other reports that the dialkyl and monoalkyl esters are completely stable in alkaline solution.

Hydrolysis data for the various alkyl phosphates discussed in this section are listed in Table XXI.

---

*Ketelaar writes a second order rate constant for the overall reaction, since his work indicated that the hydrolysis was first order with respect to both OH⁻ and ester. In the present paper, where it is not expressly stated, the concentration of acid or base is considered constant and the rate constant given for the ester alone.

**Support for Ketelaar's interpretation is his observation that the analogous compound diethyl nitrophenyl phosphorothioate, "parathion," hydrolyzed to the diethyl phosphorothioate which was stable.

TABLE XX

HYDROLYSIS OF
ISOOCTYL PHOSPHATE IN POTASSIUM HYDROXIDE SOLUTIONS

R - isooctyl; temperature - boiling point of solution; Source - Gerrard[26]

Compound	Conc. Ester, Moles per Liter Solution*	Aq. Phase	Time, hrs.	Alcohol Produced, $\underline{M}$
$(RO)_3 PO$	0.092	1 $\underline{M}$ KOH	24	0.040
		2 $\underline{M}$ KOH in EtOH	27	0.050
$(RO)_2 P(O)OH$	0.248	1 $\underline{M}$ KOH	28	0.21
$(RO)_2 P(O)OEt$	0.179	1 $\underline{M}$ KOH	25	0.532
		1 $\underline{M}$ KOH in EtOH	24	0.054
		2 $\underline{M}$ KOH in EtOH	38	0.068

*Organic phase probably present.

TABLE XXI
RATE CONSTANTS FOR THE AQUEOUS HYDROLYSIS OF ALKYL PHOSPHATES

Ester+	System	Temp, C	$k_1{}^*$ hr^{-1}	k_2 hr^{-1}	k_3 hr^{-1}	References
TMP	H_2O	88	0.063	3.6×10^{-3}	5.6×10^{-3}	(90)
TMP	0.1 $\underline{M}$ HCl	100	0.131	--	--	(94)
TMP	0.1 $\underline{M}$ HCl	25	1.6×10^{-3}	--	--	(94)
TMP	0.5 $\underline{M}$ H_2SO_4	100	--	--	8.8×10^{-3}	(97)
TMP	1.0 $\underline{M}$ HOAc	100	--	--	0.016	(97)
TEP	H_2O	25	--	3.5×10^{-4}	3.5×10^{-4}	(93)
TEP	H_2O	88	0.011	1.5×10^{-3}	3.2×10^{-3}	(90)
TEP	H_2O	44	1.1×10^{-4}	--	--	(90)
TEP	H_2O	50	3.3×10^{-4}	--	--	(91)
TEP	1 $\underline{M}$ HNO_3	100	--	--	8.9×10^{-3}	(56)
TEP	2 $\underline{M}$ HNO_3	100	--	--	0.0125	(56)
TEP	4 $\underline{M}$ HNO_3	100	--	--	0.023	(56)
TEP	0.001 $\underline{M}$ HCl	100	--	--	0.0195	(56)
TEP	0.1 $\underline{M}$ HCl	100	--	--	6.5×10^{-3}	(56)
TEP	2.0 $\underline{M}$ HCl	100	--	--	0.046	(56)
TEP	7.5 $\underline{M}$ HCl	100	--	--	0.825	(56)
TEP	0.1 $\underline{M}$ HCl	100	0.0318	--	--	(94)
TEP	1 $\underline{M}$ H_2SO_4	90	0.15	3×10^{-3}	3×10^{-3}	(92)
TEP	2 $\underline{M}$ NaOH	90	0.11	Negligible	Negligible	(92)
TPP	1 $\underline{M}$ H_2SO_4	90	--	6×10^{-3}	--	(92)

+The second letter in the code, M, E or P refers to methyl, ethyl, or propyl, respectively.

*The symbols k_1, k_2, and k_3 represent the rate constants for the hydrolysis of the triester, diester, and the monoester, respectively.

L. L. Burger