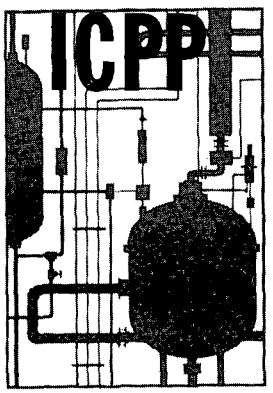

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BASIC STUDIES OF CHEMICAL STABILITY IN EXTRACTION SYSTEMS I. THE EFFECT OF ZIRCONIUM NITRATE AND NITRIC ACID UPON THE CHEMICAL STABILITY OF TRIBUTYL PHOSPHATE

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BASIC STUDIES OF CHEMICAL STABILITY IN EXTRACTION SYSTEMS
I. THE EFFECT OF ZIRCONIUM NITRATE AND NITRIC ACID UPON THE CHEMICAL STABILITY OF TRIBUTYL PHOSPHATE

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A B S T R A C T

The effect of extracted zirconium and nitric acid upon the chemical stability of tributyl phosphate was investigated using gas-liquid chromatography. Tributyl phosphate was degraded approximately 1000 times faster by the tributyl phosphate-zirconium reaction than by the tributyl phosphate-nitric acid reaction. Normal butyl nitrate was the major volatile product for both systems studied; with extracted zirconium a solid complex corresponding to the formula $Zr(NO_3)_2(DBP)_2$ was also obtained.

BASIC STUDIES OF CHEMICAL STABILITY IN EXTRACTION SYSTEMS

I. THE EFFECT OF ZIRCONIUM NITRATE AND NITRIC ACID UPON THE CHEMICAL STABILITY OF TRIBUTYL PHOSPHATE

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I. SUMMARY

The effect of extracted zirconium and nitric acid upon the chemical stability of diluent-free tributyl phosphate (TBP) was investigated using gas-liquid chromatography as a means of identifying and measuring the amounts of the volatile products. The TBP-HNO_3 reaction was found to be a dealkylation reaction forming n-butyl nitrate as the major volatile product over the organic phase nitric acid concentration range of 0.9-2.9M.

Extracted zirconium was found to degrade TBP approximately 1000 times faster than extracted nitric acid. The major products for the TBP-Zr reaction were found to be n-butyl nitrate and a solid complex corresponding to the formula $Zr(NO_3)_2(DBP)_2$.

The effect of solid $ZrO(NO_3)_2 \cdot 2H_2O$ upon the stability of pure TBP was briefly investigated.

II. INTRODUCTION

A study of process problems at the Idaho Chemical Processing Plant has shown that tri-n-butyl phosphate (TBP) will react to form a solid zirconium organic phosphate when contacted with simulated process solutions.[1] Thus, the initial purpose of this investigation was to determine the effect of both aqueous and extracted zirconium species upon the rate of "hydrolysis" of diluent-free TBP and to identify the solid zirconium organic phosphates which were produced.

Much of the information pertaining to rates of hydrolysis of TBP has been reviewed by Burger.[2] Most of the attention which has been given to the TBP hydrolysis reaction was based upon acid formation (dibutyl phosphoric acid, HDBP; monobutyl phosphoric acid, H_2MBP; and H_3PO_4) with little emphasis or interest placed upon the more volatile products

(n-butyl nitrate and n-butyl alcohol). Nichols and Siddall[3] reported that both n-butyl alcohol and n-butyl nitrate were found in the hydrolysis reaction with nitric acid. However, n-butyl nitrate was found only in significant quantities at high temperature (>100°C) and high acid concentrations.

The determination of various acid decomposition products in the presence of Zr(IV) and nitric acid by acid-base titrations is difficult. To avoid this difficulty, the course of the reaction was followed by determining the amounts of the more volatile TBP decomposition products (n-butyl alcohol and n-butyl nitrate) with a gas chromatograph. Work by Baldwin[4] would indicate that most of this volatile product might be n-butyl nitrate rather than n-butyl alcohol; in either case the rate of formation of the volatile decomposition product could be estimated by the use of gas chromatography.

III. EXPERIMENTAL

Tributyl phosphate was purified by washing with 10% sodium hydroxide followed by water washes to remove any excess caustic. The TBP was then dried and distilled under reduced pressure in a 3-foot Todd column packed with glass helices. The product was collected at 117-119°C (approximately 1.0 mm Hg; $n_D^{23} = 1.4234$).

Zirconyl chloride (from Fisher Scientific Co.) was recrystallized three times from approximately 6M HCl. An aqueous solution of the recrystallized $ZrOCl_2 \cdot 8H_2O$ was then boiled while maintaining a constant volume of liquid by the addition of 16M HNO_3. This process was continued until no trace of chloride (by testing with a solution of $AgNO_3$) was found in the Zr(IV)-$(NO_3)^-$-HNO_3 solution. This stock solution was then used to prepare the Zr-HNO_3 solutions for equilibration with TBP. In some cases the original stock solution was equilibrated directly with TBP and the resultant organic phase was diluted with TBP to obtain the desired zirconium and HNO_3 concentrations.

Organic phase zirconium and nitrate concentrations were determined by the titration of aliquots in the presence of and in the absence of excess fluoride (i.e., F/Zr >6) with standard sodium hydroxide.[5] By itself the latter yields the nitrate concentration; the difference of the two titrations is related to the zirconium concentration.

n-Butyl nitrate was prepared according to the procedure described for methyl nitrate.[6] Final purification of product was by distillation at reduced pressure (B.P. = 48°C at 30 mm Hg; n_D^{22} = 1.4017).

The rate of formation of n-butyl nitrate in TBP-nitrate systems was determined using a Pye Argon Chromatograph. Runs on unknowns were interspersed with runs with TBP solutions containing known amounts of n-butyl nitrate; and then unknown concentrations were estimated through a comparison of peak heights. Peak heights were used instead of peak areas since the n-butyl nitrate peak is rather narrow. The variation of peak heights with concentration was found to be linear over the range studied.

The column packing and stationary liquid used were the acid washed "Chromosorb" (60 to 80 mesh) and "LAC-2R446" (Research Specialties Co.) in a three to one ratio by weight, respectively.

Some difficulty was encountered using the argon ionization detector for the quantitative determination of n-butyl nitrate. Both positive and negative peaks were obtained for n-butyl nitrate depending upon the condition of the column. Freshly prepared columns gave negative peaks while those which were baked at 200-300°C for extensive periods of time gave positive peaks. The general procedure which was followed was to flush the column at 200°C for several hours each night to remove any residual materials such as TBP (which is trapped in the column at the 100°C operating temperature). Continual operation at 100°C without the periodic baking at 200°C resulted in a gradual decrease in peak amplitude with the ultimate formation of negative peaks. The reason for the peak reversal (regardless of concentration) appears to be due to the high ionization potential of n-butyl nitrate coupled with the residual column impurities such as TBP which causes increased conduction in the ionization chamber. Thus, conduction due to a continual background of impurities would lower the voltage applied to the detector such that the n-butyl nitrate would not be ionizable and would pass through the detector unnoticed (no peak) or serve as a quenching agent for the activated argon (negative peak). Improved performance was obtained by operating the chromatograph at the highest detector voltages available (1750 and 2000V). It is the opinion of the authors that the data obtained with an ionization detector are reliable, but future studies of this type will be made using a more suitable detector with possibly lower sensitivity.

The solid zirconium organic phosphates were analyzed for carbon, hydrogen, phosphorus, nitrogen,[7] and zirconium.[8] n-Butyl nitrate was identified by means of mass spectrometry.[9]

IV. RESULTS AND DISCUSSION

A. TBP-HNO_3 Reaction

TBP is a major solvent in the processing of nuclear fuels. It owes its success primarily to its chemical stability.[2] Generally, it is assumed that the primary reaction between TBP and dilute aqueous acids at temperatures less than 100°C is a hydrolysis reaction;[2] and it has been suggested that in the presence of concentrated acids the primary reaction may be a dealkylation reaction (i.e., $C_4H_9ONO_2$ and C_4H_9Cl are the products from TBP and HNO_3 or HCl, respectively).[4] Blumenthal and Herbert,[10] in studying the hydrolysis of trimethyl phosphate, stated that their results showed that when the solution was acid or neutral the O-CH_3 bond was broken preferentially. Under alkaline conditions the P-OCH_3 bond of the ester was broken. Gerrard, et al., obtained excellent yields of alkyl halides using dry hydrogen halides on tertiary phosphates.[11]

Preliminary studies by the authors have demonstrated that the principal reaction which occurs between TBP and HNO_3 or HCl is a dealkylation reaction producing n-butyl nitrate or n-butyl chloride.[12]

$$\text{TBP} + HNO_3 \longrightarrow C_4H_9ONO_2 + \text{HDBP, } H_2\text{MBP and } H_3PO_4 \qquad (1)$$

Otherwise the major volatile product would be n-butyl alcohol. It is possible that n-butyl alcohol is formed first and then rapidly converted to n-butyl nitrate; however, no n-butyl nitrate was detected when n-butyl alcohol and 5M nitric acid were contacted for several days at 50°C.

Fig. 1 shows the rate of increase of n-butyl nitrate as a function of time for the TBP-HNO_3 reaction. Most of these experiments were carried out using the organic phase; however, the presence of the aqueous phase produced no detectable change in the n-butyl nitrate formation rate. When equal volumes of pure TBP and 5M HNO_3 are equilibrated, 99% of the reaction occurs in the organic phase;[2] thus, for the TBP-HNO_3 reaction, the two phases may be left in contact after equilibration or separated, whichever is the more convenient. Samples for analysis were always withdrawn from the organic phase.

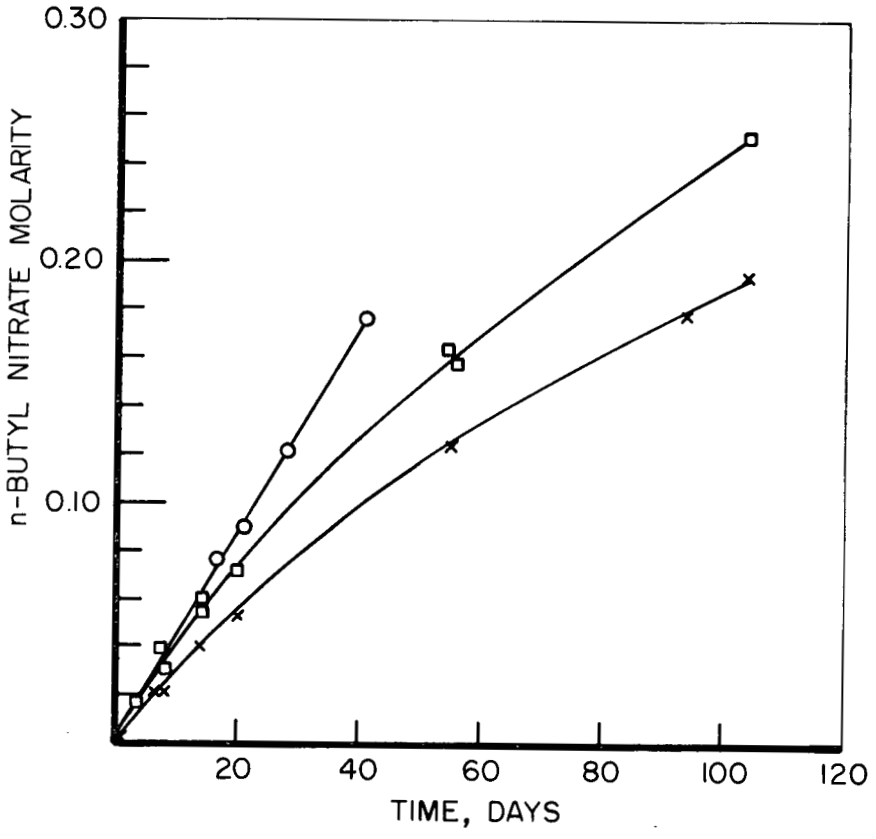

Fig. 1 - n-Butyl Nitrate Formation in TBP-HNO_3 Reagent as a Function of Time (50°C). Organic phase HNO_3 molarity O 2.92, □ 2.02, X 0.89

The TBP-HNO_3 reaction appears to be approximately first order with respect to TBP concentration. The rate constants (Table 1), which were calculated by

$$k = \frac{1}{t} \ln\left(\frac{a}{a-x}\right) \qquad (2)$$

where k is the rate constant in hr^{-1}, a is the initial TBP concentration and x is the n-butyl nitrate concentration at time t, are reasonably constant over the interval of time during which the reaction was followed. However, the rate constants appeared to be decreasing with time. This decrease in k might be the result of at least three effects: first, n-butyl nitrate is not stable in the presence of acid and may be decomposed;[6] second, after the reaction begins, HDBP and H_2MBP undergo further decomposition as they are formed, thereby complicating the reaction; and third, the role which the extracted HNO_3 plays upon the reaction is not clear (order less than one for data in Table 1) and may also account for any variations which are observed. The data at 50°C in Table 1 compare very favorably with the organic phase hydrolysis data summarized by Burger for 100% TBP.[2]

Table 1

FIRST ORDER RATE CONSTANTS FOR TBP-HNO_3 REACTION AT 50°C AS A FUNCTION OF HNO_3 CONCENTRATION

Initial Aq. HNO_3 M*	Org. HNO_3 M	k x 10^5 (hr^{-1})
2.0	0.89	3.4 ± 0.4‡
5.0	2.02	4.5 ± 0.6‡‡
8.0	2.92	6.7 ± 0.3

* Equal volumes of organic and aqueous phases were equilibrated at room temperature.

‡ Standard deviation.

‡‡ This value may be compared with the 5.5 x 10^{-5} hrs^{-1} value of Kennedy and Grimley.[12]

In spite of the large amount of data which is available on the "hydrolysis" of TBP, very little is actually known about the mechanism and the effect of water and nitric acid upon the reaction. Also, more information should be obtained about the behavior of HDBP and H_2MBP before a more complete evaluation can be made of the data obtained thus far.

B. The TBP-Zirconium Reaction

The presence of zirconium in process solutions as an alloy component, a fission product, or both, and its effect upon TBP[1,13] emphasize the need for a better understanding of the TBP-zirconium reaction.

Extracted zirconium, $Zr(NO_3)_4 \cdot 2TBP$,[14] has been found to react with TBP to produce a relatively insoluble, crystalline zirconium organic phosphate.[1] The same compound was also prepared from HDBP and a 2.0M HNO_3 solution of zirconium. Results of the latter method were not predictable and often an amorphous material of variable composition was obtained.[15] The TBP-zirconium reaction always produced a crystalline compound whose X-ray pattern and composition are given in Tables 2 and 3, respectively. This crystalline compound appears to have the formula, $Zr(NO_3)_2(DBP)_2$.

Table 2

X-RAY[16] DATA FOR $Zr(NO_3)_2(DBP)_2$

d(Å)	I/I_1
11.2	100
10.7	55
6.54	15
6.34	15
5.65	15
5.42	15
4.75	20
4.43	20
4.11	25
3.84	20
3.34	20

Table 3

COMPOSITION OF THE CRYSTALLINE Zr-TBP PRODUCT

Element	Wt% Found	Wt% Calc'd for $Zr(NO_3)_2(DBP)_2$
C	31.0	30.3
H	6.0	5.7
P	9.7	9.8
N	4.1	4.4
Zr	13.3	14.4
Total %	64.1	64.6

Since n-butyl nitrate is the volatile product which is formed, the overall reaction may be written as:

$$Zr(NO_3)_4 \cdot 2TBP \xrightarrow[HNO_3]{TBP} Zr(NO_3)_2(DBP)_2 + 2C_4H_9ONO_2. \qquad (3)$$

Thus, when extracted zirconium and acid are present, TBP may be degraded by two methods; first, the TBP-Zr reaction (Equation 3) and second, the $TBP\text{-}HNO_3$ reaction which was discussed above. Fig. 2 depicts the formation of n-butyl nitrate as a function of time for the $TBP\text{-}HNO_3$

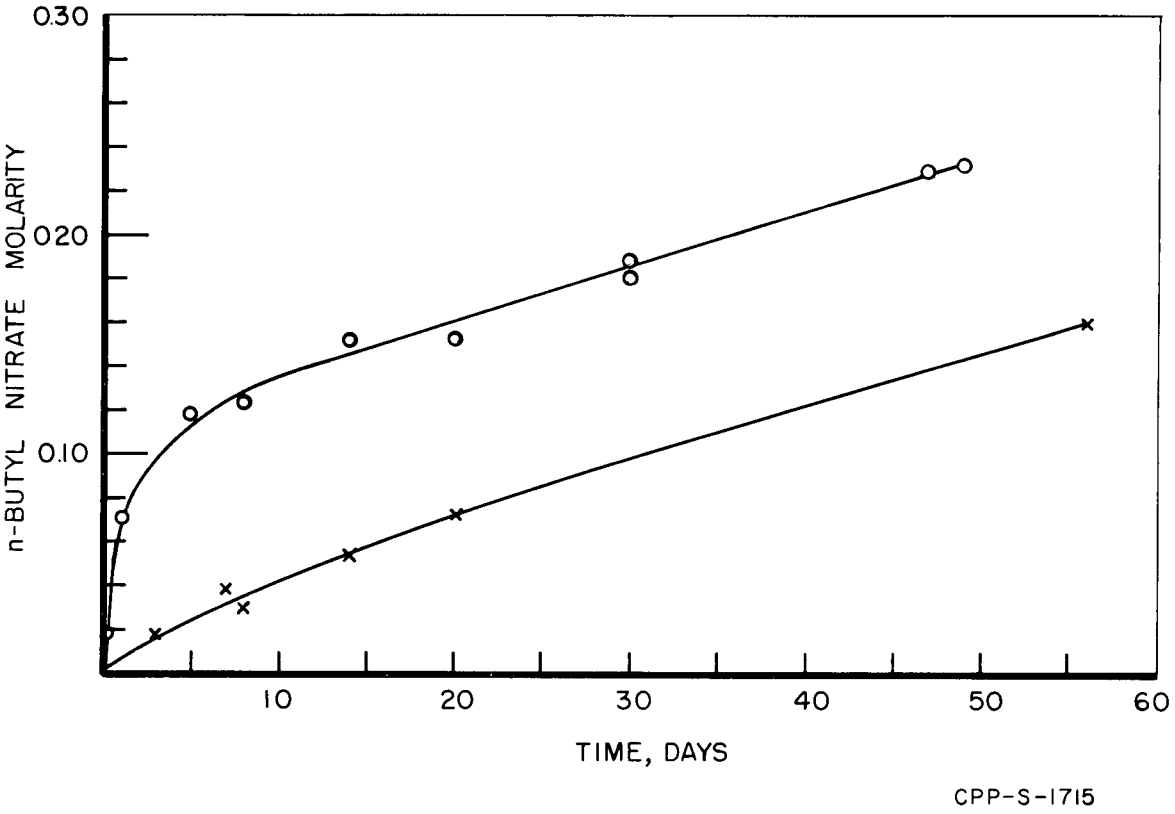

Fig. 2 - Comparison of TBP-Zr Reaction and TBP-HNO_3 Reaction at 50°C. (O-TBP Equilibrated with 0.255M Zr - 5.50M NO_3^- solution; X-TBP Equilibrated with 5.01M HNO_3).

reaction and the combined TBP-Zr, TBP-HNO_3 reactions.

According to Fig. 2 there actually is a rapid initial decomposition of $Zr(NO_3)_4 \cdot 2TBP$ followed by the slower TBP-HNO_3 reaction. It has not been established whether the zirconium tetranitrate complex undergoes rearrangement or whether additional free TBP molecules are involved in the reaction. The point where the zirconium reaction ends (i.e., the Zr is used up) and the HNO_3 reaction becomes the predominant reaction indicates that approximately one mole of n-butyl nitrate is formed per mole of zirconium.

The TBP-Zr reaction appears to be divided into two parts. This premise is based upon the fact that the solid, $Zr(NO_3)_2(DBP)_2$, does not precipitate from the TBP solution until after the TBP-Zr reaction is almost completed (approximately 3 days at 50°C). The first part of the reaction can then be represented by:

$$Zr(NO_3)_4 \xrightarrow{TBP} Zr(NO_3)_3DBP + C_4H_9ONO_2, \quad (4)$$

where $Zr(NO_3)_3DBP$ is the suggested soluble product. The organic HNO_3 concentration had no noticeable effect upon this initial phase of the zirconium reaction, as evidenced by the rate of formation of n-butyl nitrate.

The second part of the reaction appears to be tied in closely with the TBP-HNO_3 reaction:

$$TBP + HNO_3 \longrightarrow HDBP + C_4H_9ONO_2, \quad (5)$$

since it was observed that decreasing the organic HNO_3 concentration while maintaining approximately the same zirconium concentration resulted in a marked delay in both the appearance of precipitate and the approximate rate at which the precipitate was formed (see Table 4).

Table 4

TIME FOR THE FIRST APPEARANCE OF $Zr(NO_3)_2(DBP)_2$ PRECIPITATE AS A FUNCTION OF HNO_3 CONCENTRATION AT 70°C

Zr Conc.	HNO_3 Conc.	Time (hrs)
0.12	2.00	9-10
0.11	0.51	20-25

Then, HDBP could react with the soluble species $Zr(NO_3)_3DBP$ to form the insoluble $Zr(NO_3)_2(DBP)_2$ precipitate:

$$Zr(NO_3)_3DBP + HDBP \longrightarrow Zr(NO_3)_2(DBP)_2 + HNO_3 \quad (6)$$

Also, it is possible that the soluble $Zr(NO_3)_3DBP$ species may react with TBP at a much slower rate to produce the observed products.

One experiment was designed to determine the effect of water upon the TBP-Zr reaction. The organic phase (after equilibration with 0.255M Zr-5.50M NO_3^-) was divided into two equal samples. One sample was placed in the 50°C bath while the other sample was evacuated for approximately 1/2 hour at 50°C (approximately 1 mm of Hg) to remove most of the water which was present. The rate of formation of n-butyl nitrate is sufficiently slow to be neglected for this brief period. The sample from which most of the water had been removed produced n-butyl nitrate at a rate slightly greater than the sample with water. It is concluded that the rates are

not appreciably different since the evacuated sample should have a slightly higher zirconium concentration due to volume reduction.

Several experiments similar to the one for which results are shown in Fig. 2 were completed at 50, 60 and 70°C. The TBP-zirconium reaction was found to be first order with respect to the zirconium concentration. Fig. 3 depicts this first order dependency at 50°C.

Table 5 gives the rate constants for the TBP-Zr reaction at 50, 60 and 70°C. An activation energy of 20 kcal was calculated from Fig. 4,

Table 5

RATE CONSTANTS FOR THE TBP-Zr REACTION AT 50, 60 and 70°C

Temp.	k x 10^2 (hr^{-1})
50	5.0
60	13
70	35

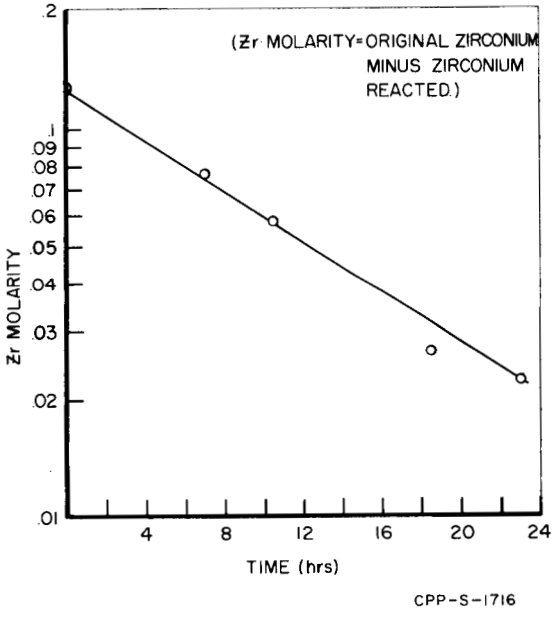

Fig. 3 - First Order Dependency of TBP-Zr Reaction Rate Upon Zr Concentration at 50°C. (Zr Molarity = Original Zr Minus Reacted Zirconium)

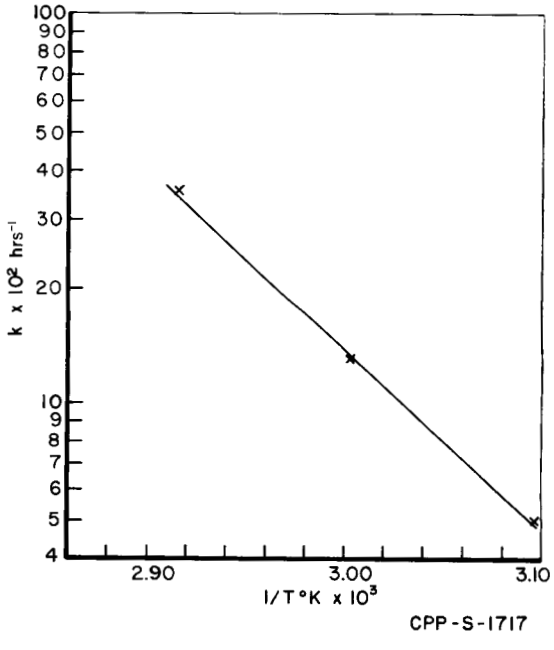

Fig. 4 - Variation of TBP-Zr Reaction Rate Constants With Temperature

which is a semilog plot of rate constants vs $1/T°k$. Generally, the reaction rate constants measured at various initial zirconium concentrations increased slightly with decreasing zirconium concentration. However, these changes in the rate constants are hardly outside of experimental error and may be explained by the fact that less TBP is available for reaction as the Zr concentration is increased because of the $Zr(NO_3)_4 \cdot 2TBP$ complex which is formed.

It should be noted that the experimental results at 70°C were complicated. The TBP-Zr reaction appeared to occur normally, but the $Zr(NO_3)_2(DBP)_2$ precipitate reacted noticeably after three or four days at 70°C to form a colloidal compound. Also, the n-butyl alcohol concentration was found to increase markedly after the TBP-Zr reaction was completed. The n-butyl nitrate concentration also increased during this time. Thus, the TBP-Zr reaction at 70°C appears to follow the same general trend as is observed at 50 and 60°C up to the time when the precipitate is formed. No reliable quantitative information is available beyond this point, and rate constants at 70°C were estimated from the data obtained prior to the point of precipitation.

From a comparison of Tables 1 and 5 it may be seen that at 50°C extracted zirconium was found to degrade TBP approximately 1000 times faster than extracted nitric acid.

C. <u>TBP-$ZrO(NO_3)_2 \cdot 2H_2O$ Reaction</u>

Experiments were performed to test the stability of TBP in the presence of solid salts of zirconium. $ZrO(NO_3)_2 \cdot 2H_2O$ and $ZrOCl_2 \cdot 8H_2O$ were found to degrade TBP very rapidly with the production of amorphous zirconium organic phosphates and n-butyl nitrate or n-butyl chloride, respectively. There was an indication (from rate of temperature rise) that the TBP-solid $ZrO(NO_3)_2 \cdot 2H_2O$ reaction would become violent at temperatures greater than 120°C. The composition of the amorphous zirconium organic phosphate product was not definitely determined. Reaction rates were not measured; however, it was noted that they were dependent upon the amount of solid used and were a function of the stirring rate.

A number of additional problems are suggested by the research to date. Since n-butyl nitrate is the major product, it would be desirable to evaluate the effect and chemical behavior of n-butyl nitrate in solvent

extraction processes. It appears to be a reasonably good emulsifying agent and is known to be unstable in the presence of acids. Second, the effect of hydrocarbon diluent on the TBP-Zr reaction and the order of the reaction with respect to TBP concentration must be evaluated. Third, the ultimate course of the TBP-Zr reaction and products at and above 70°C should be investigated. A fourth goal of a continuing program is to determine the effects of other fission products upon the chemical stability of TBP.

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