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THE HYDROLYSIS OF TRIBUTYL PHOSPHATE AND ITS EFFECT ON THE PUREX PROCESS

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THE HYDROLYSIS OF TRIBUTYL PHOSPHATE AND ITS EFFECT ON THE PUREX PROCESS

V. J. Reilly

Work by:

W. B. Lanham, V. J. Reilly

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0.0 Abstract

The rate of hydrolysis of TBP and the effect of the hydrolysis products in the Purex Process have been studied. Hydrolytic conditions may be encountered in the process which would lead to formation of dibutyl phosphoric acid, causing significant losses of tetravalent plutonium in stripping. This situation may be easily alleviated by reducing and stripping the plutonium in the trivalent state.

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1.0 Introduction

The products of hydrolysis of tributyl phosphate are known to have a marked effect on the chemistry of plutonium in the Purex Process, the dibutyl phosphoric acid for its strong complexing action of Pu IV, and monobutyl phosphoric acid for its tendency to form a precipitate with Pu IV. Due to these circumstances, information was desired on the rate of hydrolysis of tributyl phosphate under conditions which may be met in operation of the Purex Process.

2.0 Summary

The relation between DBP concentration in a TBP-kerosene solution and plutonium (IV) losses on stripping has been studied. At the plutonium concentrations expected in the IIB column, the DBP concentration will have to be kept below 0.001% unless the plutonium is reduced to the +3 state.

The strippability of plutonium (III) from a DBP-TBP-kerosene solution has been demonstrated. At DBP concentrations up to 0.01%, it has been shown that plutonium may be readily reduced and stripped.

The hydrolysis of TBP has been measured directly and also in terms of plutonium (IV) stripping losses resulting from the formation of the hydrolysis products. With only the amount of TBP present required to saturate the aqueous phase (no organic phase), the hydrolysis appears to be first order with respect to TBP concentration, with 10% hydrolyzing in 0.35, 0.55, and 1.9 hours at 8.6, 5.4, and 1.04 molar nitric acid, respectively, at the

Summary (continued)

boiling points. At 60°C with 5.4M nitric acid, only 2.9% hydrolyzes in 24 hours. With two phases present, hydrolysis takes place largely in the organic phase, and the total amount hydrolyzing per unit time and volume is much greater than for the single aqueous phase.

Where the degree of hydrolysis was measured in terms of plutonium (IV) stripping losses, the conclusion was borne out that most of the hydrolysis occurs in the organic phase. Such conditions as organic phase (30% TBP in Amsco 123-15) in equilibrium with 6M nitric acid, at 50°C for two hours, or at room temperature for 2 days, result in significant and intolerable plutonium losses (if stripped without reduction). At lower acidities, considerably longer time is required to cause appreciable hydrolysis. The hydrolysis rate is independent of the presence of an aqueous phase.

The amount of TBP distilling unchanged when dilute (1M) nitric acid is concentrated has been determined. Most of the TBP distils with the first fractions of the water, before the acid concentration rises to a destructive level. It appears feasible to limit the TBP hydrolysis during evaporation of an acid solution by designing to avoid extended contact of TBP with concentrated nitric acid, or by operating at reduced pressure. A big unknown in the amount of TBP hydrolyzed is the amount of entrained organic phase carried into the evaporator. The rate of hydrolysis of the intermediates, DBP and MBP, is not known for acidities greater than 3 molar.

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3.0 Discussion

3.1 Pu(IV) - DBP System

Since one of the principal objectives of this work has been the determination of the effect of TBP hydrolysis on plutonium losses, the effect of pure dibutyl phosphoric acid (DBP) on plutonium (IV) losses has been investigated. The DBP used in these experiments, and elsewhere in this work, was prepared by W. H. Baldwin of the Chemistry Division, according to the following scheme:

$$\mathrm{BuOH} + \mathrm{PCl_3} \xrightarrow{\mathrm{CCl_4}} (\mathrm{BuO})_2\mathrm{POH} \xrightarrow{\mathrm{Cl_2}} \underset{\mathrm{II}}{(\mathrm{BuO})_2\mathrm{POCl}}$$

$$\mathrm{II} + \mathrm{NaOH} \longrightarrow \underset{\mathrm{III}}{(\mathrm{BuO})_2\mathrm{PO}(\mathrm{ONa})} \xrightarrow{\mathrm{H}} \underset{\mathrm{IV}}{(\mathrm{BuO})_2\mathrm{PO}(\mathrm{OH})}$$

Compound II, dibutyl chlorophosphonate, was purified as an intermediate by distillation. The final product, DBP, was purified by extraction into carbon tetrachloride. After removal of solvent, it was assayed by titration with caustic to be 99 +% pure, containing no detectable amounts of MBP.

The experiments with Pu(IV) were carried out by extracting plutonium into purified TBP solution, adding small amounts of DBP (usually diluted with Amsco or TBP-Amsco to facilitate measurement), then stripping with water. The activity remaining in the organic phase after the fourth and sixth strip was determined, as well as the activity in the sixth strip solution. Only a small change was effected after the fourth strip, indicating that what remained in the organic after six strips actually represents loss. The results are given

Pu(IV) - DBP System (continued)

in Table I. The distribution coefficient on the sixth strip does not correlate well with the content of DBP. Direct correlation would be expected on the basis of the equilibrium theory discussed below. However, the results may be summarized by stating that plutonium losses are measurable and significant with as little as 0.001% DBP in the solvent, at the plutonium concentrations expected in the Purex Process. At lower Pu concentrations, percentage losses are considerably higher. It should be pointed out, however, that the DBP content is not very significant when the plutonium is reduced to the +3 state to strip.

The relation of Pu loss with variation in the DBP content may be eludidated by considering the complex formation as an equilibrium process:

$$Pu(IV)_{aq} + n\ DBP = Pu(DBP)_n\ (org)$$

The equilibrium constant for this reaction is

$$K = \frac{Pu(DBP)_n(org)}{(Pu_{aq})\ (DBP)^n}$$

If one assumes that, in the experiments described above, the stripping operation (a) has not changed the DBP concentration, and (b) has proceeded to the point where the Pu concentration in the organic is largely that due to DBP complexing (at high Pu conc. the TBP complexing is important), then K may be estimated as follows: using the data at 0.001% DBP (4.8×10^{-5} molar), we have, for the lower Pu concentration,

$$K = \frac{5.03 \times 10^4}{744\ (4.8 \times 10^{-5})^n}$$

Pu(IV) - DBP System (continued)

If n = 2 (as is believed to be the case in TBP complexing),

$$K = 3 \times 10^9 \text{ liters}^2 \text{ mols}^{-2}$$

The Pu distribution coefficient is approximately the ratio of complexed Pu to uncomplexed Pu:

$$\frac{[Pu\ (DBP)_n]}{(Pu_{aq})} \approx E\ O/A$$

At 0.001% DBP this is found experimentally to be 7. Using the value of K obtained by assuming n = 2, the O/A may be calculated for other concentrations of DBP. Thus at 0.0001% DBP, E O/A would be 0.07, and at 0.01% DBP the coefficient is calculated to be 700. The experimentally determined coefficients are 150 at 0.01% DBP, and at 0.0001% DBP, the ratio is essentially the same as with no added DBP.

If the complex involves only one DBP molecule (possibly with one or more TBP molecules) the calculated values of E O/A are 0.7, 7, and 70 for 0.0001%, 0.001% and 0.01% DBP, respectively.

At the higher Pu concentrations, the E O/A on the sixth strip does not correlate with DBP concentrations. This is most likely due to the effect of TBP complexing at the higher Pu concentrations.

3.3 Pu(III) - DBP System

In both the first and second plutonium cycles of the Purex Process, the reduction of Pu to the +3 state in stripping is contemplated or under consideration, and for this reason the behavior of Pu(III) in the presence of DBP

Pu(III) - DBP System (continued)

is of some interest. In these experiments, Pu(III) was formed by reduction of Pu(IV), then contacted with TBP-kerosene-DBP solutions. In one set of experiments the distribution coefficient E O/A was 0.2 in the presence of 0.1% DBP. In another experiment with 0.001% DBP in the organic phase, after stripping six times (before reduction of Pu IV) the E O/A was 70; stripping with dilute sulfurous acid gave a coefficient of 0.01. In several experiments performed to determine the rate of reduction of Pu(IV) by hydroxylamine, DBP was added to the 30% TBP solution to emphasize the difference in E O/A for Pu IV and III in low acid systems. When reduction was complete, at 0.4M HNO_3, the E O/A was 0.008 at 0.001% DBP, and 0.025 at 0.01% DBP. Where no reduction had taken place, the coefficients were 0.44 and 6.0 at 0.001 and 0.01% DBP, respectively. In another experiment, a plutonium (IV) nitrate solution in 30% TBP containing 0.01% DBP was stripped six times with 0.04M hydroxylamine solution. The Pu remaining in the organic after three strips was down to 0.1% of the original value. Further stripping had no effect (possibly due to a trace of Pu VI, as hydroxylamine is not a rapid reducing agent for Pu VI).

These experiments prove that DBP has no significant complexing action on Pu (III), and as much as 0.01% DBP can be tolerated in a solvent extraction system where the Pu is reduced to +3 state for stripping.

In some of the above experiments, where the reducing agent was ferrous iron, considerable difficulty was encountered due to emulsification of the two phases. This has been traced to the interaction of DBP and either Fe(II)

Pu(III) - DBP System (continued)

or Fe(III). It seems quite possible that the maximum tolerance for DBP in the 1B column may be fixed by its interaction with the iron present.

The effect of monobutyl phosphoric acid on reduced plutonium was checked in one experiment. The MBP was prepared in crude form by hydrolyzing commercial butyl acid phosphate (mixture of MBP and DBP, as well as pyrophosphates) with concentrated nitric acid. The hydrolyzed product was diluted with kerosene. The kerosene solution was washed with water several times, and the water washes extracted with diethyl ether. The ether was evaporated to yield the crude monobutyl phosphoric acid. A one percent solution of this MBP in kerosene was contacted with Pu(III). The distribution coefficient was found to be 0.25, indicating slight tendency of Pu III to be extracted by MBP.

3.4 Hydrolysis Experiments

The procedure used to determine the extent of hydrolysis of TBP relied on the use of TBP containing P-32. All of the hydrolysis products were removed from the TBP solution before the experiment using several caustic washes. In single (aqueous) phase experiments, this TBP was equilibrated with an aqueous phase of the desired composition, then the aqueous phase was subjected to hydrolytic conditions. Samples were taken periodically and separated into two parts, one being neutralized with an excess of solid sodium carbonate. The neutralized portion was scrubbed three times with equal portions of Amsco kerosene. This neutralized, washed sample has been found to be very

Hydrolysis Experiments (continued)

nearly free of TBP, and contains all the hydrolysis products of the unneutralized sample. The unneutralized sample and the treated sample were then counted in porcelain cups before evaporation. The count of the unneutralized sample gave a check on possible losses during the hydrolysis experiment.

Since this procedure does not differentiate between the intermediate (harmful) hydrolysis products and the end product, phosphoric acid, which is not particularly harmful, a second procedure was used in some of the experiments. In this procedure, after the organic phase was subjected to the desired hydrolysis conditions, it was equilibrated with a plutonium (IV) nitrate-nitric acid solution, and the Pu concentration determined. The aqueous phase was withdrawn, and the organic was stripped six times with equal volumes of water. The aqueous and organic phases were sampled and analyzed for Pu, and the Pu loss to the organic calculated. This type of data may be correlated roughly with concentration of hydrolysis products in the organic, using the data presented above on Pu loss versus DBP (dibutyl phosphoric acid) concentration (Table I).

In the experiments on the hydrolysis in the aqueous phase, the concentration was in the range of 0.01 to 0.02% TBP. Since reliable measurements were desired where only a small fraction of the TBP had hydrolyzed, P-32 labelled TBP was used to indicate concentrations of TBP and its hydrolysis products. The procedure is as outlined above. The results of the experiments are shown in Figure 1, where the fraction of TBP unhydrolyzed is plotted against time, for hydrolyses at the boiling point. One experiment at 60°C indicated a hydrolysis of 0.7, 2.9, and 5.0% in 6, 24, and 47 hours, respectively, in 5.4M nitric acid.

Hydrolysis Experiments (continued)

With a TBP-rich phase present, the hydrolysis appears to take place largely in the rich phase, or at the interface. In one experiment at 70°C with one volume of 30% TBP (in Amsco 123-15) and 2.5 volumes of 6.0M nitric acid, 0.4% of the TBP present in the system hydrolyzed in three hours. If this hydrolysis were taking place solely in the aqueous phase about 5% of the TBP in the aqueous phase would have to hydrolyze every minute. This is much faster than the rate in the aqueous phase at the boiling point, so the major share of the reaction must have occurred either at the interface or in the organic phase.

Several experiments have been carried out on the hydrolysis in a two phase system at room temperature. Equal volumes of TBP (30% in Amsco 123-15) and 7.2M nitric acid were mixed (continuous agitation) for one day and five days (two separate systems). In one day 0.052% of the TBP present in the one system had hydrolyzed. In the other system, 0.19% hydrolyzed in five days. In these experiments, the amount of hydrolysis was determined by washing with caustic several times, then removing unreacted TBP from the alkaline aqueous solution by three washes with kerosene, then counting the activity remaining in the aqueous phase.

These experiments, with either one phase or two phases present, do not show the prolonged induction period reported previously.[1] In the above two-phase experiments at room temperature, the rate data follow a logarithmic plot, which extrapolates back to zero hydrolysis at zero time. Moreover, the rate of hydrolysis found in these experiments is much faster than found in the

Hydrolysis Experiments (continued)

above-reported work.[1] In the reference work, the hydrolysis was carried out with two phases present, with the extent of hydrolysis determined by analysis for MBP and phosphoric acid. With equal volumes of both phases, pure TBP and 3M nitric acid, the rate following an induction period of eight days was 0.045% per day at 76°C; at 105°C, the rate was 0.23% per day after a two day induction period. In another equi-volume experiment at 105°C, with 6M nitric acid in the aqueous, they report 0.33% hydrolyzing in two days, and 2.25% in six days. It is believed that the analytical methods used in the present work are more accurate for low concentrations of phosphorus and therefore more reliable when only a small fraction of the TBP has hydrolyzed.

A number of hydrolysis experiments have been carried out, where the extent of hydrolysis has been measured in terms of plutonium loss such hydrolysis causes. This had been done because of the fact that the primary hydrolysis product of TBP - dibutyl phosphoric acid - is the only one which really matters from the standpoint of the effect on the Purex Process. Thus, if it were that the DBP formed by hydrolysis in turn hydrolyzes at a much faster rate than does the TBP, there would be very little DBP present at any time, and the TBP hydrolysis would be of no consequence. For this reason, the second procedure outline above was used.

The results of these experiments are given in Table II. These results indicate that the major share of the hydrolysis takes place in the organic phase, and in fact, is independent of the presence of an aqueous phase.

Hydrolysis Experiments (continued)

The major importance of these results lies in the fact that, where the plutonium is not reduced in the second cycle, the losses may be quite serious. Thus IIAP, according to the ORNL #1 flowsheet, will be in equilibrium with 4.5M nitric acid. This organic, if steam jetted to a feed tank for the IIB contactor, may be warmed to 50°C and held there occasionally for extended periods. Under these conditions, the Pu loss may reach several percent in the IIB bank. This type of loss can be avoided by reducing to Pu III in the IIB bank, but if this is undesirable, the best method to avoid solvent hydrolysis and consequent Pu loss is by keeping the temperature and acid concentration as low as consistent with the flowsheet, and to avoid any possibility for the IIAP to be stored for extended periods.

Several experiments were carried out in an attempt to estimate the relative amount of DBP in the hydrolysis products of TBP. It is understood that if the rates of hydrolysis of TBP and DBP are of the same order of magnitude, the relative proportion of DBP will vary over at least part of the hydrolysis period. The faster the rate of DBP hydrolysis in relation to that of TBP, the quicker a steady state is reached, where (TBP/DBP) will remain constant. In one experiment, a solution of 5.5M nitric acid was equilibrated with 30% TBP in Amsco 123-15, then separated completely. The aqueous was spiked with Pu(IV) and refluxed for one hour. The solution at this point was 5.0M in nitric acid and contained 1.71×10^6 Pu α c/m/ml. It was equilibrated with a 30% TBP-Amsco solution, giving an organic containing 1.64×10^6 Pu α c/m/ml. This organic was stripped six times at which point 2.5% of the Pu was still in the organic

Hydrolysis Experiments (continued)

phase. Referring to Table I, it is seen that roughly 0.001% DBP is required at this Pu level to result in a 2.5% loss. From the solubility of pure TBP in nitric acid[2,3], we estimate the aqueous phase contained roughly 0.01% TBP prior to hydrolysis. Under the conditions of this experiment, roughly 15% of the TBP should have hydrolyzed (see Figure I). Thus the concentration of hydrolysis products should be about 0.0015%. Therefore, the plutonium loss figure indicates that a major share of the hydrolysis products is DBP. This experiment is subject to large errors, especially in the original concentration of TBP in the aqueous (any entrainment of free organic phase will increase the TBP concentration greatly).

In another experiment (described above) a 7.2 molar nitric acid solution and 30% TBP solution gave 0.05% hydrolysis in one day at room temperature and 0.2% in five days. In four days, roughly 0.15% hydrolysis should occur. Since the organic is only 30% TBP, the concentration of hydrolysis products is 0.3 x 0.15 = 0.045%. In the first experiment described in Table II, a system at 5.8M nitric acid gave a Pu loss of 3.8% in 4 days. This Pu loss indicates 0.001 to 0.005% DBP. The percentage of the hydrolysis products which is DBP, under these conditions, is 10% or less.

Since the relative importance of DBP in the hydrolysis mixture may be expected to vary with the temperature (if DBP and TBP have different activation energies for hydrolysis), with acidity, and with time, the results of these few experiments should be taken only as an indication of what the DBP

Hydrolysis Experiments (continued)

concentration might be. In any case, these experiments and those shown in Table II definitely indicate the potential danger, in terms of plutonium losses, due to TBP hydrolysis.

3.5 TBP Hydrolysis During Distillation

Several streams in the Purex Process which must be evaporated, may be affected by the behavior of TBP during the evaporation. The TBP may be present in these streams either as the amount dissolved or as entrained separate phase. The two factors at work during such an evaporation are steam distillation and hydrolysis. Since the hydrolysis products are essentially non-volatile, once a particular TBP molecule hydrolyzes to DBP, it will be held in the liquid under hydrolytic conditions, so it will tend to hydrolyze further, ultimately to orthophosphoric acid. Whether it actually hydrolyzes all the way depends on the time of exposure to hydrolysis conditions. Since the rate of hydrolysis of TBP goes up as the nitric acid concentration goes up, one would expect steam distillation to become less important as the nitric acid concentration builds up, as in a batch acid evaporation. Therefore, since the beginning of the distillation is the most favorable time for TBP distillation, and since those molecules hydrolyzed to DBP will tend to hydrolyze further, it is evident that the amount of phosphate retained and also the relative porportions of the intermediate and final hydrolysis products will depend on the manner in which the distillation is carried out. A rapid distillation would be expected to distil out more TBP, while most of the hydrolyzed TBP would be present as DBP. A slow distillation, on the other hand, would

TBP Hydrolysis During Distillation (continued)

result in more hydrolysis, and with enough time, hydrolysis of DBP and MBP to phosphoric acid would be complete. The type of equipment used would also be expected to affect the amount distilled as well as the relative proportions of hydrolysis products. Thus continuous feed to a fractionating column would permit less contact with higher acid concentrations until most of the TBP distilled.

Several experiments were performed to determine the fate of TBP during concentration of an acid solution. In the first, carried out at atmospheric pressure, 1M nitric acid saturated with P-32 labelled TBP-Amsco solution was distilled for 1.7 hours. At this point, 85% of the liquid had distilled, and 97.7% of the TBP in the original charge had distilled unchanged. Of the TBP which had not distilled, 80% was hydrolyzed. The still residue was roughly 8M in nitric acid at the end of the distillation. A similar experiment with the exception that the nitric acid feed contained 1 gm UNH/liter, yielded the same results. A two hour distillation at 75 mm Hg, temperature ranging from 47° at the start to 71°C at the end, gave the following results: liquid distilled, 85%; TBP distilled, 99.1%; TBP in residue hydrolyzed, 34%; TBP hydrolyzed, based on TBP in feed, 0.24%; residue acidity, 8.1M.

From these data it is apparent that most of the TBP can be steam distilled without hydrolysis. Since in these experiments only the amount of TBP as is soluble in 1M nitric acid was present, it is obvious that only a very small amount of TBP was hydrolyzed. Since the solubility of TBP in the various

TBP Hydrolysis During Distillation (continued)

aqueous solutions that will be concentrated in the Purex Process is between 0.005 and 0.02%, the amount of TBP from entrainment will most likely be of more importance. A separation of phases that is only 99.5% complete will provide 20 to 100 times the amount of TBP as that due to its solubility. For this reason, then, we believe the completeness of separation of phases to be of prime importance in any situation where TBP hydrolysis during subsequent evaporation is likely to cause trouble.

In the proposed three-stage evaporation of IIBP for isolation of plutonium, a thousand-fold concentration is expected. Here the original acidity is about 0.2M. Negligible hydrolysis would be expected to occur at this acidity, and most of the TBP should distil out before the acid concentration reaches a destructive level. However, whatever TBP does hydrolyze will be subjected to very severe hydrolytic conditions (68% nitric acid, 120°C) for the latter part of the evaporation. The published data on hydrolysis of DBP and MBP[1] hold for conditions no more severe than 3M in nitric acid at 76°C. Using their hydrolysis rates at 76°C and at 25°C, the hypothetical half-life at 120°C in 3M nitric is estimated to be 2.8 days for MBP and 1.4 days for DBP. Although the effect of acidity on the hydrolysis of these acid esters has not been determined it is very likely that the rate will change more with acidity than does the rate of TBP hydrolysis. This is due to the fact that both MBP and DBP are fairly strong acids[4], and it is probable that the mechanism of the hydrolysis reaction involves reaction of water and hydrogen ion with the

TBP Hydrolysis During Distillation (continued)

the unionized form of the acid. This is equivalent to a second or higher order dependence of the reaction on hydrogen ion. It appears likely, then, that under the conditions toward the end of the triple evaporation of IIBP, much of the DBP and MBP formed will be hydrolyzed further to orthophosphoric acid. More quantitative conclusions must await the experimental determination of the hydrolysis of MBP and DBP in constant boiling composition nitric acid at the boiling point.

4.0 References

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

4. Kumler, W. D., J. J. Eiler, J. Am. Chem. Soc. 65, 2355-61 (1943).

Victor J. Reilly

V. J. Reilly

VJR:mp

[redacted]

Table I

Effect of Dibutyl Phosphoric Acid on Plutonium Stripping Losses

Solvent: 30% TBP - 70% Amsco 123-15
Strip: demineralized water
Equal volumes of solvent and strip batch-contacted for two minutes

DBP Conc. (% by Vol.	Plutonium Concentration (c/m/ml) Organic - Before Stripping	Organic 6th Strip	Aqueous 6th Strip	Pu D.C. (O/A) 6th Strip	Pu Loss(%)
0.0	6.5×10^5	850	120	7	0.13
0.0001	6.5×10^5	565	50	11	0.09
0.001	6.5×10^5	5.03×10^4	744	6.8	7.7
0.01	3.6×10^5	2.2×10^5	1.4×10^3	70	61.1
0.001	6.87×10^7	6.14×10^5	8.76×10^3	70	0.9
0.01	6.87×10^7	5.33×10^6	2.86×10^5	18.5	7.8

Table II

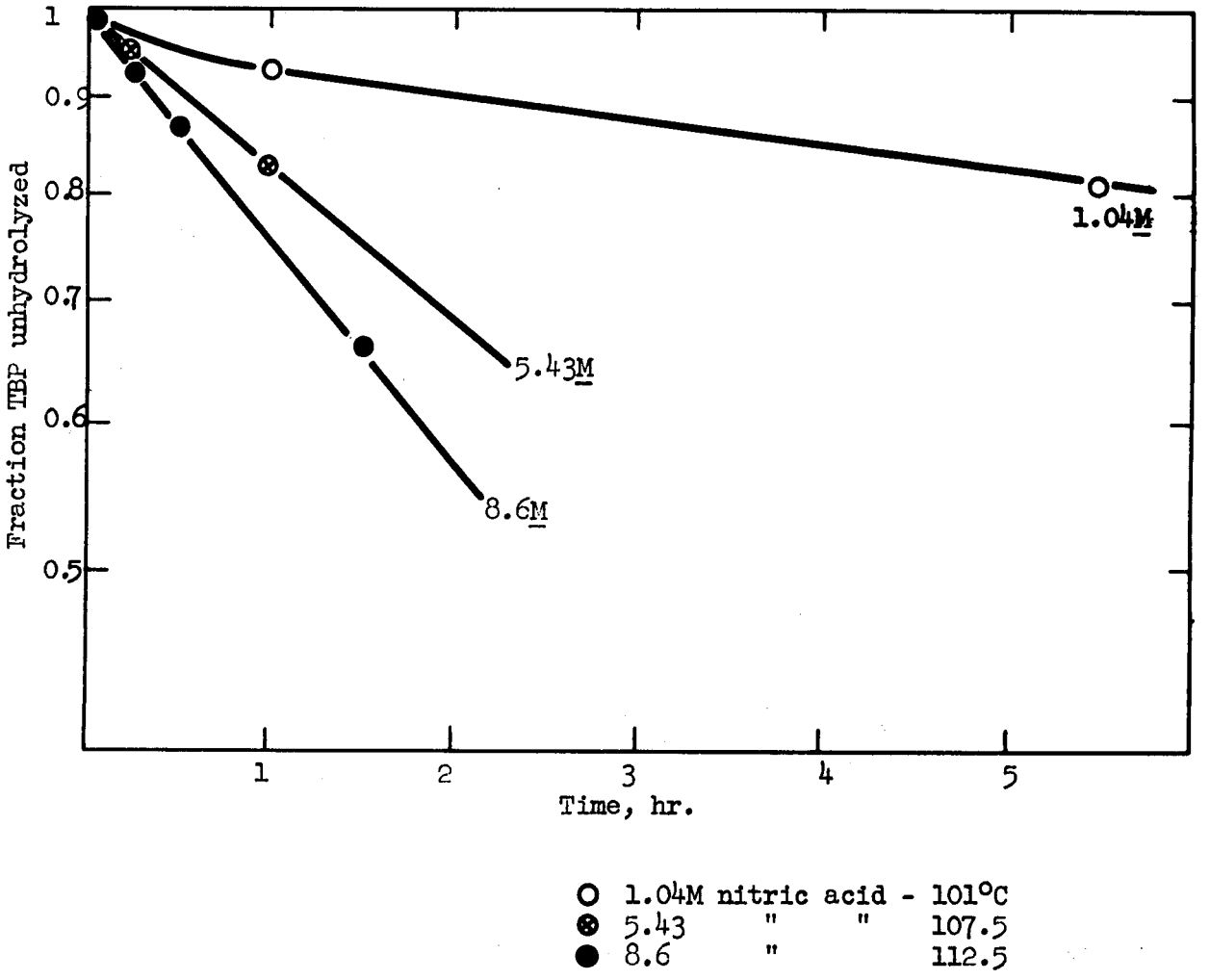
Two-phase and Organic Phase Hydrolysis of Tributyl Phosphate, using Pu Loss as Indicator

(Equal volumes of 30% TBP (in Amsco 123-15) and aqueous nitric acid; organic spiked to 5×10^6 Pu α c/m/ml after hydrolysis experiment)

Temp.	Phases Present	Aqueous phase* M-HNO_3	Time, hr.	Pu Loss, %
28°C	Org; aq.	5.8	96	3.8
"	Org; aq.	6.0	24	0.3
"	Org.	6.0	24	0.7
"	Org.	1.0	168	1.4
"	Org.	3.0	168	21.3
50°	Org; aq.	6.0	1.0	0.28
"	"	6.0	2.5	5.7
"	"	6.0	2.5	2.8
"	"	6.0	17	49
"	Org.	6.0	1.0	0.36
"	"	6.0	2.5	3.0
"	"	6.0	22	33
"	"	1.0	21.5	23.6
"	"	3.0	21.5	40.7
Control (no nitric acid treatment)				0.17

* Where only organic phase is present, the organic was equilibrated three times with fresh, equal-volume portions of acid of the normality shown.

[redacted]

Figure I

HYDROLYSIS OF TBP DISSOLVED IN NITRIC ACID
(aqueous phase at the boiling point)