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Alpha Radiolysis and Other Factors Affecting Hydrolysis of Tributyl Phosphate

M. H. Lloyd
R. L. Fellows

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Chemical Technology Division

ALPHA RADIOLYSIS AND OTHER FACTORS AFFECTING HYDROLYSIS OF TRIBUTYL PHOSPHATE

M. H. Lloyd
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ALPHA RADIOLYSIS AND OTHER FACTORS AFFECTING HYDROLYSIS OF TRIBUTYL PHOSPHATE

M. H. Lloyd and R. L. Fellows

ABSTRACT

The primary purpose of this study was to identify the principal degradation products produced by Pu(IV) loading in 30% tributyl phosphate/dodecane (TBP-DD) solutions and to determine the formation rates of these species as a function of temperature.

Experiments were also conducted to evaluate HNO_3 hydrolysis of TBP as a function of temperature and to compare the effects resulting from plutonium solvent loading with effects due to loading with uranium and zirconium. The results indicate that four factors are of particular significance: (1) dibutyl phosphate (DBP) is the principal plutonium-complexing species formed at temperatures of 50°C or lower, while significant concentrations of monobutyl phosphate (MBP) are also formed at higher temperatures; (2) the TBP degradation rate due to alpha radiolysis or chemical hydrolysis is strongly dependent on temperature; (3) plutonium promotes TBP hydrolysis by two mechanisms, alpha radiolysis and metal-ion-induced hydrolysis, and, of these, metal-ion-induced hydrolysis can be the major effect; and (4) small amounts of an unidentified plutonium-complexing species are formed in experiments using plutonium of high specific activity [$\sim 4 \times 10^8$ counts per minute per milligram (c/min·mg)]. This species cannot be removed from 30% TBP-DD by Na_2CO_3 washing or other solvent cleanup procedures.

The TBP degradation rates (determined as grams of plutonium complexed by degradation products) increased from 0.125 mg Pu/L·h at 25°C to 47.9 mg Pu/L·h at 80°C in 30% TBP-DD solutions that contained only 0.68 $\underline{M}$ HNO_3. In solutions that additionally contained ~20 g/L of plutonium (specific activity = 9×10^7 c/min·mg) TBP degradation rates increased from 2.46 mg Pu/L·h at 25°C to 127.1 mg Pu/L·h at 80°C.

1. INTRODUCTION

The objectives of this study were to investigate alpha radiolysis and other factors which promote hydrolysis of tributyl phosphate (TBP), and to determine the concomitant formation rates of dibutyl phosphate (DBP), monobutyl phosphate (MBP), or other degradation products that might form in 30% TBP-n-paraffin mixtures. As in previously reported studies,[1] the DBP and MBP were measured by direct spectrophotometric examination of the plutonium complexed species in the TBP—diluent phase.

At present, solvent extraction from nitric acid solutions with TBP is the only method used for reprocessing spent reactor fuels to recover uranium and plutonium. It is widely recognized that the radiolytic and chemical decomposition of TBP and its diluents can adversely affect processing operations, and experience has shown[2-4] that solvent quality is of prime importance in determining process performance. A number of laboratory and plant studies[5-6] that address this problem have demonstrated that TBP decomposition can be shown as:

$$TBP \rightarrow HDBP \rightarrow H_2MBP \rightarrow H_3PO_4 \ , \qquad (1)$$

and that this reaction is of major importance in degrading solvent quality. Adverse effects due to diluent degradation and the accumulation of degradation products in recycled solvent systems have also been recognized.

Many of the earlier studies concerned with TBP degradation involved only DBP or made no attempt to differentiate between DBP and MBP; during the past several years, however, sophisticated techniques have become available for the analysis of trace compounds in complicated mixtures, making it possible to conduct detailed studies that were not previously possible. Examples of such studies include the determination of hydrolysis constants for TBP, DBP and MBP in 3 $\underline{M}$ HNO_3,[7] the influence of temperature and acid concentration on acid hydrolysis,[8] and Purex diluent degradation.[9]

The primary emphasis in this study was to determine TBP and DBP decomposition rates due to plutonium loading in a 30% TBP-diluent phase as a function of temperature. Significant decomposition attributable to alpha radiolysis and metal-ion-catalyzed hydrolysis was observed. This study also examined acid hydrolysis of TBP in plutonium-containing systems and compared metal-ion-induced hydrolysis of TBP by plutonium, uranium, and zirconium. Conditions were confined primarily to those expected for LMFBR fuel reprocessing, such as 3 M HNO_3 feed solutions and plutonium loadings of 20–30 g/L.

2. EXPERIMENTAL PROCEDURE

Industrial-grade TBP was obtained from the Ashland Chemical Company. A 30 vol % TBP solution was prepared by dilution of the as-received material with reagent-grade, n-dodecane (DD) (Eastman Kodak Co.). The mixed organic solution was then purified by successive, equal-volume scrubs with Na_2CO_3 solution (10 g/L), water, and HNO_3 (3 M).

Plutonium stock solutions were purified by anion exchange with 7 M HNO_3. This treatment yielded high-purity, americium-free, Pu(IV) products in ~1 M HNO_3. The solutions were examined spectrophotometrically on a periodic basis to ensure that plutonium remained in the tetravalent state.

In all experiments, solutions of 30% TBP–DD were equilibrated with 3 M HNO_3, which produced an organic-phase HNO_3 concentration of 0.58 M. The desired metal ion was introduced by contacting the acidified organic phase with an equal volume of 3 M HNO_3 that contained the metal nitrate. This generally produced an organic-phase acid concentration of 0.68 M. The organic solutions were aged in water-jacketed, sealed, glass containers for periods ranging from 7 to 80 d. The desired temperature was maintained with a constant-temperature, recirculating water bath.

Each solution was sampled periodically and analyzed using low-acid stripping and spectrophotometric procedures that have been previously described.[1] In this procedure, organic solutions that contained plutonium were stripped with seven equal-volume stages of 0.2 M HNO_3. This effectively removes TBP-complexed plutonium, while the plutonium complexed by TBP degradation products (e.g., DBP and MBP) is not removed to any significant degree. Analysis of the stripped organic solution for plutonium, therefore, provides a quantitative determination of plutonium complexation by the TBP-DD degradation products. A direct spectrophotometric examination of the stripped organic phase was then used to identify the plutonium-complexed species.[1]

For organic feeds that do not contain plutonium, the same procedure can be used by first contacting the organic phase with 3 $\underline{M}$ HNO_3 that contains an appropriate amount of Pu(IV) nitrate. This is possible even when other metal ions are present because, in nearly all cases, Pu(IV) preferentially complexes with the TBP hydrolysis products that are most frequently encountered.

In each stripping experiment, all solutions were analyzed for plutonium by gross-alpha counting since the plutonium had been recently purified. Material balances were calculated for each stage, to ensure a counting accuracy of ±2.0%. The organic phase, after each stripping stage, was analyzed using a Cary, Model 14, recording spectrophotometer with quartz cells. The absorption spectra were recorded from 410 to 1200 nm. The reference solution was 30% TBP-DD that had been equilibrated with 0.2 $\underline{M}$ HNO_3. All experiments and analytical procedures were conducted at ambient temperature.

For the solutions that contained plutonium, the radiation dose was calculated by assuming that all the decay radiation from the plutonium dissolved in the organic phase was absorbed by that organic phase. The decay energy for each plutonium stock solution was calculated from the radioisotope decay energies shown below and the isotopic distribution in the plutonium solution used.

Isotope	Decay energy, W/g
^{238}Pu	0.570
^{239}Pu	1.913×10^{-3}
^{240}Pu	7.047×10^{-3}
^{241}Pu	4.06×10^{-3}
^{242}Pu	1.13×10^{-4}

The radiation dose is calculated as the product of the decay energy (in watts per gram), the plutonium concentration in the organic phase (in grams per liter), and the irradiation time (hours).

3. RESULTS AND DISCUSSION

The primary purpose of this study was to identify and determine the formation rates of complexing species induced by Pu(IV) loading in TBP-DD solutions. Some of the results obtained were expected, e.g., DBP was the principal degradation product formed, particularly at the lower temperatures, and the rate of TBP hydrolysis increases rapidly with increasing temperature. Somewhat unexpectedly, it was found that plutonium promotes TBP hydrolysis by two mechanisms, alpha radiolysis and metal-ion-induced hydrolysis. Of these, the metal-ion-induced hydrolysis is the major effect for plutonium of moderate specific activity.

3.1 ACID-CATALYZED HYDROLYSIS OF TBP

Figure 1 presents the rates of TBP degradation due to HNO_3 hydrolysis for reaction temperatures of 25, 50, and 80°C, as indicated by the total plutonium concentrations complexed by degradation products. These results were obtained by periodic analysis of the acidified organic phase. In all cases, the HNO_3 concentration in the organic phase was 0.68 $\underline{M}$, to match conditions of the subsequent plutonium-containing experiment. The rate of TBP hydrolysis is definitely a function of temperature, increasing by a factor of nearly 400 as the temperature is increased from 25 to 80°C.

Our determinations of the plutonium-complexing species by direct spectrophotometric analysis of the organic phase, and of the total DBP and MBP concentrations by spectrophotometric and low-acid-stripping data, indicate that the plutonium was totally complexed by DBP at 50°C and lower temperatures, and that only trace amounts of the MBP complex formed at 80°C ($<2\%$ of the complexed plutonium). The DBP formation rates can therefore be calculated from the data in Fig. 1, based on the relationship (ref. 1):

$$\frac{\text{moles DBP}}{\text{moles Pu}} = 1.75 \pm 0.1 \ .$$

The DBP formation rates determined as mg DBP/L·h are shown (as a function of temperature) in Fig. 2.

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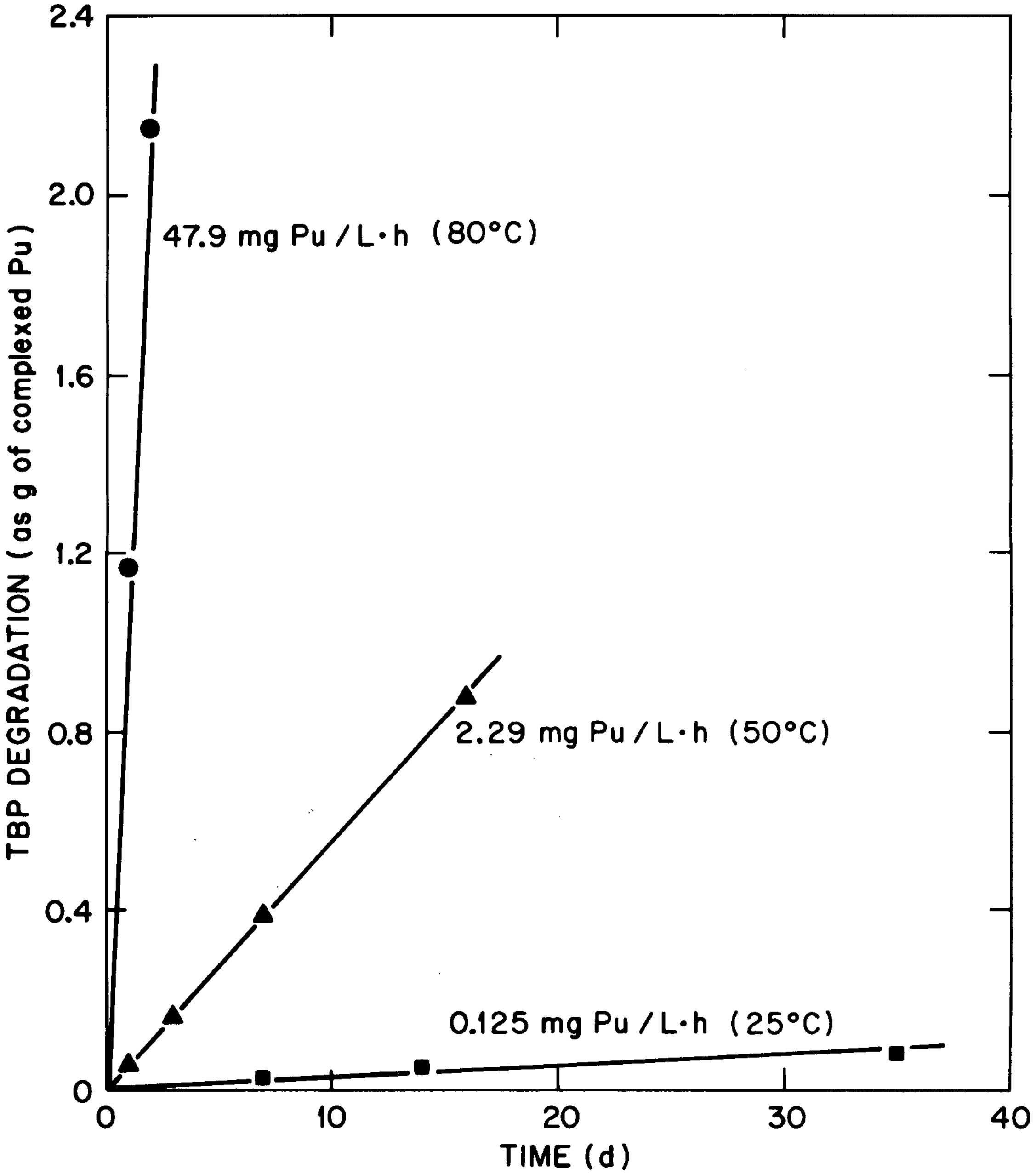

Fig. 1. Tributyl phosphate (TBP) degradation rates at 25, 50, and 80°C in 0.68 M HNO_3.

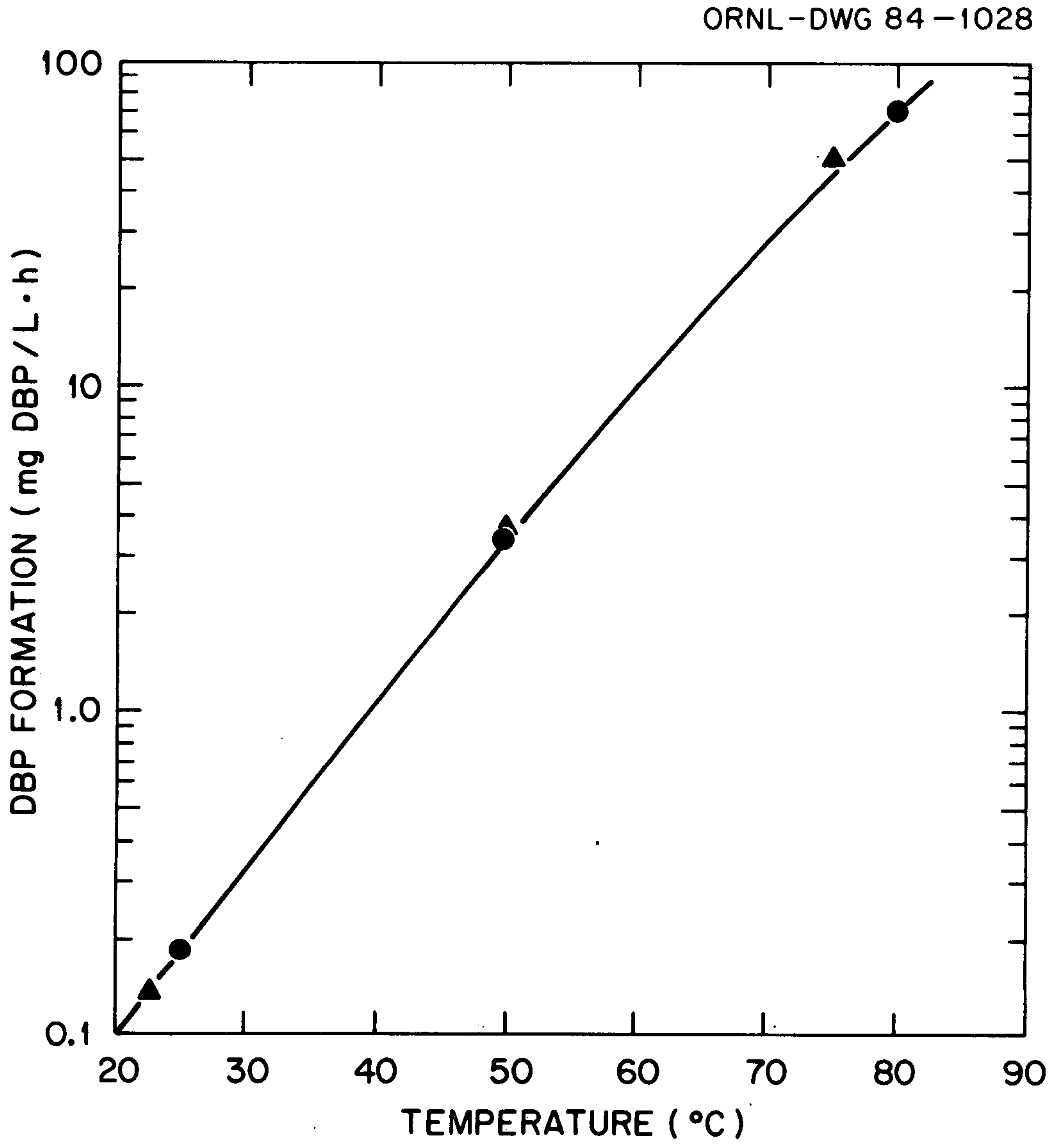

Fig. 2. Dibutyl phosphate (DBP) formation rates in 30% TBP-DD that contains 0.68 M HNO_3 as a function of temperature. [● our data; ▲ calculated from data reported by L. Stieglitz et al.][8]

Detailed studies of acid-catalyzed hydrolysis of TBP have been previously reported by L. Stieglitz et al.[7,8] They report data from two-phase experiments (30% TBP-n-alkane; 3 M HNO_3) with organic-to-aqueous (O/A) phase ratios of 3/1 for reaction temperatures of 23, 50 and 75°C. In their study, HDBP formation was found to proceed almost linearly with time, first order with respect to TBP, and first order with respect to HNO_3 concentration. They also found MBP formation to be below the limits of detection ($<3 \times 10^{-3}$ mg/L·h) at 23 and 50°C and to have a very low formation rate at 75°C (~0.5% of the DBP formation rate). Their data on DBP formation rates are comparable with our data, if a correction is made for the difference in organic-phase acid concentration.

The organic-phase acid concentration in their experiments can be calculated to be 0.42 M when the aqueous-phase HNO_3 is 3 M, the O/A phase ratio is 3, and the organic phase is not preacidified. When it is then assumed, as reported, that HNO_3 shows a first-order dependence, the DBP formation rates at 0.68 M acid can be calculated, and these results (solid triangles) are shown in Fig 2. The agreement between the two data sets is excellent, particularly so when it is considered that single-phase experiments are being compared with two-phase experiments and that the DBP analytical procedures used were significantly different.

3.2 THE EFFECT OF PLUTONIUM ON TBP HYDROLYSIS RATES

The effect of plutonium on TBP degradation was evaluated in single-phase experiments (30% TBP-DD). Plutonium concentrations were varied from 16.5 to 26.5 g/L, using plutonium feeds in which the isotopic compositions provided plutonium specific activities of 8.9×10^7 and 3.81×10^8 c/min·mg. The organic-phase nitric acid concentration was ~0.68 M in all experiments, and reaction temperatures of 25, 50 and 80°C were used.

Figure 3 presents our data on the TBP degradation rates for experiments using plutonium of low specific activity (8.9×10^7 c/min·mg) at reaction temperatures of 25, 50, and 80°C; comparable data for plutonium of high specific activity (3.81×10^8 c/min·mg) at reaction temperatures of 50 and 80°C is shown in Fig. 4. The data are given in terms of total grams of plutonium complexed by the TBP degradation products. It should

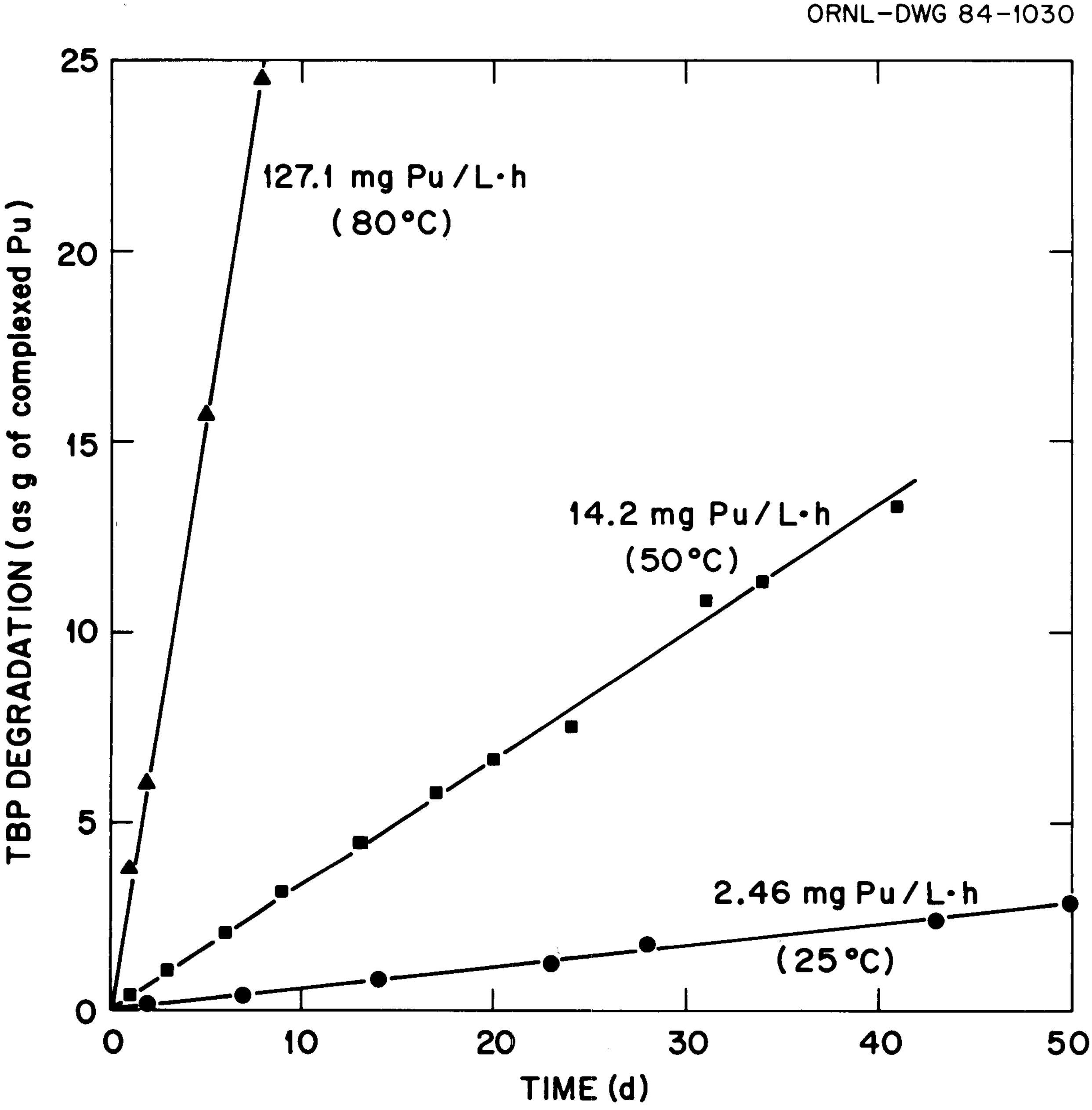

Fig. 3. Effects of low-specific-activity plutonium (S.A. ≈8.9 × 10^7 c/min·mg) on TBP degradation rates in 30% TBP-DD that contains 0.68 $\underline{M}$ HNO_3. [● Pu = 20.18 g/L; ■ Pu = 26.5 g/L; ▲ Pu = 25.9 g/L.]

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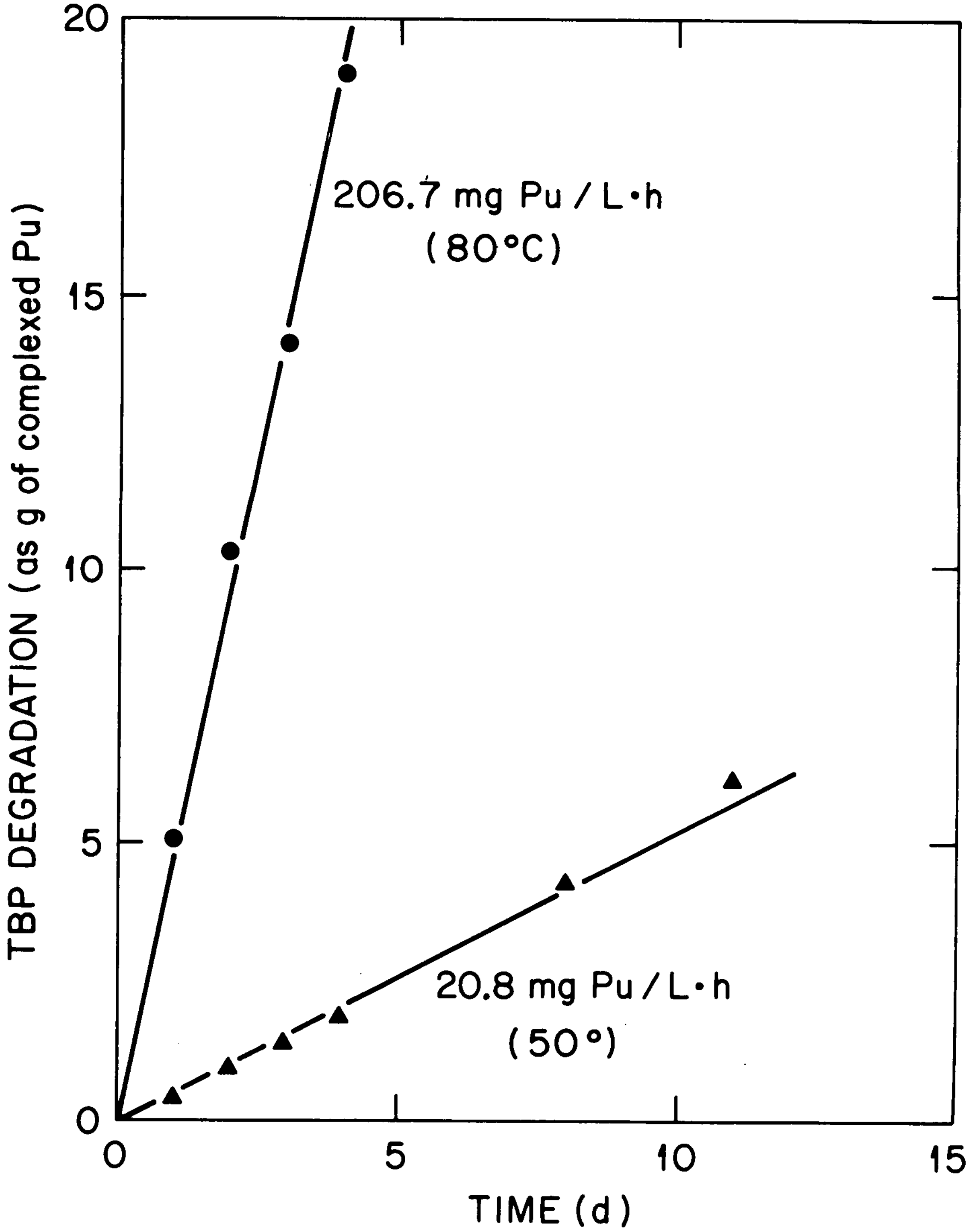

Fig. 4. Effects of high-specific-activity plutonium (S.A. = 3.81×10^8 c/min·mg) on TBP degradation rates in 30% TBP-DD that contains 0.68 M HNO_3. [▲ Pu = 16.54 g/L; ● Pu = 20.87 g/L.]

be noted that constant plutonium feed concentrations were not used in these experiments; however, if it is assumed, as discussed in the following sections, that TBP degradation due to acid hydrolysis is not affected by small changes in acid concentration, the data can be normalized for a constant plutonium concentration by first subtracting the contribution due to acid hydrolysis from the total due to both acid and plutonium concentration. The resultant variation in total grams of plutonium complexed for plutonium feeds of a given specific activity should then be due only to variations in the reaction temperature. Table 1 summarizes the results obtained when the data are normalized for a plutonium organic-phase concentration of 20 g/L.

Table 1. Effects of plutonium on TBP degradation rates at various temperatures

Plutonium specific activity (c/min·mg)	Temperature (°C)	TBP degradation rate[a] (mg Pu/L·h)
8.87×10^7	25	2.5
8.92×10^7	50	11.3
8.92×10^7	80	109.1
3.81×10^8	50	24.7
3.81×10^8	80	200.1

[a] Degradation rate is indicated by the rate of complexation of plutonium; data are normalized for a constant organic-phase plutonium concentration of 20 g/L.

As shown in Figs. 3 and 4, the temperature effect is very pronounced. The TBP degradation rate is increased by factors of ~4.5 and ~9.5 as the temperature is increased from 25 to 50°C and from 50 to 80°C, respectively.

The data in Table 1 suggest that TBP degradation is not due entirely to acid hydrolysis and alpha radiolysis; since an increase in the specific activity of the plutonium by a factor of ~4, with a corresponding increase in total dose, causes the degradation rate to increase by only a factor of ~2. This is verified by the data shown in Fig. 5, where the degradation rate is plotted as a function of total dose (W·h/L) for the experiments at 50 and 80°C. As shown, the rate of TBP degradation is significantly greater for the experiments using plutonium with the lower specific activity. This is true even though the total dose is much greater for experiments with plutonium of the higher specific activity (2.9 and 3.7 times greater at 50 and 80°C, respectively). It is reasonable to assume, therefore, that a third factor affects TBP degradation, and that this factor is metal-ion-induced hydrolysis of TBP resulting from the plutonium concentration in the organic phase. Other studies[10] have demonstrated similar behavior for zirconium, and both zirconium and uranium were shown in this study (Sect. 3.3) to increase the rate of TBP hydrolysis.

From the data on TBP degradation rates for the four experiments described above, the relative contributions from alpha radiolysis and from plutonium-induced hydrolysis can be determined if the effect of acid-catalyzed hydrolysis is considered to be constant for each temperature — that is, if the rate of acid hydrolysis is assumed to be unaffected by variations in organic-phase plutonium concentration from 16 to 26 g/L.

Assuming the total TBP degradation results from acid hydrolysis, alpha radiolysis, and metal-ion-induced hydrolysis, equations can be written for each temperature in terms of dose (W·h/L), plutonium concentration (g/L), total grams of plutonium complexed by degradation products, and grams of plutonium complexed by degradation products due to HNO_3 hydrolysis:

$$Pu_A + Pu_R \cdot D + Pu_c \cdot C = Pu_T , \tag{2}$$

where

Pu_A = Pu complexed by HNO_3 hydrolysis, g,
Pu_R = Pu complexed by alpha radiolysis, $g(W \cdot h/L)^{-1}$
Pu_c = Pu complexed by metal-ion-induced hydrolysis, g/L
Pu_T = total Pu complexed by TBP degradation products, g
C = concentration, g Pu/L,
D = radiation dose, W·h/L.

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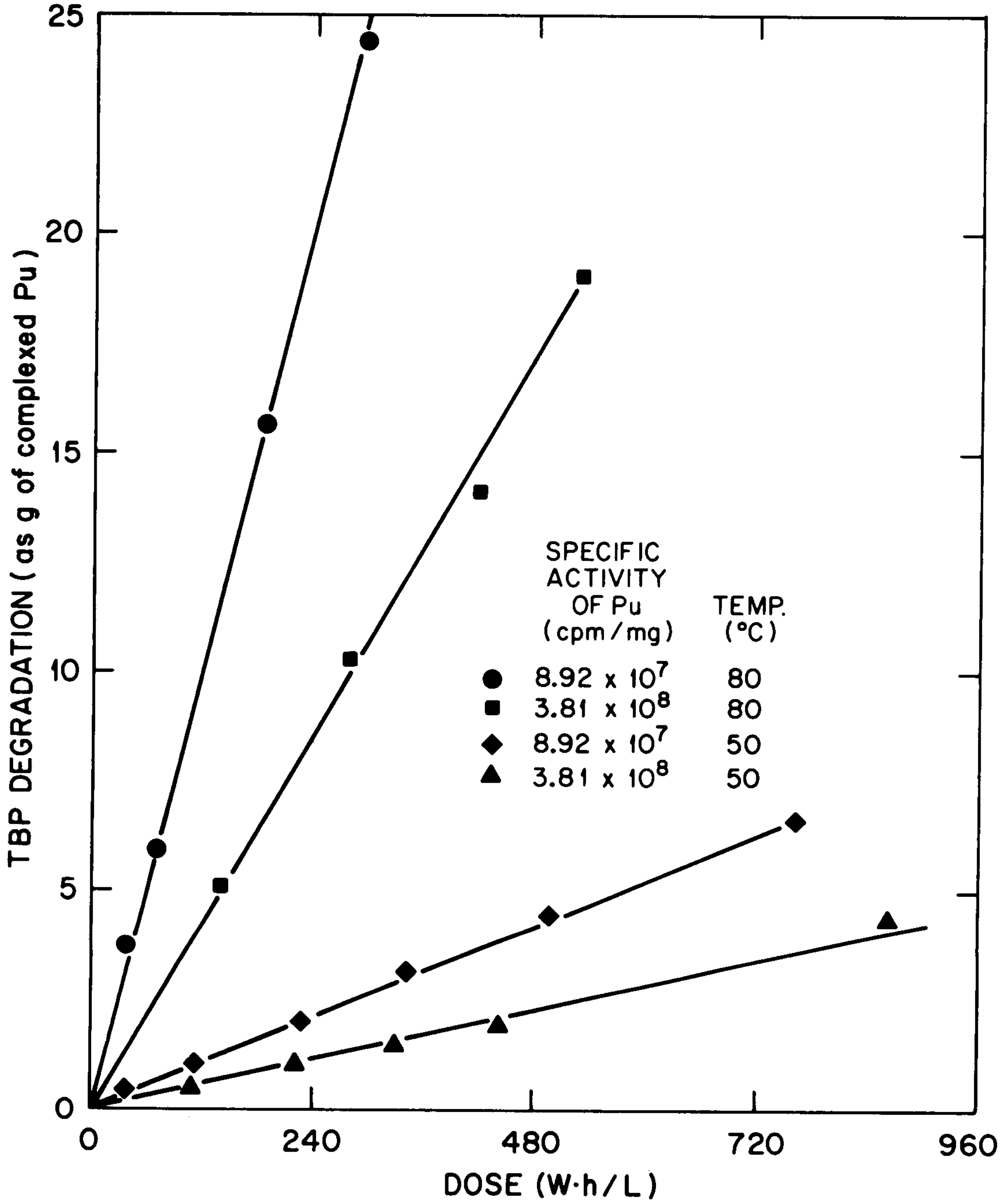

Fig. 5. Plutonium-induced degradation of TBP as a function of radiation dose (W·h/L) at 50 and 80°C. [● Pu = 25.9 g/L; ■ Pu = 20.87 g/L; ◆ Pu = 26.5 g/L; ▲ Pu = 16.54 g/L.]

For the two experiments at 80°C and exposure times of 24 h, with plutonium of low specific activity, substituting in Eq. (2) gives:

$$1.15 \text{ g Pu} + Pu_R \text{ (1.55 W·h/L)} + Pu_c \text{ (25.9 g Pu/L)} = 3.05 \text{ g Pu},$$

and, with plutonium of high specific activity

$$1.15 \text{ g Pu} + Pu_R \text{ (5.82 W·h/L)} + Pu_c \text{ (20.87 g Pu/L)} = 4.96 \text{ g Pu} .$$

Simplifying and solving these as simultaneous equations gives the relative contribution of each factor, as grams of plutonium complexed:

$$Pu_R (1.55) + Pu_c (25.9) = 1.90 \text{ g Pu},$$

$$Pu_R (5.82) + Pu_c (20.87) = 3.81 ,$$

$$Pu_R = 0.499 \text{ g Pu} ,$$

$$Pu_c = 0.0435 \text{ g Pu} .$$

Similar calculations were done for the experiments at 50°C.

The grams of plutonium complexed and the percentages of total plutonium complexed by each factor are given in Table 2 for each of the four experiments in this series.

These results are also shown graphically in Figs. 6 and 7 for the plutonium of low specific activity and for reaction temperatures of 80 and 50°C, respectively. The TBP degradation rates for each factor are given as mg of plutonium complexed by that factor's TBP degradation products. The data show that the relative contribution from HNO_3 hydrolysis is significantly greater at 80°C than at 50°C, indicating that temperature has a greater effect on acid-catalyzed hydrolysis than on the other mechanisms. If the TBP degradation is considered that is due only to plutonium concentration and alpha radiolysis, the relative complex concentrations from each factor are essentially constant with temperature (e.g., the contributions due to radiolysis were found to be 40.5 and 41.0% for 80 and 50°C, respectively, while the contributions due to metal-ion-induced hydrolysis were 59.5 and 59%).

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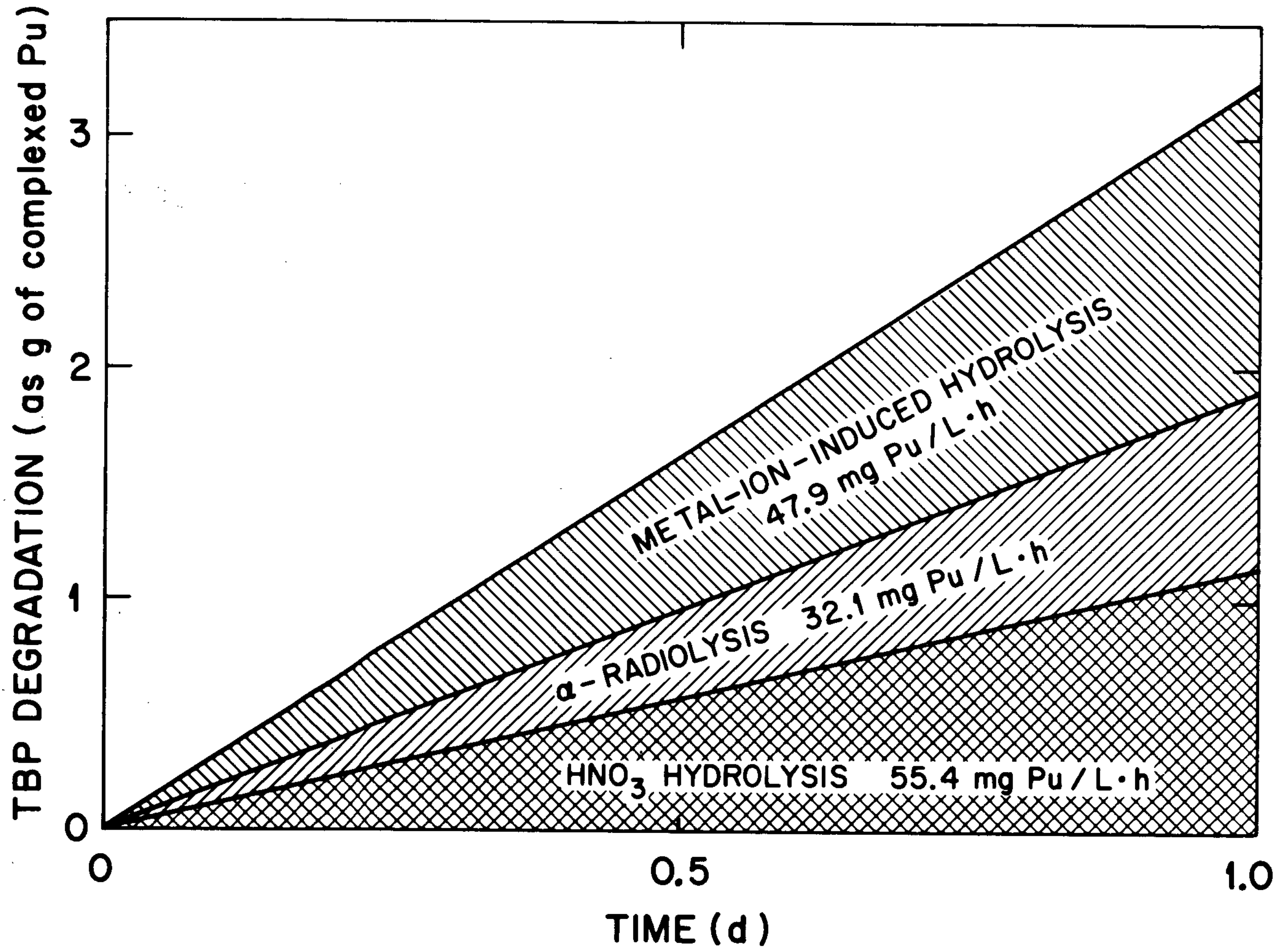

Fig. 6. TBP degradation rates due to acid hydrolysis, alpha radiolysis, and metal-ion-induced hydrolysis at 80°C (shown as mg of plutonium complexed by degradation products for each factor).

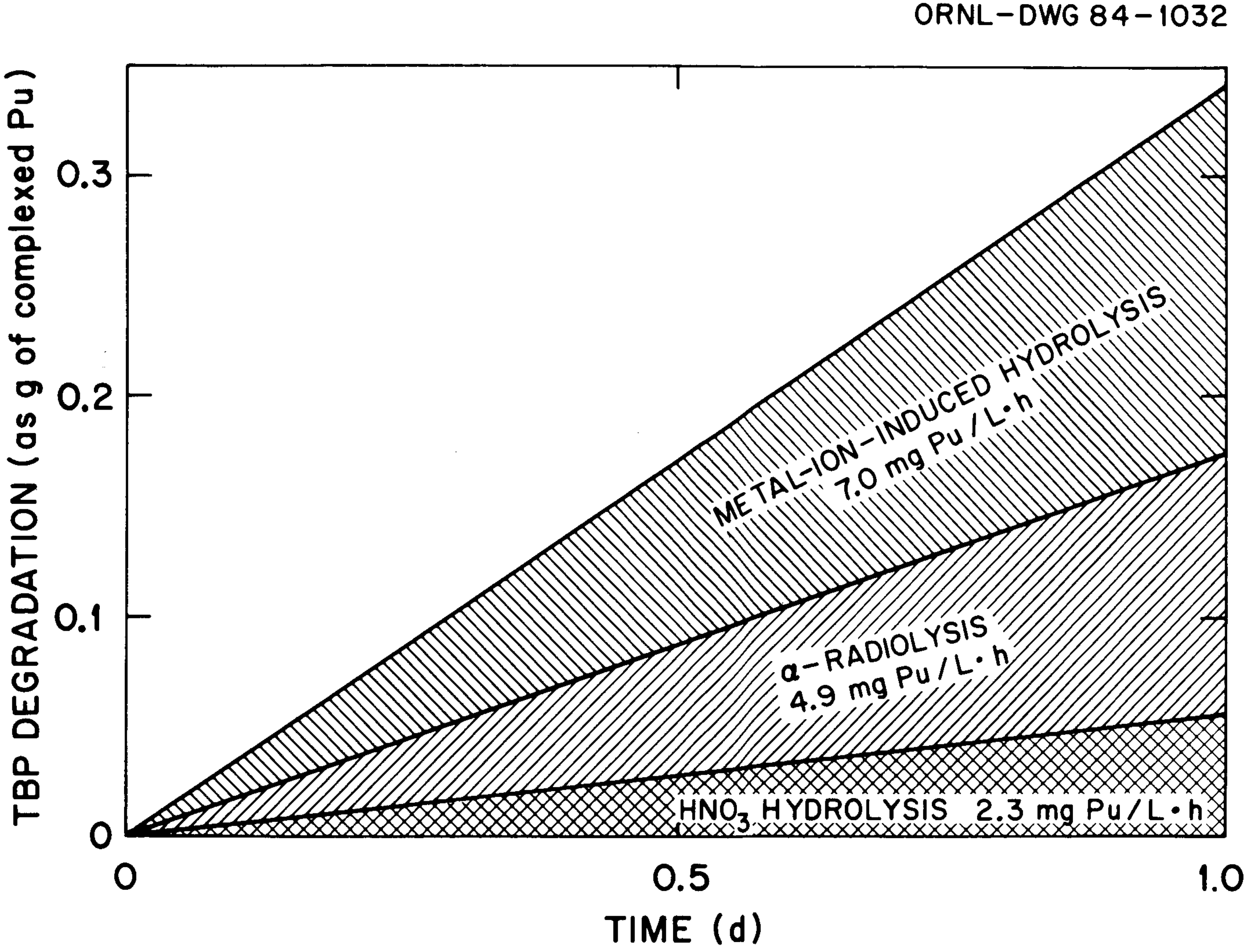

Fig. 7. TBP degradation rates due to acid hydrolysis, alpha radiolysis, and metal-ion-induced hydrolysis at 50°C (shown as mg of plutonium complexed by degradation products for each factor).

Table 2. Results of TBP degradation studies with plutonium[a]

Temperature (°C)	Plutonium specific activity (c/min·mg)	Acid hydrolysis, g Pu (%)	Metal-ion-induced hydrolysis, g Pu (%)	Alpha radiolysis, g Pu (%)
80	Low	1.15 (38%)	1.13 (37%)	0.77 (25%)
80	High	1.15 (23%)	0.91 (18%)	2.90 (58%)
50	Low	0.056 (17%)	0.17 (49%)	0.12 (34%)
50	High	0.056 (11%)	0.10 (20%)	0.34 (69%)

[a] Results are given as grams of plutonium complexed by degradation products for each factor and as a percentage of the total plutonium complexed. Calculation methods are discussed in the text preceding this table.

A spectrophotometric analysis of each stripped organic phase in the five plutonium experiments indicated that DBP is the primary degradation product formed; however, the MBP concentration and the MBP/DBP concentration ratio varied directly with temperature, specific activity, and aging time. The details of these analyses have been previously described.[1] Calculations were based on the evaluation of standard spectra of Pu(IV) in solutions of DBP and MBP in 30% TBP-DD. Two wavelengths (666 and 793 nm) were chosen because use of the ratio of absorbances increased the sensitivity of the measurements, making the use of molar extinction coefficients unnecessary and thereby increasing self-consistency. Unfortunately, the lengthy aging times altered the spectral characteristics of the solutions used in these experiments, which reduced the precision and accuracy of the measurements. The aging can cause, for example, the formation of nitrite ions that could alter the spectra. Nevertheless, the data were reproducible to ±4%. The accuracy of these spectroscopic measurements could be significantly improved if additional experiments were performed.

The results obtained after 20 d of aging are shown in Table 3. For each temperature and each specific activity, however, the MBP/DBP concentration ratio increases directly with aging time and, therefore, the MBP concentrations and MBP/DBP concentration ratios are much lower with

Table 3. TBP degradation products produced after 20-d aging of 30% TBP-DD containing $Pu(NO_3)_4$ and HNO_3

Specific activity (c/min·mg)	Temperature (°C)	DBP (%)	MBP (%)
8.87×10^7	25	96	4
8.92×10^7	50	92	8
8.92×10^7	80	60	40
3.81×10^8	50	80	20
3.81×10^8	80	60[a]	40[a]

[a] Solution aged 10 d.

short aging times. In the experiments using plutonium of low specific activity, the MBP concentration is below the limit of detection for the first 14 d of aging at 25°C and for ~4 d at 50°C; at 80°C, the MBP concentration was 6% after one day of aging. When plutonium of the higher specific activity was used, the MBP concentrations were 3 and 10% after one day of aging at 50 and 80°C, respectively.

Apparently, when the 30% TBP-DD solutions contain plutonium, the MBP formation rate is actually greater than the DBP formation rate. This could be due to a higher radiation exposure for DBP than for TBP, because as DBP is formed it will preferentially complex the plutonium.

At the conclusion of each plutonium experiment, the aged solvent that had been stripped with 0.2 $\underline{M}$ HNO_3 was washed twice with 0.5 $\underline{M}$ Na_2CO_3 to remove the plutonium complexed by DBP and MBP. In experiments with plutonium of low specific activity (8.9×10^7 c/min·mg), essentially complete plutonium removal was effected by this procedure. However, in the two experiments with plutonium of high specific activity, a small but significant concentration of plutonium could not be removed by washing with Na_2CO_3 or hydrazine carbonate or by sorption on macrorecticular resins. The concentration of plutonium remaining in the organic phase was ~0.0006 $\underline{M}$, when the initial concentration of plutonium in the experiment was about 0.1 $\underline{M}$. Spectrophotometric examination of the plutonium-containing organic exhibited a spectrum that was significantly different from that of DBP or MBP plutonium complexes. The precise nature of the species is not known.

3.3 METAL-ION-CATALYZED HYDROLYSIS OF TBP

The rates of metal-ion-induced hydrolysis of TBP in 30% TBP-DD at 25°C were determined using zirconium and uranium. These results are presented in Fig. 8, along with comparable data obtained for plutonium and for HNO_3 hydrolysis. The only hydrolysis product detected in these experiments was DBP, and its concentration could therefore be directly determined from the concentration of plutonium complexed by degradation products. Even though the metal loadings and acid concentrations that are compared are not identical, it is obvious from the data in Fig. 8 that plutonium and zirconium promote TBP hydrolysis far more effectively than uranium.

The adverse effect of zirconium on TBP stability is particularly significant, and it was found that the TBP degradation rate due to zirconium increases rapidly with increasing temperature. The results of our experiments on zirconium-catalyzed TBP degradation rates are presented in Table 4, along with comparable data for plutonium-induced hydrolysis.

The data in Table 4 indicate that zirconium promotes TBP hydrolysis ~30 times more effectively than plutonium (on an equal weight basis) and >10 times more effectively on an equimolar basis.

Table 4. Effects of zirconium and plutonium on TBP degradation rates

Metal[a]	Temperature (°C)	mg Pu/L·h[b]	mg DBP/L·h[c]
Zirconium	25	3.45	5.31
Plutonium	25	0.12	0.18
Zirconium	50	19.40	29.88
Plutonium	50	0.57	0.83

[a] Calculations are based on a metal loading of 1 g/L.

[b] Calculated as mg of plutonium complexed by all degradation products.

[c] Calculation based on plutonium complexation due only to DBP.

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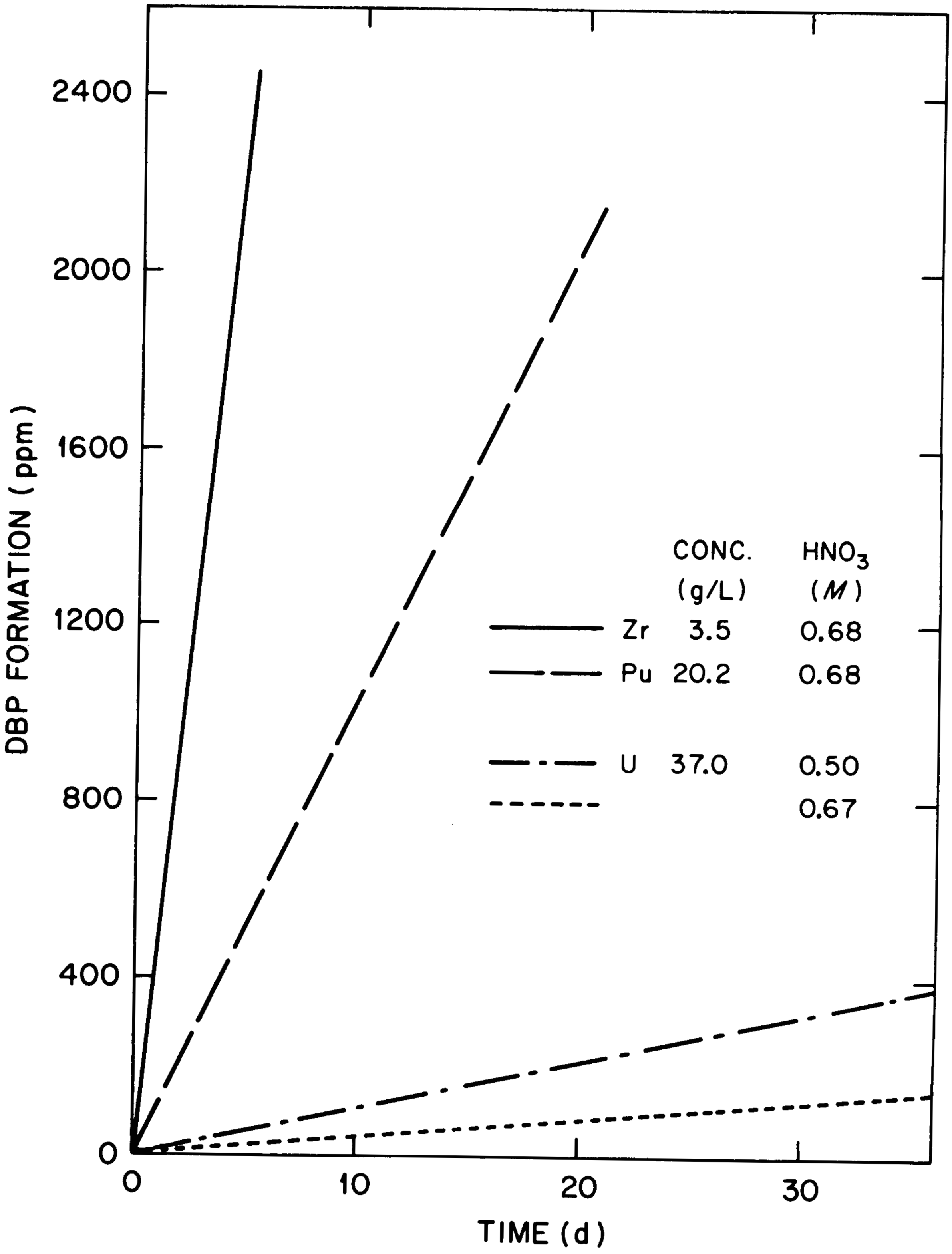

Fig. 8. DBP formation rates due to metal-ion-induced hydrolysis of TBP.

4. SUMMARY

The principal effect encountered when HNO_3 or polyvalent metal ions were extracted into 30% TBP-DD was shown to be an increase in the rate of hydrolysis of TBP, according to the equation:

$$TBP \rightarrow HDBP \rightarrow H_2MBP \rightarrow H_3PO_4.$$

These and other studies have shown that the rate of hydrolysis increases with increasing HNO_3, metal-ion concentration, and radiation dose, and increases very rapidly with increasing temperature.

In this study, the TBP degradation rates due to acid hydrolysis (determined as grams of plutonium complexed by degradation products) increased from 0.125 mg Pu/L·h at 25°C to 47.9 mg Pu/L·h at 80°C in 30% TBP-DD solutions that contained 0.68 $\underline{M}$ HNO_3. In solutions that additionally contained ~20 g/L of plutonium (specific activity = 9×10^7 c/min·mg), TBP degradation rates increased from 2.46 mg Pu/L·h at 25°C to 127.1 mg Pu/L·h at 80°C.

In addition to collecting data on the TBP degradation rate, our studies have suggested four factors of particular importance in the degradation process: (1) DBP is the principal plutonium-complexing species formed at temperatures of 50°C or lower, while significant concentrations of monobutyl phosphate (MBP) are also formed at higher temperatures; (2) the TBP degradation rate due to alpha radiolysis or chemical hydrolysis is strongly dependent on temperature; (3) plutonium promotes TBP hydrolysis by two mechanisms, alpha radiolysis and metal-ion-induced hydrolysis, and, of these, metal-ion-induced hydrolysis is the major effect; and (4) small amounts of an unidentified plutonium-complexing species are formed in experiments using plutonium of high specific activity (~4×10^8 c/min·mg). This species cannot be removed from 30% TBP-DD by Na_2CO_3 washing or other solvent cleanup procedures such as washing with hydrazine carbonate or sorption on macroreticular resins. Formation of this species was not observed in experiments which utilized plutonium of low specific activity.

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