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**AQUEOUS-PHASE DECOMPOSITION OF TRIBUTYL PHOSPHATE
AT 35 TO 75°C IN NITRIC ACID SOLUTIONS**

W. Davis, Jr., and A. H. Kibbey

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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

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ABSTRACT

The decomposition of tributyl phosphate (TBP) dissolved in the aqueous phase was studied by heating two-phase systems of TBP with 1 to 5 M HNO_3 at 35 to 75°C and subsequently analyzing for decomposition products by a methylation--gas chromatographic method. Phase ratios were maintained in the range 50 to more than 10,000 volumes of aqueous solution per volume of separate TBP phase to assure that most of the decomposition occurred in the aqueous phase. The present results are consistent with those obtained by extrapolating literature data at 75 to 115°C to the lower temperatures, and show that the rate constant for TBP decomposition in the aqueous phase is tenfold higher than that in the organic phase. However, in process applications, where the organic volume will equal or exceed the aqueous volume, the TBP decomposition rate in the organic phase will be one hundredfold higher than in the aqueous phase. The decomposition mechanism may not be as simple as a series of successive first-order reactions whereby hydrogen atoms replace butyl groups, or hydroxyl groups replace butoxy groups.

1. INTRODUCTION

The decomposition of tributyl phosphate (TBP) in solvent extraction plants for the recovery of uranium and plutonium has been a constant cause for concern* because the primary decomposition product, dibutyl phosphoric acid (HDBP), forms strong complexes with uranium, plutonium, and zirconium, thereby increasing the losses of uranium and plutonium and decreasing the zirconium decontamination

*References 1-5 provide a concise description of the status of the problem to 1963. Many reports on solvent stability have been written since these papers were presented at the Gatlinburg Conference on Solvent Extraction in 1962.

factors. Since most of the decomposition occurs in the organic phase,⁶⁻¹¹ the rate of decomposition of TBP dissolved in the aqueous phase (which contains nitric acid, uranyl nitrate, and fission products) has not been studied extensively, particularly at temperatures below 75°C. The purpose of this report is to present data on the decomposition of TBP dissolved in nitric acid solutions at 35 to 75°C, a temperature range that includes expected process temperatures.

2. EXPERIMENTAL

Experiments to evaluate the aqueous-phase decomposition of TBP were performed in vessels (Fig. 1) maintained at 35, 50, or 75°C. The reactants were 1, 3, or 5 M HNO_3 plus enough second-phase TBP to assure a TBP-saturated aqueous phase. In many of the experiments, 1 cc of TBP was used with 300 cc of the acid solution. As the result of removing 4 to 17 aqueous samples of 10 to 20 cc each and, in a few instances, adding further quantities of TBP, the phase volume ratio, $V_{\text{org}}/V_{\text{aq}}$, increased from an initial value of about 3×10^{-3} to 1×10^{-2} in many experiments, and to 5×10^{-2} in a few.

Three experiments in which the phase ratio varied from about 10^{-4} to 0 cc TBP (second phase) per cubic centimeter of HNO_3 solution were performed at 50°C. The solubilities of TBP in 1, 3, and 5 M HNO_3 at 50°C were estimated from the data of Higgins, Baldwin, and Soldano¹² to be 322, 415, and 532 mg/liter respectively. To three 400-cc portions of the aqueous acid solutions, we added 160, 200, and 260 microliters of TBP, respectively, corresponding to 31.2, 34.0, and 47.2 microliters of undissolved TBP per 400 cc of acid solution. Thus, the initial phase ratios were 0.78×10^{-4} , 0.85×10^{-4} , and 1.18×10^{-4} . The quantity of TBP in the second phase decreased to almost zero during the approximately 1500 hr of reaction time.

One experiment was performed using 15% TBP in *n*-dodecane as the second phase. In two other experiments, the solutions were exposed to ^{60}Co gamma irradiation at dose rates of the order of 0.03 whr/liter.

Fig. 1. Thermostat-Reactor System Used in Studies of TBP Decomposition.

All aqueous solutions were sampled three or more times during the 500- to 1500-hr duration of the experiments. These samples were taken after cessation of stirring to avoid withdrawing undissolved TBP. Sample solutions were stored in separatory funnels in a refrigerator until they could be transferred to equipment for freeze-drying preparatory to gas chromatographic analysis. Storage in the separatory funnels served as a means for further reducing (or eliminating) the quantity of undissolved TBP associated with the aqueous samples.

The freeze-drying and methylation treatment that was used to prepare the aqueous samples for gas chromatographic analysis has been described in detail elsewhere.¹³ The method involves converting dibutyl phosphoric acid (HDBP) to methyl dibutyl phosphate (MeDBP), the monobutyl phosphoric acid (H_2MBP) to dimethyl monobutyl phosphate (Me_2MBP), and phosphoric acid to trimethyl phosphate (TMeP). Only in the experiments at 75°C were Me_2MBP and TMeP present in sufficiently large quantities to be significant in the data analysis.

3. RESULTS

Examples of data obtained in this study are given in Fig. 2, which shows the HDBP concentrations formed during the decomposition of TBP dissolved in a 3 M HNO_3 aqueous phase at 50°C. Experiments 5139-69 and 5586-62 were performed with time-averaged ratios V_{org}/V_{aq} of the order of 10^{-2} or less; in experiment 5836-16-3, this ratio was less than 10^{-4} , as described in the Experimental section above.

All of the data are summarized in Table 1, which contains values of the following functions: (1) the rate of HDBP formation and the minimum standard deviation of this rate (column 5); (2) the solubility of TBP in the aqueous solutions, estimated by interpolation and extrapolation of literature data¹² (column 6); and (3) a first-order rate constant for HDBP formation and the minimum standard deviation of this constant (column 7). The rates in column 5 were obtained by fitting the gas chromatographic data on HDBP concentration vs time in Eq. (7) below, by use of

Fig. 2. HDBP Concentration in the Aqueous Phase During Decomposition of TBP at 50°C. Volumetric phase ratio ($V_{\text{org}}/V_{\text{aq}}$): ■ and ○, $\sim 10^{-2}$; ●, $\leq 10^{-4}$.

Table 1. Rate Constants for the (Primarily Aqueous Phase) Decomposition of TBP

Notebook Ref.	HNO ₃ Conc. (M)	Temp. (°C)	No of Points	$[k_1 S_o + \sigma(k_1 S_o)] \times 10^4$ (millimoles/liter-hour) ^a	S_o^b (millimoles/liter)	$[k_1 \pm \sigma(k_1)] \times 10^4$ (hr ⁻¹)	Phase Ratio (V _{org} /V _{aq})	Remarks
	1	101				370.	0. ^c	Ref. 8
5139-75	1	75	4	48. ± 16.			~10 ⁻²	
5139-71	1	50	4	3.4 ± 1.6	1.21	2.8 ± 1.3	~10 ⁻²	
5586-62	1	50	6	3.5 ± 1.8	1.21	2.9 ± 1.5	~10 ⁻²	
5836-16-1	1	50	4	2.6 ± 0.3	1.21	2.1 ± 0.2	<10 ⁻⁴	
5586-25	1	35	4	0.87 ± 0.49	1.21	0.72 ± 0.40	~10 ⁻²	
	3 ^d	105				400.	1. and 5 × 10 ⁻³	Ref. 7
	3 ^d	76				75.	1.	Ref. 7
5586-11	3	75	4	256 ± 19.			~10 ⁻²	
5139-69	3	50	4	8.6 ± 0.6	1.56	5.5 ± 0.4	~10 ⁻²	
5586-62	3	50	7	6.4 ± 2.2	1.56	4.1 ± 1.4	~10 ⁻²	
5836-16-3	3	50	4	6.4 ± 0.2	1.56	4.1 ± 0.1	~10 ⁻⁴	
5139-63	3	50	11	13. ± 2.	1.56	8.4 ± 1.2	~10 ⁻²	⁶⁰ Co, 0.0334 watt/liter
5139-73	3	50	3	2.8 ± 0.6	0.58 ^e	4.8 ± 1.0	1.5 to 8	15% TBP in n-dodecane
5586-14	3	35	3	0.84 ± 0.60	1.23	0.68 ± 0.49	~10 ⁻²	
	5	75				140.		Ref. 14
5139-61	5	75	17	183. ± 12.			~10 ⁻²	
5139-68	5	50	4	9.9 ± 1.0	2.00	5.0 ± 0.5	~10 ⁻²	
5586-63	5	50	5	8.9 ± 4.8	2.00	4.4 ± 2.3	~10 ⁻²	
5836-16-5	5	50	5	9.3 ± 1.5	2.00	4.6 ± 0.7	<10 ⁻⁴	
5586-57	5	50	9	6.8 ± 1.8	2.00	3.3 ± 0.9	~10 ⁻²	⁶⁰ Co, 0.0262 watt/liter
5586-28	5	35	4	1.1 ± 0.2	1.25	0.9 ± 0.2	~10 ⁻²	
	5.4	108				1900.	0. ^c	Ref. 8
	5.4	60				11.5	0. ^c	Ref. 8
	6 ^d	105				720.	1.	Ref. 7
	8.6	116				2800.	0. ^c	Ref. 8

^aBased on Eq. (9) and Ref. 15.^bSolubilities of TBP in aqueous acid solutions calculated by interpolating or extrapolating the data of Higgins, Baldwin, and Soldano (ref. 12).^cAqueous phase was contacted with TBP, and the separate aqueous phase was then subjected to hydrolytic conditions.^dThese are acid concentrations before contacting with TBP.^eInterpolated from the data of Kennedy and Grimley (ref. 9).

POLFIT II.¹⁵ Except at 75°C, the H_2MBP and H_3PO_4 concentrations were so small and uncertain that they were assumed to be zero. The straight lines in Fig. 2 were drawn from the intercept and the slope calculated in this manner for the three experiments shown.

The data plotted in Fig. 2 are based on the calibration data previously reported.¹³ If no bias in our experimental techniques developed during repeated use of the freeze-drying--methylation--gas chromatography sequence of operations, then we would expect all of the data, or lines, to intersect (within experimental accuracy) at zero millimoles of HDBP per liter at time zero. This is the case for two of the three experiments, but not for experiment 5836-16-3.

Only 3 experiments were performed at 75°C; of these, only the one involving 5 M HNO_3 was run long enough and sampled frequently enough to permit detailed numerical analysis (Fig. 3). At the earliest sampling time (i.e., after less than two days of reaction), H_2MBP was readily detectable, but no significant quantity of H_3PO_4 was present until after an induction period of about 300 hr. Further mathematical analyses of this experiment were based on the usual assumptions that the successive hydrolytic reactions are:

From these equations, we derived the mathematical relationships listed below. These relationships apply to systems in which the aqueous phase remains saturated with TBP (at a concentration S_0) and in which the extent of decomposition of TBP in the separate TBP phase can be neglected.

Fig. 3. Experimental and Calculated Concentrations of TBP Decomposition Products in 5 M HNO₃ at 75°C as a Function of Time. Upper straight line is sum of product concentrations from Eq. (7). ○ - HDBP; curve is calculated from Eq. (4), ● - H₂MBP; curve is calculated from Eq. (5), ■ - H₃PO₄; curve is calculated from Eq. (6). See Table 2 for parameters.

$$[\text{HDBP}] = \frac{k_1 S_o}{k_2} (1 - e^{-k_2 t}) + I(\text{HDBP}) \quad (4)$$

$$[\text{H}_2\text{MBP}] = k_1 S_o \left\{ \frac{1}{k_3} + \frac{e^{-k_2 t}}{(k_2 - k_3)} - \frac{k_2 e^{-k_3 t}}{k_3 (k_2 - k_3)} \right\} + I(\text{H}_2\text{MBP}) \quad (5)$$

$$[\text{H}_3\text{PO}_4] = k_1 S_o \left\{ \left(t - \frac{1}{k_2} - \frac{1}{k_3} \right) - \left(\frac{k_3}{k_2} \right) \frac{e^{-k_2 t}}{(k_2 - k_3)} + \left(\frac{k_2}{k_3} \right) \frac{e^{-k_3 t}}{(k_2 - k_3)} \right\} + I(\text{H}_3\text{PO}_4) \quad (6)$$

$$[\text{HDBP}] + [\text{H}_2\text{MBP}] + [\text{H}_3\text{PO}_4] = k_1 S_o t + I^o \quad (7)$$

In Eqs. (4) - (7), the $I(\text{HDBP})$, $I(\text{H}_2\text{MBP})$, $I(\text{H}_3\text{PO}_4)$, and I^o are intercept terms that we have added to the normal equations to provide for potential bias in the analytical data. The I values should be zero. Although they are not zero in the numerical analyses (Tables 1 and 2), zero is included within the standard error of I (indicating that there is no real bias).

Considerable care must be exercised in the nonlinear least-squares analysis of data according to Eqs. (4)-(6). First,

$$e^{-k_2 t} \approx 1 - k_2 t \quad k_2 t \leq 0.2, \quad (8)$$

in which case Eq. (4) reduces to

$$[\text{HDBP}] = k_1 S_o t. \quad (9)$$

Equation (9) involves $k_1 S_o$, but k_2 has been eliminated. Thus, unless the value of $k_2 t$ is at least as large as 0.4, Eq. (4) can be used to determine only one of the constants, $k_1 S_o$. This is the basis of the linear least-squares analysis with POLFIT II,

Table 2. Rate Constants^a for the Hydrolysis of TBP, HDBP, and H₂MBP in 5 M HNO₃ at 75°C

Component Analyzed	Equation No.	$[k_1 S_o \pm a(k_1 S_o)] \times 10^2$ (millimoles liter·hour)	$[k_2 \pm \gamma(k_2)] \times 10^3$ (hr ⁻¹)	$[k_3 \pm \gamma(k_3)] \times 10^3$ (hr ⁻¹)	Intercept Conc. (millimoles liter)	Standard Error of Fit (millimoles liter)
HDBP + H ₂ MBP + H ₃ PO ₄	7	1.83 ± 0.12			-0.173 ± 0.471	0.905
HDBP	4	1.83 ± 0.98	3.52 ± 1.63		-0.180 ± 0.741	0.654
H ₂ MBP	5	0.43 ± 0.16	38. ± 155.	-1.10 ± 0.73	0.266 ± 0.327	0.244 (15.7%) ^b
		0.46 ± 0.13	21. ± 30.	-1.03 ± 0.57	0.274 ± 0.174	
H ₂ MBP + H ₃ PO ₄	11	1.71 ± 0.22	3.40 ± 0.01		0.290 ± 0.484	0.484
H ₃ PO ₄	6	1.48 ± 10.8	3.60 ± 529.	3.24 ± 493.	0.013 ± 0.164	0.333

^aAll 17 sets of data were used in all of the numerical analyses, which are based on the assumption that the uncertainties of the concentrations are independent of the concentrations, except as noted.

^bNumerical analysis based on the assumption of a constant-percentage uncertainty in analysis of the species.

although we modified it, as indicated in Eq. (7), by adding an intercept term.

We previously mentioned that the HDBP and H_2 MBP were formed in significant quantities in our experiments at 75°C. By using the data from these experiments and the nonlinear least-squares program of D. W. Marquardt,^{16,17} we attempted to evaluate k_2 and k_3 as well as $k_1 S_o$. Values of $k_1 S_o$ determined in this manner agreed rather closely with those listed in Table 1; however, the uncertainty of $k_1 S_o$, namely $\sigma(k_1 S_o)$, and both k_2 and $\sigma(k_2)$ were meaningless except for the experiments at 75°C. When there are a sufficient number of points, as in run 5139-61, the data can be combined for the purpose of estimating $k_1 S_o$, k_2 , and k_3 . In Table 2 we have listed rate constants for the experiment run at 75°C with 5 M HNO_3 . The values of the constants are based only on HDBP, H_2 MBP, or H_3PO_4 analyses; for comparison, we have also listed values for $k_1 S_o$, estimated from the sum of all decomposition products [Eq. (7)] and from the sum H_2 MBP plus H_3PO_4 . In attempting to evaluate the constants from the sum of the HDBP and H_2 MBP concentrations, we found that, while the data fit the resulting summation equation, it was not possible to obtain a set of constants from this combination. The summation equations involve the rate constants as follows:

$$[HDBP] + [H_2MBP] = k_1 S_o t - [H_3PO_4] = k_1 S_o \left\{ \left(\frac{1}{k_2} + \frac{1}{k_3} \right) + \left(\frac{k_3}{k_2} \right) \frac{e^{-k_2 t}}{(k_2 - k_3)} - \frac{k_2}{k_3} \frac{e^{-k_3 t}}{(k_2 - k_3)} \right\} + I_1^o. \quad (10)$$

$$[H_2MBP] + [H_3PO_4] = k_1 S_o t - [HDBP] = k_1 S_o \left\{ t - \frac{1}{k_2} + \frac{e^{-k_2 t}}{k_2} \right\} + I_2^o. \quad (11)$$

The temperature dependence of the rate of formation of HDBP ($k_1 S_o$ of Table 1) in the present studies is shown in Fig. 4, whereas the temperature dependence of the rate constant (k_1 of Table 1) of the present and literature data^{7,8,10,14} is shown in Fig. 5. Figure 5 also includes a straight line that passes reasonably well through

Fig. 4. Rate of Formation of HDBP, Primarily in the Aqueous Phase, as a Function of Temperature (This Study). $\bigcirc$ - 1 M HNO_3 , $\bullet$ - 3 M HNO_3 , $\square$ - 5 M HNO_3 . Horizontal lines are drawn through the 3 rates at 50 $^{\circ}\text{C}$ corresponding to organic/aqueous volumes $\leq 10^{-4}$.

Fig. 5. Effects of Temperature on Decomposition in Both Aqueous and TBP Phases. Non-referenced points are for the present work at 35 and 50°C. + - 5 M HNO₃, Δ - 1 M HNO₃, ○ - 3 M HNO₃, ● - 1 M HNO₃, □ - 5 to 6 M HNO₃, X - 8.4 M HNO₃.

the data. Regression analysis was not applied since the data of the different authors are not readily comparable. The line is described by the equation

$$\left. \begin{aligned} k_1 &= e^{(30.0187 - 12,260/T)} \\ \text{or} \\ k_1 &= 1.1 \times 10^{13} e^{-12,260/T} \end{aligned} \right\} \quad (12)$$

4. DISCUSSION AND CONCLUSIONS

One objective of the work reported here was to evaluate the rate of decomposition of TBP in the aqueous phase at temperatures encountered in Purex process operations, namely, below 50°C. Based on estimated solubilities, more than 80% of the TBP was dissolved in the aqueous phase in the three experiments having an initial organic/aqueous phase ratio of 10^{-4} . During the course of these experiments, the quantity of TBP that dissolved in the aqueous phase approached 100% of the TBP that was present. Table 1 shows that the estimated rates of HDBP formation, namely $k_1 S_o$, at 50°C are the same (within experimental errors) for phase ratios of approximately 10^{-2} as for ratios of 10^{-4} and lower. They do not differ as much as a factor of 2. Thus, 50%, or more, of the HDBP in the aqueous phase is formed by the decomposition of TBP dissolved therein when the organic/aqueous volume ratio does not exceed about 10^{-2} . Values of $k_1 S_o$ appear to increase as the acidity increases in the range 1 to 5 M HNO_3 (Fig. 4). However, our data are not accurate enough to permit us to suggest a quantitative description of the effect of acidity.

To our knowledge, no studies have been made of the decomposition of TBP dissolved in aqueous nitric acid solutions at temperatures in the range 25 to 50°C, which are used in solvent extraction plant equipment. Wagner⁷ studied the decomposition of TBP: (1) at 76 and 105°C for systems initially containing equal volumes of TBP and 3 M HNO_3 ; (2) at 105°C for systems initially containing equal volumes of TBP and

6 M HNO_3 ; and (3) at 105°C for a system consisting of 1 volume of TBP per 200 volumes of 3 M HNO_3 . He reports the solubilities of TBP in 3 M HNO_3 at 25, 76, and 105°C to be 0.2, 0.35, and 0.40 g/liter respectively. The quantity of HDBP that was formed during these experiments was never determined; further, as Burger¹⁰ notes, there are serious doubts raised by Wagner's methods of calculation, "by this 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 TBP decomposed."

Our data in Fig. 3 and Table 2 show that the hydrolysis of TBP to HDBP, Eq. (1), is not the rate-controlling step at 75°C. They also show (Fig. 3) that only about half of the decomposition products at 75°C exist as $\text{H}_2\text{MBP} + \text{H}_3\text{PO}_4$. Wagner's estimates of k_1 fall within a factor of 2 of the line value [Eq. (12) and Fig. 5].

Lanham and Reilly⁸ performed four measurements of the rate of hydrolysis of TBP in a separate aqueous phase that was first saturated with TBP and then separated and heated to 60°C or the boiling temperature, namely 101 to 116°C for the 1 to 8.6 M HNO_3 solutions employed (Table 1). Phosphorus-32 was used to determine the total quantities of decomposition products. Data obtained by these authors also lie close to the line defined by Eq. (12) and shown in Fig. 5.

In two experiments, both radiation and heat were used to decompose TBP (Table 1). The dose rates, approximately 0.03 whr/liter, were not of sufficient magnitude to produce a measurable effect. Thus, while the estimated value of $k_1 S_0$, 13×10^{-4} millimole liter⁻¹ hr⁻¹, for the experiment with 3 M HNO_3 is greater than the corresponding unirradiated value, 6.4×10^{-4} , by a factor of about 2, the situation with 5 M HNO_3 is reversed; here, $k_1 S_0$ for the irradiated solution is 6.8×10^{-4} vs about 9×10^{-4} for the unirradiated solution.

While the three successive, first-order decomposition reactions of Eqs. (1)–(3) have generally been accepted as descriptive of the production of HDBP, H_2MBP , and H_3PO_4 from TBP, there are practically no data to support this scheme. The 17 points of experiment 5139–61 (Tables 1 and 2) provide the most extensive set

of data for TBP decomposition with which we are familiar. Yet the analyses of these data (Table 2 and Fig. 3) indicate that Eqs. (1)-(3) represent no more than an educated guess concerning the nature of the mechanisms of formation of TBP decomposition products. In particular, the quantity $k_1 S_o$ for 75°C and 5 M HNO_3 is probably $(1.7 \text{ to } 1.8) \times 10^{-2}$ millimole liter⁻¹ hr⁻¹; however, numerical analyses of the sum $[\text{HDBP}] + [\text{H}_2\text{MBP}]$ or of $[\text{H}_2\text{MBP}]$ alone do not support this value. The constant k_2 is probably about 3.5×10^{-3} hr⁻¹, although the HDBP concentrations do not support this value. Finally, the value of k_3 is essentially unknown.

The net effect of the present study is to cast doubt on the validity of the concept of the series of successive, first-order reactions described by Eqs. (1)-(3), and to support the concept that the overall rate of decomposition of TBP in the aqueous phase is much smaller than it is in the organic phase when the organic volume exceeds about one-tenth of the aqueous volume, a situation that applies during nuclear fuel processing in the Purex process. The second feature is a result of the much higher concentration of TBP in the organic phase, which more than offsets the fact that the rate constant, k_1 , for decomposition in the aqueous phase is greater than its value in the organic phase (Fig. 5).

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