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A Pulse Radiolysis Investigation of the Reactions of Tributyl Phosphate with the Radical Products of Aqueous Nitric Acid Irradiation

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Tributyl phosphate (TBP) is the most common organic compound used in liquid−liquid separations for the recovery of uranium, neptunium, and plutonium from acidic nuclear fuel dissolutions. The goal of these processes is to extract the actinides while leaving fission products in the acidic, aqueous phase. However, the radiolytic degradation of TBP has been shown to reduce separation factors of the actinides from fission products and to impede the back-extraction of the actinides during stripping. As most previous investigations of the radiation chemistry of TBP have focused on steady state radiolysis and stable product identification, with dibutylphosphoric acid (HDBP) invariably being the major product, here we have determined room temperature rate constants for the reactions of TBP and HDBP with the hydroxyl radical [$(5.00 \pm 0.05) \times 10^{9}$, $(4.40 \pm 0.13) \times 10^{9}$ M^{-1} s^{-1}], hydrogen atom [$(1.8 \pm 0.2) \times 10^{8}$, $(1.1 \pm 0.1) \times 10^{8}$ M^{-1} s^{-1}], nitrate radical [$(4.3 \pm 0.7) \times 10^{6}$, $(2.9 \pm 0.2) \times 10^{6}$ M^{-1} s^{-1}], and nitrite radical ($<2 \times 10^{5}$, $<2 \times 10^{5}$ M^{-1} s^{-1}), respectively. These data are used to discuss the mechanism of TBP radical-induced degradation.

Introduction

Tributyl phosphate (TBP) is the most important chemical in nuclear solvent extraction and has been used on a process scale for decades. In the PUREX (Plutonium Uranium Extraction) process, 30% TBP in alkane diluent is used to extract actinides from aqueous nitric acid. One of the major advantages of this ligand is its low nitric acid hydrolysis rate; for example, Williams and Wilkinson[1] reported no production of acid phosphates after several days of exposure of TBP to 5 M HNO_3, and Egorov et al.[2] reported a rate constant for TBP hydrolysis of 9×10^{-7} h^{-1} for 30% TBP in decane refluxed with 1.5 M HNO_3. Therefore, TBP thermal degradation is slow and can be safely neglected under the short-contact, moderate-temperature conditions often used in extractions.

However, these extraction processes are also subjected to radiation dose rates in the kGy h^{-1} range. Dibutylphosphoric (HDBP) acid is invariably the major product, regardless of whether TBP is irradiated neat, in alkane diluents, or in contact with an aqueous phase (see Scheme 1). Other products measured are methylated and hydroxylated phosphates, some of high molecular weight.[3] Since HDBP is also a complexing agent, its production interferes with uranium stripping and fission product separation factors, especially for zirconium.[4] The adverse effects of the buildup of HDBP and related compounds are mitigated during process extractions by washing the solvent with aqueous Na_2CO_3 solutions[5,6] which extract residual radioactivity and acidic complexing agents from the organic solvent. However, with continued recycling, washing becomes less effective, and the degraded solvent shows increased retention of Pu, Zr, and Ru, and increases in viscosity.[7] In addition, alkylphosphoric acids contribute to emulsion formation[8,9] and decreased phase separation performance.[9] Continued degradation by radiolysis produces monobutyl phosphoric acid (H_2MBP) from HDBP and phosphoric acid (H_3PO_3) from H_2MBP.

SCHEME 1: Structures of Tributyl Phosphate (TBP, left) and Dibutyl Phosphoric Acid (HDBP, right)

Various mechanisms have been proposed to explain the radiolytic degradation of TBP.[10–16] However, previous investigations of TBP radiation chemistry have mainly focused on steady state radiolysis using isotopic γ-ray or accelerator electron sources, followed by stable product identification. In the absence of verified kinetic data for the reactions of the radical species produced in irradiated aqueous nitric acid, the validity of these proposed mechanisms is speculative. Given the worldwide importance of TBP in nuclear solvent extraction and the interest in its radiation chemistry, there have been surprisingly few attempts made to determine the fundamental kinetics involved.

Moreover, the little kinetic data available show significant discrepancies. The reaction kinetics of the hydroxyl radical ($^{\bullet}$OH) with TBP have been previously reported as 1.03×10^{10} [14] and 4.8×10^{9} M^{-1} s^{-1}.[13] A single measurement of the hydrated electron (e_{aq}^{-}) reaction rate constant ($< 1 \times 10^{6}$ M^{-1} s^{-1} [13]) has also been determined, but there are no reports for the reactions of the hydrogen atom or any nitrogen centered radicals.

In this study, we present the methods and results of a pulse radiolysis investigation of the reactions of TBP and HDBP with the hydroxyl radical, hydrogen atom, and the nitrogen trioxide ($^{\bullet}NO_3$) and nitrogen dioxide ($^{\bullet}NO_2$) radicals. The implications of these results for the postulated radiolysis mechanisms are also discussed.

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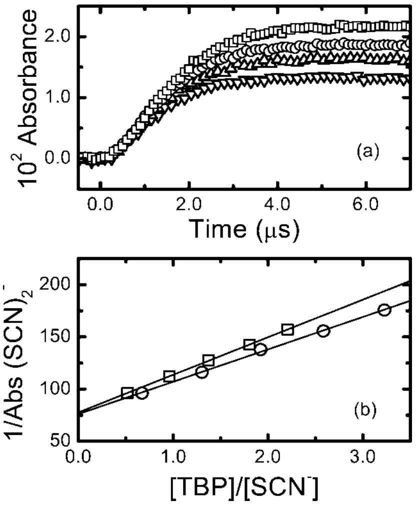

Figure 1. (a) Measured $(SCN)_2^{\bullet-}$ absorbance for N_2O-saturated 100.0 μM KSCN with 220.6 μM (▽), 180.4 μM (△), 137.4 μM (○), and 51.8 μM (□) added TBP. (b) Transformed plots for TBP (□, slope = 35.99 ± 0.14, intercept = 77.73 ± 0.21, $R^2 = 1.000$) and HDBP (○, slope = 31.01 ± 0.69, intercept = 76.1 ± 1.5, $R^2 = 0.998$) corresponding to reaction rate constants of $k_6 = (5.00 \pm 0.05) \times 10^9$ and $k_8 = (4.40 \pm 0.13) \times 10^9$ M^{-1} s^{-1}, respectively.

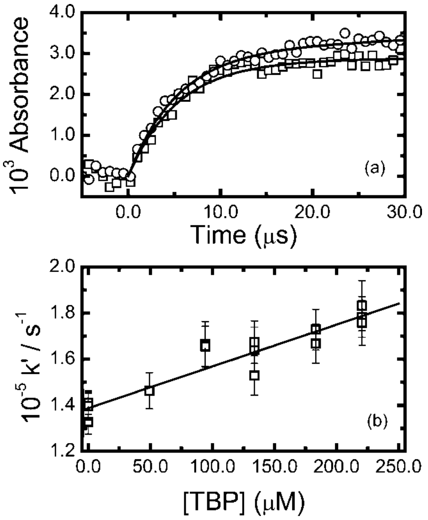

Figure 2. (a) Kinetics observed for hydrogen atom reaction of 34.9 μM tetracycline with 49.2 μM (□) and 220.6 μM (○) TBP in N_2-saturated solution containing 0.10 M *tert*-butyl alcohol at pH 1.84. Solid lines correspond to fitted pseudo-first-order growths, with rate constants of $(1.40 \pm 0.06) \times 10^5$ and $(1.83 \pm 0.11) \times 10^5$ s^{-1}, respectively. (b) Second-order determination of hydrogen atom reaction with TBP from values in part a. The solid line corresponds to a weighted linear fit, giving a rate constant of $k_9 = (1.8 \pm 0.2) \times 10^8$ M^{-1} s^{-1}.

Experimental Methods

Tributyl phosphate from Sigma-Aldrich Chemical Co. was further purified prior to use by a series of aqueous washes, consisting of 1 M Na_2CO_3, 1 M NaOH, 0.1 M HNO_3, and pure water, each at a 2:1 volume ratio[17] to remove trace amounts of HDBP, H_2MBP, and/or H_3PO_4. This purification was necessary as using unpurified reagent resulted in impossibly high reaction rate constants. Aqueous TBP solutions for pulse radiolysis were then prepared within 10 days, by stirring 30 μL of the purified TBP in 500 mL of ≥18.0 MΩ Milli-Q water for 24 h. The resulting solution was 220.6 μM in TBP, and dilutions of this solution were used to measure pseudo-first-order rate constants with selected radicals.

HDBP (Fluka Chemical) was purified by dissolution in CCl_4 at a 4:1 volume ratio, followed by two extractions with an equal volume of pure water[18] to remove trace amounts of H_2MBP and/or H_3PO_4. The CCl_4 was then removed from the resulting HDBP-containing organic phase by nitrogen blow-down. Aqueous solutions were made by adding 30 μL aliquots of the purified chemical to 500 mL of water, followed by stirring for 24 h to give 322.7 μM HDBP.

All solutions were completely sparged with high-purity N_2O (for hydroxyl radical experiments) or N_2 (hydrated electron experiments) to remove dissolved oxygen.

The linear accelerator (LINAC) electron pulse radiolysis system at the Radiation Laboratory, University of Notre Dame, was used for the reaction rate constant determinations of this study. This irradiation and transient absorption detection system has been described in detail previously.[19] During rate constant measurements, the solution vessels were sparged with only the minimum amount of gas necessary to prevent air ingress. Solution flow rates in these experiments were adjusted so that each irradiation was performed on a fresh sample. Dosimetry[20] was performed using N_2O-saturated, 1.00×10^{-2} M KSCN solutions at $\lambda = 475$ nm, ($G\varepsilon = 5.2 \times 10^{-4}$ m^2 J^{-1}) with average doses of 3−5 Gy per 2−3 ns pulse. Throughout this paper, G is defined in μmol J^{-1}, and ε is in units of M^{-1} cm^{-1}. All measurements were conducted at a room temperature of 18 ± 1°C. The uncertainties reported for rate constant determinations are $\pm 1\sigma$.

Results and Discussion

The radiolysis of water produces free radicals in pure water according to the stoichiometry[21]

$$H_2O \rightsquigarrow [0.28]^{\bullet}OH + [0.06]^{\bullet}H + [0.27]e^-_{aq} + [0.05]H_2 + [0.07]H_2O_2 + [0.27]H^+ \quad (1)$$

where the numbers in brackets are the G-values (yields in μmol J^{-1}) for each species production. The total radical concentrations typically used in our kinetics radiolysis experiments were ∼2−8 μM per pulse. Under process conditions, the solvated electron reaction with TBP is not important, due to the effectively quantitative reaction of this radical with H^+ [21]

$$e^-_{aq} + H^+ \rightarrow {}^{\bullet}H \quad k_2 = 2.3 \times 10^{10}\ M^{-1}\ s^{-1} \quad (2)$$

and also due to its low measured bimolecular rate constant (<1 × 10^6 M^{-1} s^{-1}).[13]

Hydroxyl Radical Reactions. The reaction of only hydroxyl radicals was achieved by presaturating the solutions with N_2O, which quantitatively converts the hydrated electrons, e^-_{aq}, and hydrogen atoms, $^{\bullet}H$, to this radical via the reactions:[2]

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + OH^- + {}^{\bullet}OH \quad k_3 = 9.1 \times 10^9\ M^{-1}\ s^{-1} \quad (3)$$

$${}^{\bullet}H + N_2O \rightarrow {}^{\bullet}OH + N_2 \quad k_4 = 2.1 \times 10^6\ M^{-1}\ s^{-1} \quad (4)$$

As no direct transient absorbance was observed in the reaction of the hydroxyl radical with TBP in water, these rate constants were determined using SCN^- competition kinetics,[21] monitoring the decrease in absorbance of the produced $(SCN)_2^{\bullet-}$ transient at 475 nm upon increasing addition of TBP (see Figure 1a). This competition

$${}^{\bullet}OH + SCN^- (+SCN^-) \rightarrow OH^- + (SCN)_2^{\bullet-} \quad k_5 = 1.05 \times 10^{10}\ M^{-1}\ s^{-1} \quad (5)$$

$$^{\bullet}\mathrm{OH} + \mathrm{TBP} \rightarrow (\mathrm{C_4H_9O})_2(^{\bullet}\mathrm{C_4H_8O})\mathrm{PO} + \mathrm{H_2O} \quad k_6 \tag{6}$$

can be solved to give the following expression:

$$\frac{1}{\mathrm{Abs(SCN)_2^{\bullet -}}} = \frac{1}{\mathrm{Abs^0(SCN)_2^{\bullet -}}} + \frac{k_6[\mathrm{TBP}]}{\mathrm{Abs^0(SCN)_2^{\bullet -}}\, k_5[\mathrm{SCN^-}]} \tag{7}$$

where $\mathrm{Abs^0(SCN)_2^{\bullet -}}$ and $\mathrm{Abs(SCN)_2^{\bullet -}}$ are the absorbances of $\mathrm{(SCN)_2^{\bullet -}}$ in the absence and presence of added TBP, respectively. From a plot of $1/\mathrm{Abs(SCN)_2^{\bullet -}}$ versus $[\mathrm{TBP}]/[\mathrm{SCN^-}]$ (Figure 1b) we obtain a straight line with the slope/intercept quotient corresponding to the ratio k_6/k_5. Since the value of $k_5 = 1.05 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ is known,[21] the value of the TBP rate constant can be determined.

Previous attempts to measure the $^{\bullet}$OH radical reaction with TBP using steady state radiolysis and competition kinetics in 0.1 M $\mathrm{HNO_3}$ have been made by Clay and Witort,[14] who reported a value of $1.03 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$. Khaikin[13] performed pulse radiolysis with $\mathrm{SCN^-}$ competition kinetics at pH 6.5 to find a value of $4.8 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$. Our determination gave a value of $k_6 = (5.00 \pm 0.05) \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$, in very good agreement with Khaikin.[13] It is important to note that all our rate constant errors include contributions from the precision of the second-order determinations and also the uncertainty in the concentrations. All of the rate constants determined in this work are summarized in Table 1.

A survey of the literature shows that hydroxyl radical reaction rate constants that have been measured for alkanes in aqueous solution increase with carbon chain length, from butane ($4.6 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$) to heptane ($7.7 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$).[22] The rate constant for butane is comparable to that measured here for TBP, as expected for hydrogen atom abstraction from a TBP butyl group. A slightly slower value of $k_8 = (4.40 \pm 0.13) \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$ was found for hydroxyl radical reaction with HDBP (see Figure 1b):

$$^{\bullet}\mathrm{OH} + \mathrm{HDBP} \rightarrow \mathrm{H_2O} + \text{products} \quad k_8 \tag{8}$$

No previous value for this rate constant has been reported.

Hydrogen Atom Reactions. The rate constants for the $^{\bullet}$H atom reactions with TBP or HDBP have also not been previously reported; however, the generation of the TBP radical by hydrogen abstraction has traditionally been reported to be due to $^{\bullet}$H atom reaction because of the large amounts of hydrogen gas generated during TBP radiolysis.[10–12,16]

To determine the hydrogen atom reaction rate constant for TBP

$$^{\bullet}\mathrm{H} + \mathrm{TBP} \rightarrow (\mathrm{C_4H_9O})_2(^{\bullet}\mathrm{C_4H_8O})\mathrm{PO} + \mathrm{H_2} \quad k_9 \tag{9}$$

we used 34.88 μM tetracycline in $\mathrm{N_2}$-sparged solution containing 0.10 M *tert*-butyl alcohol adjusted to pH 1.8 with perchloric acid as a standard[23] and measured the increase in rate of the tetracycline−H adduct absorbance (see Figure 2a) with added TBP. By plotting this rate constant change against TBP concentration (Figure 2b) this value was determined to be $k_9 = (1.8 \pm 0.2) \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$. The reactions of the $^{\bullet}$H atom with various alkanes have previously been measured for butane through hexane using EPR techniques,[24] again showing increasing rates with increasing chain length. The corresponding literature value for butane, $3.6 \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$,[24] was somewhat slower than our TBP value. Our corresponding value for the $^{\bullet}$H atom reaction with HDBP

$$^{\bullet}\mathrm{H} + \mathrm{HDBP} \rightarrow \mathrm{H_2} + \text{other products} \quad k_{10} \tag{10}$$

was slightly slower than for TBP, giving $k_{10} = (1.1 \pm 0.1) \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}}$.

Nitrate Radical Reactions. Steady-state radiolysis of TBP in the presence of $\mathrm{HNO_3}$ would be expected to result in additional products. These include nitrated phosphates, which also impede stripping efficiency.[3] The TBP radical product of hydrogen abstraction (eq 9) was postulated to undergo reaction with $^{\bullet}\mathrm{NO_3}$ radical to produce nitrated TBP:[3]

$$^{\bullet}\mathrm{NO_3} + (\mathrm{C_4H_9O})_2(^{\bullet}\mathrm{C_4H_8O})\mathrm{PO} \rightarrow (\mathrm{C_4H_9O})_2(\mathrm{OC_4H_8NO_3})\mathrm{PO} \quad k_{11} \tag{11}$$

Nitrated phosphates ($\mathrm{RONO_2}$ and $\mathrm{RNO_2}$) have been identified in infrared and mass spectrometric analyses of postirradiation 30%-TBP/dodecane/$\mathrm{HNO_3}$ solutions,[3] and although hydrogen abstraction reactions by the $^{\bullet}\mathrm{NO_2}$ radical are slow, they might be expected to undergo radical addition reactions in the same way as shown for $^{\bullet}\mathrm{NO_3}$ radical above:

$$^{\bullet}\mathrm{NO_2} + (\mathrm{C_4H_9O})_2(^{\bullet}\mathrm{C_4H_8O})\mathrm{PO} \rightarrow (\mathrm{C_4H_9O})_2(\mathrm{OC_4H_8NO_2})\mathrm{PO} \quad k_{12} \tag{12}$$

In this study, the reaction of $^{\bullet}\mathrm{NO_3}$ with TBP was measured in $\mathrm{N_2O}$-sparged 6 M $\mathrm{HNO_3}$ solution, where production of $^{\bullet}\mathrm{NO_3}$ is favored over $^{\bullet}\mathrm{NO_2}$ by direct radiolysis of the high concentration of nitric acid and nitrate anion[25,26]

$$\mathrm{HNO_3} \rightsquigarrow \mathrm{e^-} + \mathrm{HNO_3^{\bullet +}} \rightarrow \mathrm{H^+} + \mathrm{e^-} + {}^{\bullet}\mathrm{NO_3} \tag{13}$$

$$\mathrm{NO_3^-} \rightsquigarrow \mathrm{e^-} + {}^{\bullet}\mathrm{NO_3} \tag{14}$$

and also by the reaction of the formed hydroxyl radicals with $\mathrm{HNO_3}$[26]

$$\mathrm{HNO_3} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{H_2O} + {}^{\bullet}\mathrm{NO_3} \quad k_{15} = 1.4 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}} \tag{15}$$

Our measured spectrum of the $^{\bullet}\mathrm{NO_3}$ radical is given in the inset of Figure 3. This spectrum was converted to absolute ε values using the measured *G*-value for $^{\bullet}\mathrm{NO_3}$ radical production of 0.46 μmol $\mathrm{J^{-1}}$, as measured by Katsumura et al.[26] This gave a peak absorption coefficient at 640 nm of $\varepsilon = 1200\ \mathrm{M^{-1}\ cm^{-1}}$, in good agreement with the previous measurement of $1300 \pm 100\ \mathrm{M^{-1}\ cm^{-1}}$. We saw evidence of the reaction in eq 15 as a decrease in the intensity of the $^{\bullet}\mathrm{NO_3}$ radical absorbance spectrum (Figure 3a, inset) upon the addition of 76 mM methanol. The $^{\bullet}\mathrm{NO_3}$ radical transient absorbance was directly observed at 640 nm (see Figure 3a). The rate of change of the decay of this radical was found to be of mixed first- and second-order. We therefore fitted these absorbances to the integrated rate equation[27]

$$\frac{A_0 k_{18}}{k_{18}\exp(k_{18}t) - 2A_0 k_{17}(1 - \exp(k_{18}t))} \tag{16}$$

where k_{17} corresponds to the self-combination of $^{\bullet}\mathrm{NO_3}$ radicals[28]

$$^{\bullet}\mathrm{NO_3} + {}^{\bullet}\mathrm{NO_3} \rightarrow \text{products} \quad k_{17} = 7.9 \times 10^{5}\ \mathrm{M^{-1}\ s^{-1}} \tag{17}$$

and k_{18} is the reaction of $^{\bullet}\mathrm{NO_3}$ with TBP

$$^{\bullet}\mathrm{NO_3} + \mathrm{TBP} \rightarrow \text{products} \quad k_{18} \tag{18}$$

By plotting the fitted first-order component against TBP concentration (Figure 3b), a second-order rate constant of $k_{18} = (4.3 \pm 0.7) \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}}$ was determined.

TABLE 1: Summary of Rate Constants (M^{-1} s^{-1}) Measured for the Reactions of Important Radicals Produced in Irradiated Aqueous Nitric Acid with TBP and DBP

	TBP	HDBP
$^\bullet$OH	$(5.00 \pm 0.05) \times 10^9$	$(4.40 \pm 0.13) \times 10^9$
$^\bullet$H	$(1.8 \pm 0.2) \times 10^8$	$(1.1 \pm 0.1) \times 10^8$
$^\bullet NO_3$	$(4.3 \pm 0.7) \times 10^6$	$(2.9 \pm 0.2) \times 10^6$
$^\bullet NO_2$	$<2 \times 10^5$	$<2 \times 10^5$

The only previous measurement of this rate constant was that of He et al.,[29] who used laser flash photolysis in mixed aqueous/acetonitrile ceric ammonium nitrate solution. A rate constant of 7.4×10^5 M^{-1} s^{-1} was reported at the lowest acetonitrile concentration of 0.146 mole fraction, about a factor of 2 slower than determined here. Comparison of that rate constant with that for the $^\bullet NO_3$ radical reaction with hexane,[30] 5.9×10^5 M^{-1} s^{-1}, again in acetonitrile, suggests that the $^\bullet NO_3$ radical reaction with TBP is one of oxidative hydrogen atom abstraction from a butyl group. For the analogous HDBP reaction:

$$^\bullet NO_3 + HDBP \rightarrow \text{products} \quad k_{19} \tag{19}$$

we found a slightly slower value than that for TBP of $k_{19} = (2.9 \pm 0.2) \times 10^6$ M^{-1} s^{-1} (see Figure 3b).

NO_2 Radical Reactions. The reaction with $^\bullet NO_2$ radical was measured in N_2O-sparged 0.1 M $NaNO_2$ solution, which quantitatively produces $^\bullet NO_2$ radicals through the reaction of hydroxyl radicals:[21]

$$^\bullet OH + NO_2^- \rightarrow OH^- + {}^\bullet NO_2 \quad k_{20} = 1.1 \times 10^{10}\ M^{-1}\ s^{-1} \tag{20}$$

The change in the decay of the $^\bullet NO_2$ transient absorbance was directly observed at 450 nm. However, there was no substantial change in the rate of decay even at the highest concentrations of TBP, or HDBP, and therefore we only report upper-limit rate constants of $<2 \times 10^5$ M^{-1} s^{-1} for both.

TBP Radiolysis Mechanism. Burr[10] proposed that HDBP was formed from the decay of the TBP radical

$$(C_4H_9O)_2({}^\bullet C_4H_8O)PO \rightarrow {}^\bullet C_4H_8{}^+ + (C_4H_9O)_2OPO^- \tag{21}$$

where the TBP radical is produced by hydrogen atom abstraction.[10] Subsequently, Khaikin[13] suggested that HDBP was also the stable product of dissolved oxygen addition to the TBP radical, to produce the TBP peroxyl radical:

$$(C_4H_9O)_2({}^\bullet C_4H_8O)PO + O_2 \rightarrow (C_4H_9O)_2P(O){-}O{-}(C_4H_8)OO^\bullet \tag{22}$$

A possible fate of this peroxyl radical is superoxide elimination, followed by hydrolysis to produce HDBP and butyraldehyde (also a measured product):[14]

$$(C_4H_9O)_2P(O){-}O{-}(C_4H_8)OO^\bullet \rightarrow O_2^{\bullet -} + [(C_4H_9O)_2P(O){-}O{-}(C_4H_8)]^+ \tag{23}$$

$$[(C_4H_9O)_2P(O){-}O{-}(C_4H_8)]^+ + H_2O \rightarrow (C_4H_9O)_2P(O){-}O^- + C_3H_7CHO + 2H^+ \tag{24}$$

Alternately, Wilkinson and Williams[12] proposed a mechanism for HDBP formation based upon the decomposition of the TBP radical cation, the product of direct TBP radiolysis:

$$(C_4H_9O)_3PO \rightsquigarrow e^-_{sol} + (C_4H_9O)_3PO^{\bullet +} \tag{25}$$

The radical cation product of eq 25 then undergoes intramolecular hydrogen bonding between the phosphoryl oxygen and a butoxy hydrogen atom, to form a six- or seven-membered ring structure. The ring species then decomposes to produce protonated HDBP and the butene radical, as shown in eq 26. Loss of the proton then creates HDBP, as shown in eq 27:[12]

$$(C_4H_9O)_3PO^{\bullet +} \rightarrow (C_4H_9O)_2P(OH)OH^+ + CH_2{=}CHCH^\bullet CH_3 \tag{26}$$

$$(C_4H_9O)_2P(OH)OH^+ \rightarrow (C_4H_9O)_2P(O)OH + H^+ \tag{27}$$

Canva and Pages[31] attempted to distinguish between free-radical and direct radiolysis HDBP production in irradiated TBP and concluded that the radical cation mechanism does occur in neat TBP. Since TBP is used at a process concentration of 30% by volume, direct radiolysis may play a role in real applications. To determine its extent, we next used our measured rate constants to calculate whether radical yields in the irradiated biphasic system are sufficient to explain TBP radiolysis without a direct radiolysis component.

The sources of $^\bullet$H atom are organic diluent radiolysis, which has been measured at 0.07 μmol J^{-1} for $C_6{-}C_{10}$ hydrocarbons[32] (γ-radiolysis) plus that produced from water radiolysis (0.06 μmol J^{-1} in eq 1) and the acidic conversion of the solvated electron yield (0.27 μmol J^{-1} in eq 1) in eq 2. However, the water radiolysis yields will be lower in aqueous nitric acid. To estimate the $^\bullet$H atom yield under these conditions, energy deposition due to radiolysis was assumed to be proportional to electron density. The yield was corrected accordingly.[33] The electron fraction of water (f_w) in aqueous nitric acid solution is calculated according to eq 28[33]

$$f_w = [(wt\%_w)(N_w)/M_w]/[(wt\%_w)(N_w)/M_w] + (1 - wt\%_w)(N_a/M_a) \tag{28}$$

where $wt\%_w$ is the weight percent water (0.81 for 3 M nitric acid), N_w is the number of valence electrons for water (8), M_w is the molecular weight of water (18), N_a is the number of valence electrons in nitric acid (24), and M_a is the molecular weight of nitric acid (63). The resulting electron fraction of water in 3 M nitric acid is 0.83. The $^\bullet$H atom yield would thus be $[0.83(0.06 + 0.27) + (0.07)] = 0.35$ μmol J^{-1}. This assumes that the aqueous electron yield in this highly acidic solution is equivalent to that of water at 0.27 μmol J^{-1}. The maximum value (assuming complete acid scavenging of all formed electrons, $G = 0.48$) would be 0.52 μmol J^{-1}. This will be discussed more later.

However, some of this $^\bullet$H atom yield will be scavenged by the alkane diluent. Assuming a $^\bullet$H atom reaction rate constant for the diluent to be that of hexane at 1.4×10^8 M^{-1} s^{-1},[24] and a mole ratio of approximately 4:1 dodecane:TBP in the 30% TBP process solvent, about 24% of produced $^\bullet$H atom will be available for the hydrogen abstraction reaction with TBP. Dissolved oxygen will also scavenge $^\bullet$H atoms; however, its low concentration in this system precludes any significant loss by this pathway. This results in a final yield for the H atom TBP reaction of $(0.24 \times 0.35) = 0.08$ μmol J^{-1}.

Next, assuming an irradiated volume of 1 L and unit density, with appropriate unit conversions the product of this yield and our measured rate constant gives a first-order rate for the $^\bullet$H and TBP reaction of 11.6 s^{-1} Gy^{-1}. If we assumed the full scavenged yield above, the corresponding value would be 17.2 s^{-1} Gy^{-1}.

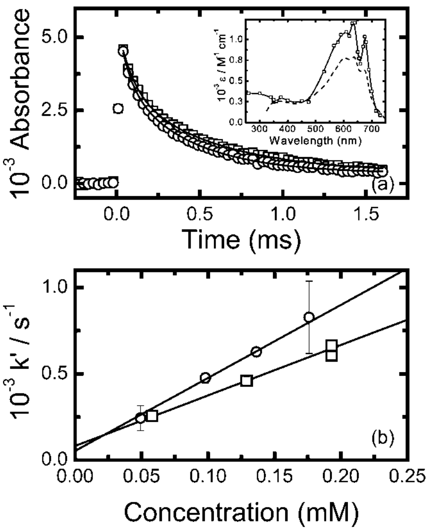

Figure 3. (a) Decay of $^{\bullet}NO_3$ radical absorbance at 640 nm for N_2O-saturated 6.0 M HNO_3 solution containing 49.3 (□) and 176.6 (○) μM TBP. Inset: Transient spectrum of $^{\bullet}NO_3$ radical in the absence (○) and presence (dashed line) of 76 mM methanol. (b) Second-order plots for $^{\bullet}NO_3$ radical reaction with TBP (○) and HDBP (□). Solid lines represent weighted linear fits, corresponding to reaction rate constants of $k_{18} = (4.3 \pm 0.7) \times 10^6$ and $k_{19} = (2.9 \pm 0.2) \times 10^6$ M^{-1} s^{-1}, respectively.

A similar analysis for the reaction of TBP with the $^{\bullet}OH$ radical suggests that hydrogen abstraction by that species will also occur under process conditions in competition with the diluent (7.7×10^9 L mol^{-1} s^{-1} for pentane)[21] and nitric acid (eq 15). It can be calculated that only 14% of $^{\bullet}OH$ radical will be available for reaction with TBP. This value must be further reduced on the basis of the electron fraction of water in 3 M nitric acid, resulting in a yield available for TBP reaction of 0.031 μmol J^{-1}, corresponding to a first-order rate of 155 s^{-1} Gy^{-1}.

The yield of $^{\bullet}NO_3$ radical in 3 M nitric acid is approximately 0.46 μmol J^{-1}.[26] Assuming that the rate constant for $^{\bullet}NO_3$ radical reaction with hexane[30] of 5.9×10^5 M^{-1} s^{-1} applies to the diluent, it may be calculated that 65% of $^{\bullet}NO_3$ radical, or 0.30 μmol J^{-1}, will be available for reaction with TBP, resulting in a first-order reaction rate of 1.3 s^{-1} Gy^{-1}. Thus, it can be seen that 92% of the radiolytic decomposition of TBP under process conditions is due to reaction with the $^{\bullet}OH$ radical and that the contribution from the $H^{\bullet}$ atom yield assumptions is not important.

The *G*-value for the radical-induced radiolysis of 30% TBP under process conditions can be estimated on the basis of this analysis. Assuming that the sum of the above yields reacts to convert TBP to HDBP, a maximum G_{HDBP} of 0.40 μmol J^{-1} is calculated. Many experimental HDBP yields have been reported in the literature, but only a few have been reported for irradiation of ~30% TBP in the presence of nitric acid. Those are in the range of 0.05−0.5 μmol J^{-1},[1,2,34–36] with only Blanco et al.[36] reporting a yield above 0.26 μmol J^{-1}. However, G_{HDBP} is reported to decrease with increasing absorbed dose,[1,14,16] probably since the rate constants for reaction with $^{\bullet}OH$, $^{\bullet}H$, and $^{\bullet}NO_3$ with HDBP are only slightly lower than those for TBP. Still, it can be seen that the maximum G_{HDBP} measured is similar to that calculated here on the basis of free radical hydrogen abstraction. Thus, on the basis of our kinetic data, it is not necessary to postulate the direct radiolysis TBP cation mechanism of HDBP formation in this system.

Conclusions

Electron pulse radiolysis techniques were used to evaluate reaction rate constants for the common radicals produced in irradiated aqueous nitric acid with the nuclear solvent extraction ligand TBP and its main degradation product HDBP. By comparison with reaction rates with *n*-alkanes, these radicals are believed to react by hydrogen atom abstraction from a TBP butyl group, resulting in a TBP carbon-centered radical that eventually produces HDBP. A maximum possible yield of HDBP was calculated on the basis of the yields of these radicals corrected for scavenging by the alkane diluents and for the electron fraction of water in aqueous nitric acid. This maximum yield is larger than actually measured, and thus it is not necessary to postulate any contribution to the HDBP yield through the direct radiolysis of TBP in the process solvent formulation.

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