

# $\alpha$ -Radiolysis of the Tributyl Phosphate–Hydrocarbon Diluent–Nitric Acid System

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**Abstract**— $\alpha$ -Radiolysis of tributyl phosphate in Sintin *n*-paraffin diluent in equilibrium with HNO<sub>3</sub> solutions at single “internal” irradiation from the extracted <sup>238</sup>Pu was studied. The radiation-chemical yields (molecules/100 eV) of butyl hydrogen phosphates (BHP), carboxylic acids, carbonyl compounds, and nitro compounds upon irradiation of 20% TBP in the treated Sintin in equilibrium with 3 M HNO<sub>3</sub> were 0.4 (at dibutyl hydrogen phosphate to monobutyl dihydrogen phosphate ratio HDBP : H<sub>2</sub>MBP = 4.3), 1.4, 0.2–0.3, and 0.2–0.3, respectively. The degradation and oxidation processes occur more deeply than under  $\gamma$ -irradiation. A simple volumetric method for determining carboxylic acids in the extract was developed. In the course of irradiation, the Pu(IV) oxidation state in the extract does not change, and its retention is due to the interaction with BHP at the ratio BHP : Pu = 2 in stripping with 0.02 M HNO<sub>3</sub> and BHP : Pu = 4 in stripping with Fe(II). The retention can be eliminated by the displacing action of Np(IV).

*Keywords:* tributyl phosphate, paraffin diluents,  $\alpha$ -radiolysis

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The modern technology for reprocessing NPP spent nuclear fuel (SNF) is based on the PUREX process. The solvent in the process is a 20–40% solution of tributyl phosphate in an inert diluent, most frequently in natural or synthetic saturated hydrocarbons (SHC) [1–4] of linear and/or branched structure. Irradiation of the solvent in contact with nitric acid solutions leads to the formation and accumulation of impurities deteriorating its hydrodynamic characteristics and selectivity. Therefore, the solvent is constantly regenerated within the extraction cycle by scrubbing with a sodium carbonate solution [1, 5], but some of the diluent degradation products are not removed in the process and are gradually accumulated in the solvent. The main components responsible for deterioration of the hydrodynamic characteristics of the solvent are hydrocarbon oxidation and nitration products. These compounds are acidic and in the course of regeneration by alkali treatment can form surface-active sodium salts [6] causing stable emulsification of the two-phase system. On the other hand, the major researchers’ attention is still focused on the formation of TBP radiolysis products and on the Pu oxidation state in the organic phase [7]. In

some other studies, the main investigation objects are polymerization products formed with the participation of diluent degradation products and/or gaseous products [8–10].

In reprocessing of SNF from NPP with thermal reactors, high radiation and chemical loads experienced by the solvent are mainly due to the action of the  $\beta$ -radiation of the fission products in the course of phase mixing and, to a lesser extent, of their  $\gamma$ -radiation in settling chambers of the contactors [4]. At expected transition to nuclear power generation using fast reactors, the content of well extractable  $\alpha$ -emitting Pu nuclides in SNF will increase by an order of magnitude [11], so that their action on the solvent will become comparable to that of the  $\beta, \gamma$ -radiation. On the other hand, the radiation-chemical yield of radiolysis products depends not only on the absorbed dose, but also on the linear energy transfer (LET) [12, 13]. Therefore, it is difficult to predict the result of the action of the “internal”  $\alpha$ -radiation on the solvent.

It should be additionally noted that today such studies are usually performed with external initiation of the

$\alpha$ -irradiation [14, 15]; otherwise, particular measures should be taken to ensure the radiation safety in experiments on “internal” irradiation by extractable actinides, with contamination of the measurement compartments of expensive scientific devices.

Available data mainly concern external manifestations of the consequences of such irradiation [16–18]. However, by the beginning of this study the influence of the irradiation (primarily  $\gamma$ -irradiation) conditions on the yield of radiolysis products has already been revealed [19, 20], which is very important for simulation of the industrial conditions with respect to both retention of radionuclides in the recycled solvent and correlation of the external manifestations of the radiolysis (hydrodynamic properties of the system, retention of radionuclides in the stripping step) with the composition of products of the radiation-chemical transformations of the extractant and diluent.

In this connection, a study performed at the Research Institute of Atomic Reactors by the joint group of researchers of that institute and the Khlopin Radium Institute for checking the suitability of the TBP–SHC solvent [21] for reprocessing irradiated Np with the aim of isolation and purification of  $^{238}\text{Pu}$  can be of interest. No detailed information on the radiation-chemical yields of radiolysis products of TBP and diluent in the course of  $\alpha$ -radiolysis under the conditions of extraction operations has been published up to now. The results obtained in that study are presented below.

The paper deals with the formation of products in the course of  $\alpha$ -radiolysis of TBP in the hydrocarbon diluent used at that time, Sintin (mixture of saturated  $\text{C}_8$ – $\text{C}_{15}$  hydrocarbons with a maximum at  $\text{C}_{11}$  after additional purification). Data on the retention of Pu by the irradiated solvent and on the cause of this effect are presented. The results obtained are compared with the available data [5, 6, 22, 23] on the radiation resistance of the TBP–diluent system subjected to  $\beta, \gamma$ -irradiation of different power with different particle energy.

## EXPERIMENTAL

### *Specific Features of the Experimental Procedures*

The experiments involved “internal irradiation” of the organic phase equilibrated with the corresponding aqueous phase, provided by the extraction of the required amount of the  $\alpha$ -emitter,  $^{238}\text{Pu}(\text{IV})$ , from the aqueous phase.  $^{238}\text{Pu}$  has a half-life of 88 years and is characterized by the mean  $\alpha$ -decay energy of ap-

proximately 5.45 MeV. The  $^{238}\text{Pu}$  concentration of  $1 \text{ mg mL}^{-1}$  ensures the dose rate of  $3.4 \times 10^{15} \text{ eV cm}^{-3} \text{ s}^{-1}$  ( $0.44 \text{ Gy s}^{-1}$ ). The experiments were performed with 90 mg of  $^{238}\text{Pu}$  (1.7 Ci), which was constantly regenerated for repeated use.

Because of the need for regenerating  $^{238}\text{Pu}$  and ensuring safety, the analyses were performed after Pu stripping. It was necessary to perform this operation without loss of the radiolysis products being analyzed. A single control experiment was performed without Pu stripping. To study the Pu stripping from the irradiated solvent, we performed a series of parallel experiments with the corresponding concentrations of  $^{239}\text{Pu}$  and butyl hydrogen phosphates.

High aerosol-generating ability of  $^{238}\text{Pu}$  preparations, caused by the recoil nuclei, severely complicates the analyses and other operations even compared to  $^{239}\text{Pu}$  solutions of equal activity and does not allow wide use of instrumental methods of the experiment and sample analysis because of inevitable contamination of the equipment.

### *Irradiation Conditions*

In the course of experiments, the dose rate was varied from  $3.4 \times 10^{15}$  to  $3.4 \times 10^{16} \text{ eV cm}^{-3} \text{ s}^{-1}$ . Up to 50 mg (0.9 Ci) of  $^{238}\text{Pu}$  was used in one experiment. The volume of the irradiated solution portions was 2.5–5 mL. The integral irradiation dose was in the range  $5 \times 10^{20}$ – $4 \times 10^{21} \text{ eV cm}^{-3}$  (70–550 kGy). A total of 27 “internal irradiation” experiments were performed.

### *Chemicals and Radionuclides*

**Plutonium-238.** The sample containing  $^{238}\text{Pu}$  was purified by anion exchange followed by twofold reprecipitation with ammonia, washing, and dissolution in 12 M  $\text{HNO}_3$  on heating. The resulting solution contained  $20 \text{ g L}^{-1} \text{ }^{238}\text{Pu}$  in the form of Pu(IV) at an  $\text{HNO}_3$  concentration of approximately 4–5 M. Also, recycled  $^{238}\text{Pu}$  solutions with a concentration of  $4 \text{ mg mL}^{-1}$ , obtained by reductive stripping from the solvent products, were used. These solutions were washed with the diluent (Sintin) to remove organophosphorus compounds and were then treated with crystalline  $\text{NaNO}_2$  at room temperature and kept in an open vessel for 24 h to remove nitrogen oxides.

In the course of the study, we performed several operations of the Pu regeneration by precipitation with

alkali on iron present in the solution, followed by dissolution in 12 M HNO<sub>3</sub>, extraction into 20% TBP in Sintin, stripping into 0.02 M HNO<sub>3</sub>, and preconcentration by precipitation with ammonia.

**Plutonium-239.** A nitric acid <sup>239</sup>Pu(IV) solution was purified by extraction into 20% TBP in Sintin, followed by stripping into water and evaporation in the presence of HNO<sub>3</sub>. The valence state was monitored by spectrophotometry.

**Inorganic chemicals.** Analytically and chemically pure grade chemicals, except Fe(NO<sub>3</sub>)<sub>2</sub>, were used in the study. Fe(NO<sub>3</sub>)<sub>2</sub> solutions were prepared by dissolving iron powder (reduced with hydrogen) in 2 M HNO<sub>3</sub> in the presence of hydrazine nitrate. Fresh Fe(II) solutions were prepared before each experimental series.

**TBP** was purified by washing with a 0.3 M KMnO<sub>4</sub> + 1 M KOH solution, followed by drying and vacuum distillation.

**Sintin** was repeatedly contacted with concentrated H<sub>2</sub>SO<sub>4</sub> at 60°C for 30 min and washed two times with a 1 M KOH solution and with water. The emulsion layer was discarded. The product obtained was free of unsaturated and oxygen- and sulfur-containing compounds.

**Monobutyl dihydrogen phosphate (H<sub>2</sub>MBP) and dibutyl hydrogen phosphate (HDBP).** Butyl hydrogen phosphates (BHP) were synthesized according to [24] and purified according to [25].

**Organic chemicals.** Benzene, carbon tetrachloride, acetone, cyclohexanone, pyridine, methanol, ethanol, and nitrodecane, used in the analyses, were purified by standard procedures. Methanol was treated with 2,4-dinitrophenylhydrazine to remove carbonyl compounds prior to distillation.

### *Experimental Procedures*

**Extraction.** The extraction and stripping were performed in a small one-step glass contactor with stirring and subsequent settling. The Pu extraction in most cases was performed with 20% TBP in Sintin. The amount of BHP in the initial solvent was taken into account in accordance with the analysis results, or BHP were removed by scrubbing the solvent with a 1 M NaOH solution.

To ensure the complete recovery of Pu in oxidation state +4, we performed four or five successive contacts

( $m = 4-5$ ). The volume ratio of the organic and aqueous phases  $n$  was chosen so as to obtain the preset Pu concentration after combining the organic phases. The combined solvent phase was washed with 3 M HNO<sub>3</sub> at  $n = 5$  for its conditioning with respect to HNO<sub>3</sub>.

The distribution coefficient of both <sup>238</sup>Pu and <sup>239</sup>Pu between 20% TBP in Sintin and 3 M HNO<sub>3</sub> was 5–6 at the solvent loading with Pu lower than 12%, which is consistent with published data [26].

The dose rate was calculated from the Pu amount in the organic phase minus the Pu amount (2.5–3.5%) that passed into the above-indicated scrubbing solution.

In some cases, when it was necessary to vary the composition of the organic phase, the extraction was performed with 100% TBP with the subsequent scrubbing with 3 M HNO<sub>3</sub>, after which the organic phase was diluted with the calculated amount of Sintin and TBP containing the known amount of HNO<sub>3</sub>.

**Irradiation.** In most cases, the Pu-containing organic phase sample was left for the required time in a glass test tube. In the case of radiolysis in the two-phase system, the scrubbing solution remained in contact with the organic phase throughout the irradiation period. Irradiation occurred at a free access of air into the test tube through a narrow tube. No appreciable self-heating of the solutions was observed under the conditions of the experiments.

**Stripping.** Depending on the goals of the experiment, stripping was performed into aqueous solutions containing 0.02 M HNO<sub>3</sub>, 0.1 M Fe(NO<sub>3</sub>)<sub>2</sub> + 0.1 M N<sub>2</sub>H<sub>5</sub>NO<sub>3</sub> + 2 M HNO<sub>3</sub>, or 0.5 M Na<sub>2</sub>CO<sub>3</sub>. As a rule, stripping was performed into the reductant solution ( $m = 4$  at  $n = 2-3$ ). The phase contact time ( $\tau$ ) was 1–1.5 min. Both phases were analyzed.

### *Analysis*

In our experiments, we used methods of organic micro- and semimicroanalysis with sequential determination of several products from one aliquot by adapted procedures.

**BHP (HDBP, H<sub>2</sub>MBP).** The BHP content was determined by the improved photometric method [27] in the blue region of the spectrum after converting BHPs into the phosphovanadatomolybdate complex. The accuracy of the method was 5–10%. The minimum determinable amount was 1.5  $\mu$ mol of any BHP.

**Table 1.** Determination of butyl hydrogen phosphates in the presence of Pu

Reductive stripping conditions		Preset concentration, mM				Found, mM		
<i>m</i>	<i>n</i>	Pu	HDBP	H <sub>2</sub> MBP	HDBP/H <sub>2</sub> MBP	HDBP	H <sub>2</sub> MBP	HDBP/H <sub>2</sub> MBP
No stripping		4	12.2	2.8	4.3	11.6	2.7	4.3
No stripping		10	12.2	2.8	4.3	11.7	2.5	4.7
3	2	4	12.2	2.8	4.3	12.3	1.8	6.9
3	2	10	8.1	1.9	4.3	8.1	1.2	6.7
3	2	10	16.2	3.8	4.3	15.2	1.8	8.7
3	4	10	6.1	1.4	4.3	6.4	1.2	5.2
3	2	0	12.2	2.8	4.3	10.4	0.9	11.6

**Table 2.** Titration of organic acids with 0.01 M KOH in pyridine–acetone (1 : 1). Initial solutions of acids in paraffins. Volumes: sample 1, medium 5 mL

Acid	Concentration, mM	Taken for analysis, $\mu$ mol	Found, $\mu$ mol				Final error of visual determination, %
			visually with indicator			potentiometrically, – BS <sup>a</sup>	
			Bromocresol Purple	thymolphthalein			
				directly	– BS <sup>a</sup>		
Blank sample	–	–	5.0	4.2	0	0.8	–
Palmitic	22.0	44	–	47.2	43.0	–	–2.3
	19.5	22	–	27.0	22.8	–	+3.6
	19.5	19.5	25.0; 27.0	23.6; 23.3	19.4; 19.1	20.0; 19.0	–0.5; +2.0
Caproic	28.0	14.0	–	17.5	13.3	–	–5.0
		28.0	–	32.8	28.6	–	+2.1
HDBP	6.1	6.1	6.0	10.33	6.13	–	+0.5
HDBP + palmitic	6.1 + 16.0	22.1	6.2	–	22.3	–	+1
Average							$\pm 2.2$

<sup>a</sup> Minus data for the blank sample.

The determination of HDBP and H<sub>2</sub>MBP in the presence of Pu in the organic phase at reductive Pu stripping deserves separate discussion. As follows from Table 1, the presence of Pu does not interfere with the direct determination of BHP. A minor fraction of H<sub>2</sub>MBP passes into the aqueous phase, with no appreciable loss of HDBP. Without Pu, 70% of H<sub>2</sub>MBP and 10–15% of HDBP are lost in the course of stripping into the Fe(II) solution. For H<sub>2</sub>MBP to be retained in the organic phase, the Pu concentration in it prior to stripping should exceed the total BHP concentration. Higher accuracy of the analysis is favored by an increase in the phase volume ratio  $n = O : W$  to 3–4 at the number of stripping operations  $m = 2$ –3 (see below).

**Carboxylic acids.** Higher carboxylic acids (HCA) are still the most difficult-to-analyze radiolysis products, including analysis with instrumental methods (GLC, IR spectroscopy [5, 6]). We have specially de-

veloped a procedure for their determination in the presence of BHP by titration in a pyridine–acetone medium (1 : 1) with 0.1 or 0.01 M aqueous KOH solution using thymolphthalein as indicator against the yellowish background of the irradiated organic phase. The results are given in Table 2. As can be seen, in determination of low HCA concentrations it is necessary to take into account the alkali consumption for the blank sample. The accuracy of the titration with 0.01 M KOH is 5%.

To remove HNO<sub>3</sub> from the organic phase, the irradiated organic phase sample was scrubbed with water to neutral reaction prior to titration. The HDBP amount remaining in the sample was determined from the difference between the amounts of BHP in the organic phase and aqueous extract. The limited volume of the irradiated organic phase did not allow direct determination of HDBP in the scrubbed organic phase. On the whole, the uncertainty of HCA determination was 10% on the average.

**Table 3.** Influence of the irradiation conditions on the formation of the radiolysis products.  $^{238}\text{Pu}$  concentration in the organic phase  $10\text{ g L}^{-1}$ , experiment time 21 h, sample volume 2.0 mL (integral dose  $2.5 \times 10^{21}\text{ eV cm}^{-3}$ , or 350 kGy)

Irradiated system	Product concentration, mM					
	$\Sigma\text{BHP}$	HDBP/H <sub>2</sub> MBP	carboxylic acids	carbonyl compounds	carboxylic acids + carbonyl compounds	nitro compounds
Single-phase	16.4	4.6	70	18	88	8.5
	16.4	4.2	80	8	88	–
Two-phase settled	17.1	4.0	59	17	78	6.3
	16.6	–	61	10	71	9.2
Two-phase disperse	17.0	4.7	86	10	96	6.4
	16.4	–	59	15	74	7.9
Average	$16.6 \pm 0.3$	$4.4 \pm 0.3$	$70 \pm 10$	$13 \pm 3$	$82 \pm 8$	$7.8 \pm 1.0$
Yield, molecules/100 eV	0.40	$4.4 \pm 0.3$	1.7	0.3	2.0	0.2
Mean error, %	2	7	14	23	10	13

**Carbonyl compounds** were determined by colorimetry in the form of 2,4-dinitrophenylhydrazones; the sample was prepared as described in [28]. To exclude occasional outliers, analyses were performed with a replicate sample, and each series included a reference sample and a blank sample of the unirradiated solvent. The uncertainty was 10–20%.

**Nitro compounds.** Analysis was performed after BHP stripping in accordance with the improved procedure [28] by conversion of the nitro compounds into *aci* form salts via the reaction with an aqueous-alcoholic KOH solution, followed by spectrophotometry of the iron complex in benzene after its extraction from an acetic acid solution at  $\lambda = 480\text{ nm}$  in a 20-mm-thick cell. The sensitivity of the method was 1.5 mM, and the determination accuracy was 10–15%.

**Other components.** We performed several determinations of alcohols by spectrophotometry of the product of their reaction with 3,5-dinitrobenzoyl chloride in acetone in accordance with [28]. Qualitative analysis for hydroxamic acid was performed by colorimetry of the crimson-red iron complex of the acid [28].

**UV absorption.** To remove Pu and HNO<sub>3</sub>, an irradiated organic phase sample was diluted by a factor of 100, washed with water and sodium carbonate solution, and acidified with a drop of concentrated HCl. The spectrum was measured using 10-mm-thick quartz cells with a ground-quartz stopper.

**Spectrophotometry of the irradiated solvent containing Pu.** We performed a series of experiments on measuring the spectrum of the irradiated solvent that contained about 10 mM  $^{238}\text{Pu}$  in the interval 400–

1400 nm. We also recorded the spectra of model solutions that contained the corresponding amounts of HDBP, H<sub>2</sub>MBP, and  $^{239}\text{Pu}$ .

**Radiometric determination of Pu.** Neutral, sodium carbonate, and acidic reducing Pu solutions were sequentially diluted with 1.5 M HNO<sub>3</sub>. Because of multiple dilution, the presence of salts in the initial sample did not play a significant role. The radiometric determination of Pu in the organic phase was performed mainly by Pu stripping into a 0.5 M Na<sub>2</sub>CO<sub>3</sub> solution after dilution of the organic phase aliquot with Sintin. The strips were combined and analyzed as described above for aqueous solutions. The  $\alpha$ -counting was performed on a scintillation installation.

## FORMATION OF RADIOLYSIS PRODUCTS

### *Irradiation of 20% TBP Solution in Sintin*

Table 3 shows how the irradiation conditions influence the formation of radiolysis products. As can be seen, the irradiation in both single-phase and two-phase (settled and disperse) systems leads to essentially similar results. This is due to the fact that the aqueous phase is subjected to relatively weak irradiation (97% of the  $\alpha$ -emitter is in the organic phase). The results obtained also indicate that, even at the highest dose rate used in this study,  $3.4 \times 10^{16}\text{ eV cm}^{-3}\text{ s}^{-1}$  ( $4.6\text{ Gy s}^{-1}$ ), the oxygen diffusion occurs at sufficient rate and does not affect the results. Therefore, all the subsequent studies were performed with single-phase organic systems.

It also follows from Table 3 that the reproducibility of the TBP decomposition products was  $\pm 3\%$  for the

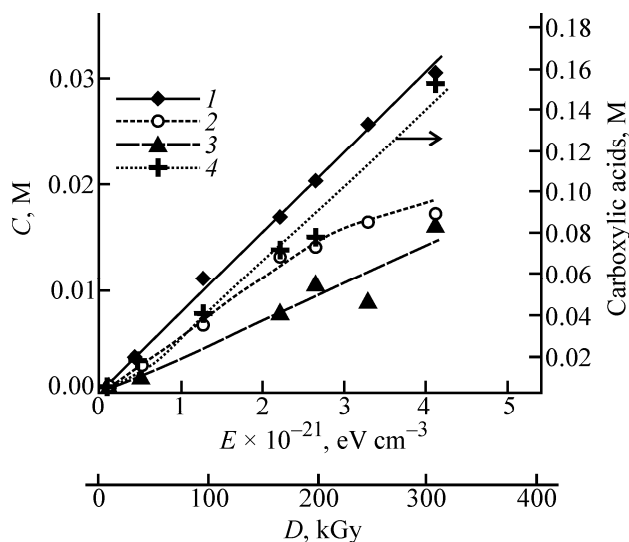
**Table 4.** Yield of radiolysis products at different dose rates of  $\alpha$ -irradiation of a 20% TBP solution in Sintin, equilibrated with 3 M HNO<sub>3</sub>

<sup>238</sup> Pu concentration, mM	Dose rate $\times 10^{-15}$ , eV cm <sup>-3</sup> s <sup>-1</sup>	Integral dose $\times 10^{-21}$ , eV cm <sup>-3</sup>	Yield of radiolysis products $G$ , molecules/100 eV				
			$\Sigma$ BHP	HDBP/H <sub>2</sub> MBP	carboxylic acids	carbonyl compounds	nitro compounds
0.4	3.4	1.5	0.45	4.4	1.65	0.29	0.20
0.8	6.8	3.7	0.43	4.1	-	0.16	0.15
1	8.2	3.0	0.40	5.0	1.55	0.28	0.22
1	8.2	4.6	0.38	-	1.95	0.20	0.21
4	34	0.5	0.42	3.8	1.75	0.30	-
4	34	2.5	0.39	4.4	1.8	0.30	0.17
Average			0.41	4.3	1.75	0.26	0.19

sum of alkyl hydrogen phosphates and  $\pm 10\%$  for their ratio, and for Sintin radiolysis products it was  $\pm 10$ – $15\%$ , which is acceptable for such studies.

Figure 1 shows the dependence of the concentration of the radiolysis products on the integral dose for 20% TBP in Sintin, equilibrated with 3 M HNO<sub>3</sub> (HNO<sub>3</sub> concentration in the organic phase 0.42 M). It follows from these data that the yield of the radiolysis products remains almost constant in the interval of integral doses from  $5 \times 10^{20}$  to  $4 \times 10^{21}$  eV cm<sup>-3</sup>. The yield of carbonyl compounds somewhat decreases at doses higher than  $3 \times 10^{21}$  eV cm<sup>-3</sup>, whereas the yield of carboxylic acids, apparently, somewhat increases. As seen from Table 4, the dose rate does not influence the formation of radiolysis products either.

Thus,  $\alpha$ -irradiation of a 20% TBP solution in Sintin



**Fig. 1.** Concentration of radiolysis products as a function of the integral dose of irradiation of the 20% TBP–Sintin–0.4 M HNO<sub>3</sub> system. (1) BHP, (2) carbonyl compounds, (3) nitro compounds, and (4) carboxylic acids.

in the presence of HNO<sub>3</sub> and air results in formation of products in the following amounts (per 100 eV of the absorbed energy): 0.41 BHP molecule at the HDBP : H<sub>2</sub>MBP ratio of 4.3, two molecules of the sum of the oxidation products with the prevalence of carboxylic acids (85–90%) over carbonyl compounds, and 0.2 molecule of nitro compounds.

The UV spectra of the irradiated solvent are characterized by a strong absorption band at 355–365 nm, an absorption minimum at 340 nm, and a sharp decrease in the absorption intensity to 400 nm. Strong absorption is observed at  $\lambda < 320$  nm. At similar measurement conditions, the absorption intensity is approximately proportional to the dose. The position of the band near 360 nm corresponds to nitrites [29], but the intensity of this band, taking into account the extinction coefficient that we measured for isoamyl nitrite in 20% TBP in Sintin ( $50 \text{ L mol}^{-1} \text{ cm}^{-1}$  at  $\lambda = 356 \text{ nm}$ ), corresponds to unrealistically high nitrite yields (more than 20–50 molecules per 100 eV). Apparently, the absorption should be attributed to the formation of an unknown radiolysis product exhibiting (itself or as a complex with Pu) a highly intense absorption band. As the absorption intensity and HNO<sub>3</sub> concentration vary in opposite directions (see below), this species does not contain nitrogen atoms.

Episodic analyses showed that virtually no hydroxamic acids were formed upon single irradiation of the solvent. The yield of alcohols can be estimated at  $\sim 0.1$  molecule per 100 eV.

#### *Irradiation of Solutions with Variable TBP Content*

Data on the formation of radiolysis products upon irradiation of systems with the TBP content varied in the interval 10–100% are given in Table 5. The HNO<sub>3</sub>

**Table 5.** Yield of radiolysis products at different TBP concentrations. Dose  $1.4 \times 10^{21}$  eV cm<sup>-3</sup>, initial organic phase contains 0.32 M HNO<sub>3</sub>

Radiolysis products	Yield <i>G</i> , molecules/100 eV, at indicated TBP concentration, %					
	10	20	30 (calculation)	50	75	100
ΣBHP	0.22	0.41	0.62	0.88	1.75	1.95
HDBP/H <sub>2</sub> MBP	4.5	4.4	4.2	3.9	3.7	3.0
Carboxylic acids	1.75	1.70; 1.65	1.4	0.85	0.6	1.7
Carbonyl compounds	0.3	0.25	0.28	0.30	0.05–0.1	0.3
Nitro compounds	0.25	0.2	0.17	0.12	0.1	–
<i>D</i> at 360 nm <sup>a</sup>	130	–	105	85	200	15

<sup>a</sup> Measured optical density (cell thickness 10 mm) multiplied by the dilution factor of 100; the same in Tables 6 and 12.

**Table 6.** Influence of the HNO<sub>3</sub> concentration on the radiolysis of the 50% TBP–Sintin system. Dose  $1.4 \times 10^{21}$  eV cm<sup>-3</sup>

Radiolysis products	Yield <i>G</i> , molecules/100 eV, at indicated HNO <sub>3</sub> concentration in organic/aqueous phase, M			
	0.16/0.5	0.32/1.0	0.9/2.5	1.6/5.0
ΣBHP	0.91	0.88	0.87	0.89
HDBP/H <sub>2</sub> MBP	4.4	3.9	4.9; 5.1 <sup>a</sup>	5.2
Carboxylic acids	0.7	0.85	1.15	1.75
Carbonyl compounds	0.30	0.25	0.25	0.20
Nitro compounds	0.05	0.12	0.17	0.5
<i>D</i> at 360 nm	85	70	52	21

<sup>a</sup> Determination of butyl hydrogen phosphates without Pu stripping.

concentration in the organic phase was 0.82 M in all the cases, and the irradiation dose was  $1.4 \times 10^{21}$  eV cm<sup>-3</sup> at a dose rate of  $3.4 \times 10^{15}$  eV cm<sup>-3</sup> s<sup>-1</sup>. As seen from the table, the BHP yields increase in proportion with the TBP concentration in its interval 0–100%. The yields of carboxylic acids and nitro compounds linearly decrease in this interval. A sharp increase in the yield of carboxylic acids in the region of 100% TBP is most probably due to the formation of butyric acid. The HDBP : H<sub>2</sub>MBP ratio slowly decreases in the TBP concentration interval 10–75% and then sharply decreases to 3.0 for 100% TBP. The yield of carbonyl compounds varies only slightly. The UV extinction depends in a complex fashion on the TBP concentration.

#### *Influence of the Concentration of HNO<sub>3</sub> and Nitrogen Oxides*

To study the influence exerted by the HNO<sub>3</sub> concentration, we chose the 50% TBP–Sintin system in which the HNO<sub>3</sub> concentration could be varied from 0.16 to 1.6 M. The results are given in Table 6. As can be seen, with increasing HNO<sub>3</sub> concentration the yield of nitro compounds and carboxylic acids linearly in-

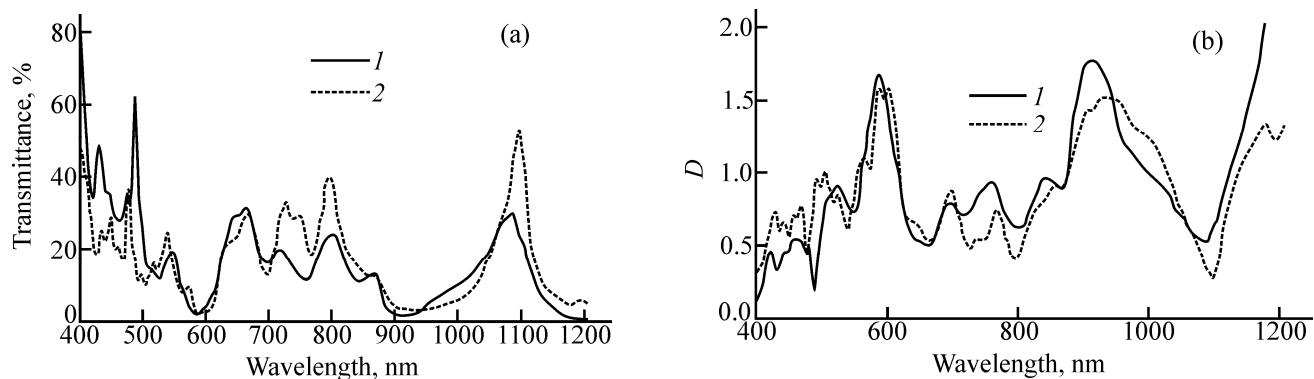
creases, but for carboxylic acids the dependence does not pass through the origin. The light absorption at  $\lambda = 360$  nm decreases with increasing HNO<sub>3</sub> concentration.

The yield of BHP and their ratio remain constant. This is also confirmed by the experiment with direct determination of the acids without Pu stripping. The yield of carbonyl compounds also remains essentially constant.

We performed two experiments with aqueous solutions from which Pu was extracted with a 20% TBP solution 1 h after adding 10 g L<sup>-1</sup> NaNO<sub>2</sub>. In this case, irradiation to small doses (up to  $5 \times 10^{20}$  eV cm<sup>-3</sup>) led to an increase in the yield of carboxylic acids to 2.2 and of nitro compounds to 0.8 against 1.7 and 0.2 molecules/100 eV, respectively. The yields of BHP and carbonyl compounds did not change noticeably.

#### STATE OF Pu IN THE ORGANIC PHASE UPON IRRADIATION

Figures 2 and 3 show the absorption spectra of the <sup>238</sup>Pu and <sup>239</sup>Pu solutions without irradiation and of <sup>238</sup>Pu solutions irradiated to a dose of  $3.7 \times 10^{21}$  eV cm<sup>-3</sup>. The spectra of the model solutions con-



**Fig. 2.** Combined (a) original and (b) processed absorption spectra of an 8 mM solution of  $^{238}\text{Pu}$  in 20% TBP-Sintin (1) before irradiation and (2) after self-irradiation to a dose of  $3.7 \times 10^{21} \text{ eV cm}^{-3}$ . Layer thickness 1 cm.

taining  $^{239}\text{Pu}$  and the corresponding amounts of BHP are also shown. As follows from comparison of these spectra, irradiation does not lead to the appearance of new absorption bands that could suggest the presence of Pu in oxidation states +3 and +6.

Irradiation of the organic solution leads to changes in the intensity and to certain changes in the shape of the Pu absorption bands. The characteristic band at 490 nm is shifted to shorter wavelengths (482 nm) and drastically decreases in the intensity. The band at 550 nm is also blue-shifted (by 8 nm), but without appreciable change in the intensity. The band at approximately 660 nm does not change its position and peak intensity, but changes the shape. The bands at 790 and 1080 nm appreciably increase in the intensity without noticeable changes in the positions. Such a change in the band intensity occurs on introducing BHP (the most significant changes at the Pu : BHP ratios in the range 0.6–1.8) into the unirradiated organic phase containing Pu(IV). The results obtained show that the changes in the Pu spectrum upon irradiation of the solvent are associated with the accumulation of acidic products of TBP radiolysis with preservation of the Pu(IV) oxidation state.

### $^{238}\text{Pu}$ STRIPPING FROM THE IRRADIATED SOLVENT

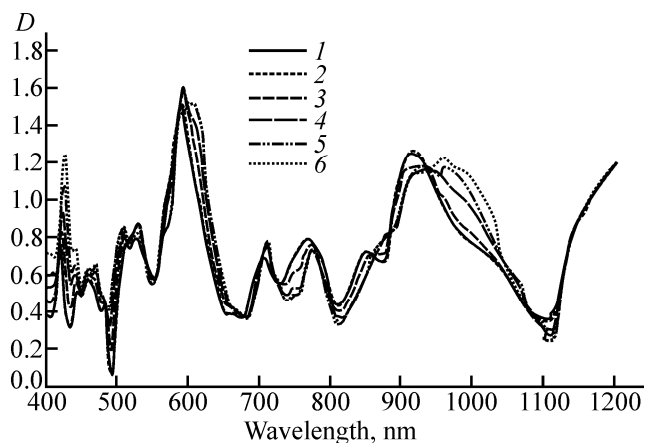
#### *Reductive Stripping*

A hydrazine solution without Fe(II) does not strip Pu at 25°C. Therefore, to find the best stripping conditions, we performed experiments with a model solvent product using a solution containing 0.1 M  $\text{Fe}(\text{NO}_3)_2$  + 0.1 M  $\text{N}_2\text{H}_5\text{NO}_3$  + 2 M  $\text{HNO}_3$  at the phase ratio  $n \sim 2$ , phase contact time  $\tau \sim 1$  min, number of steps  $m = 3$ ,

and initial  $^{239}\text{Pu}$  concentration of  $2.4 \text{ g L}^{-1}$  (10 mM), and also at the initial  $^{238}\text{Pu}$  concentration of  $8 \text{ g L}^{-1}$  and  $m = 5$  (Table 7). We also examined the dependence of stripping on the phase contact time (Fig. 4).

As follows from these data, at a contact time of 1 min and relatively low BHP concentration, Pu is retained in the organic phase by BHP at the BHP : Pu ratio of approximately 4, i.e., predominantly in the form of the Pu salt with HDBP. However, as the concentration of the sum of BHP increases, the Pu retention increases to the BHP : Pu ratio of 3.2–3.5, i.e.,  $\text{H}_2\text{MBP}$  gradually (nonlinearly) increases its effect as dibasic acid.

More attentive consideration of this effect (Fig. 4) shows that, in the course of the first contact, the degree of the Pu stripping is relatively low and is limited to the BHP : Pu ratio of 2 virtually irrespective of the phase contact time. However, in subsequent contacts,



**Fig. 3.** Absorption spectra of  $^{239}\text{Pu}$  (12 mM) in 20% TBP-Sintin solvent with BHP added in concentration, mM: (1) 0, (2) 5, (3) 10, (4) 16, (5) 20, and (6) 40.

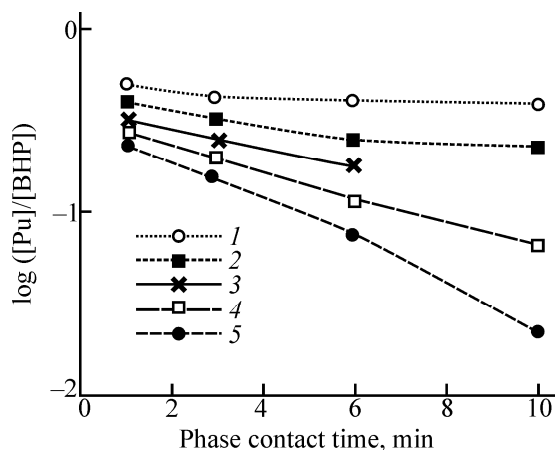


**Table 7.** Reductive stripping of  $^{239}\text{Pu}$  at its different initial concentrations from 20% TBP in Sintin containing BHP (HDBP :  $\text{H}_2\text{MBP} = 4.3$ ). Stripping solution: 0.1 M  $\text{Fe}(\text{NO}_3)_2$  + 0.1 M  $\text{N}_2\text{H}_5\text{NO}_3$  + 2 M  $\text{HNO}_3$ ,  $n = 2$ ,  $\tau = 1$  min

Step no.	Pu concentration in the aqueous phase ( $\text{mg L}^{-1}$ ) in stripping steps at indicated initial Pu concentration and $\Sigma\text{BHP}$ concentration			
	2400 $\text{mg L}^{-1}$ Pu		8000 $\text{mg L}^{-1}$ Pu	
	3 mM $\Sigma\text{BHP}$	10 mM $\Sigma\text{BHP}$	10 mM $\Sigma\text{BHP}$	40 mM $\Sigma\text{BHP}$
1	3730	2520	5600	4700
2	530	530	5020	2750
3	250	320	3100	1350
4	–	–	750	800
5	–	–	330	470
$0.5\Sigma[\text{Pu}]$	2255	1685	7400	5030
$\Delta\text{Pu}(\text{org})$ , calculation	145	715	600	2970
Pu(org) in fifth step	165	680	730	3000
$\Sigma\text{BHP}/\text{Pu}(\text{org})$	4.3	3.5	3.3	3.2

**Table 8.** Effect of Np(IV) on the reductive stripping of  $^{239}\text{Pu}$  from 20% TBP in Sintin, containing 10 mM BHP, 0.4 M  $\text{HNO}_3$ , and 10 mM  $^{239}\text{Pu}$  (2400  $\text{mg L}^{-1}$ ). Stripping solution: 0.1 M  $\text{Fe}(\text{NO}_3)_2$  + 0.1 M  $\text{N}_2\text{H}_5\text{NO}_3$  + 2 M  $\text{HNO}_3$  + 4 mM (9600  $\text{mg L}^{-1}$ ) Np(IV) or without Np;  $n = 2$ ,  $m = 5$ 

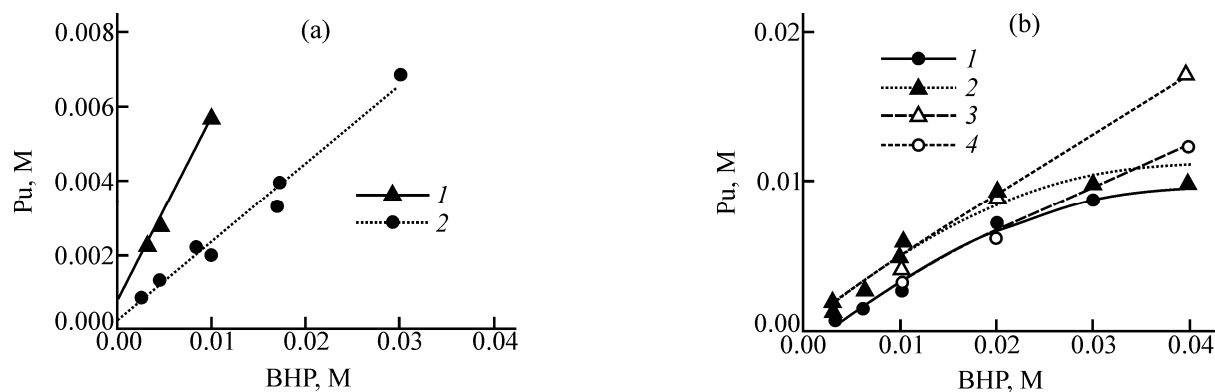
Step no.	Pu concentration in aqueous phase, $\text{mg L}^{-1}$ , at indicated $\tau_{\text{mix}}$ , min			
	without Np		in the presence of Np	
	1	6	1	6
1	2520	2900	1300	1700
2	530	770	1500	2100
3	300	370	810	920
4	210	320	640	210
5	160	190	330	20
$0.5\Sigma[\text{Pu}]$	1860	2280	2300	2470
$\Delta\text{Pu}(\text{org})$ , calculation	650	220	200	30
Pu(org) in fifth step	570	170	200	50
$\Sigma\text{BHP}/\text{Pu}(\text{org})$	4.2	14	12	40

**Fig. 4.** Logarithm of the Pu to  $\Sigma\text{BHP}$  concentration ratio in reductive stripping steps (indicated as numerals at curves) as a function of the phase contact time (the initial solvent presumably contained 2400  $\text{mg L}^{-1}$   $^{239}\text{Pu}$ ). Reducing solution composition 0.1 M  $\text{Fe}(\text{NO}_3)_2$  + 0.1 M  $\text{N}_2\text{H}_5\text{NO}_3$  + 2 M  $\text{HNO}_3$ ,  $n = 2$ .

this ratio is overcome to a greater extent, the longer is the time and the larger is the number of contacts. Ultimately, the BHP : Pu ratio of 50 can be reached. This may be due not only to slow reduction of Pu with Fe(II) at the phase boundary, but also to simultaneous slow displacement of Pu with Fe(III) accumulated in side reactions, because, as shown in later studies [30], Fe(III) forms stable salts with alkyl hydrogen phosphates.

This assumption is indirectly confirmed by the effect of Np(IV) on the reductive stripping of Pu (Table 8). In the presence of Np(IV), the stripping is less efficient in the first two steps than the stripping performed with Fe(II) solutions without Np. However, in the subsequent steps the efficiency of this process appears to be considerably higher, and considerably lower amount of Pu is retained in the organic phase.

Figure 5a (curve 1) shows the dependence of the



**Fig. 5.** Retention (a) of <sup>238</sup>Pu in the irradiated solvent and (b) of <sup>239</sup>Pu in the model solvent in the course of stripping as a function of the BHP concentration. Stripping solution: (1) 0.1 M Fe(NO<sub>3</sub>)<sub>2</sub> + 0.1 M N<sub>2</sub>H<sub>5</sub>NO<sub>3</sub> + 2 M HNO<sub>3</sub> (for conditions, see text); (2) 0.02 M HNO<sub>3</sub>; (3, 4) as for 1 and 2, respectively, with additional introduction of palmitic acid into the model solvent in a concentration equal to 4.2ΣBHP.

<sup>238</sup>Pu retention in the organic phase on the total BHP concentration. As can be seen, the concentration of Pu retained in the irradiated organic phase after stripping with Fe(II) is a linear function of the total BHP concentration and amounts to 1/4 of the latter. The corresponding model experiments with organic phases containing <sup>239</sup>Pu and BHP demonstrate the maximum ratio, 1 : 3.5 (Fig. 5b, curve 1). On adding excess palmitic acid, this limit disappears, the line becomes straight, and complete analogy with the <sup>238</sup>Pu stripping is reached.

The <sup>238</sup>Pu distribution between the stripping steps is shown in Table 9. As can be seen, the major fraction of Pu is transferred in the first two or three steps, after which the stripping from the irradiated solvent continues with low efficiency, similarly to the model organic phase (Table 7; Figs. 4, 5). The <sup>238</sup>Pu stripping from the irradiated solvent is virtually independent of the acidity of the stripping solution.

No problems with mixing or phase separation were observed in reductive stripping performed both with the real irradiated solvent and with model solutions.

Data on the <sup>238</sup>Pu stripping from the irradiated solvent into a 0.02 M HNO<sub>3</sub> solution (*n* = 1) are given in Table 10. As can be seen, the stripping occurs practically only in the first two steps. The Pu retention in the organic phase in the process is determined by the formal ratio BHP : Pu = 1.6 (Fig. 4, curve 1).

The corresponding studies with model solutions showed that, in the presence of BHP only, the Pu retention was determined by the Pu : BHP ratio of 1 : 2.2. On adding palmitic acid to the solvent in an

amount corresponding to the formation of carboxylic acids in the course of radiolysis (4 times larger compared to BHP), the irreversible retention of Pu was characterized by the Pu : BHP formal ratio of 1 : 1.7, which is consistent with the actually observed pattern.

In multistep stripping into weakly acidic solutions, the organic phase became turbid, and at high irradiation doses (of the order of 1.5 × 10<sup>21</sup> eV cm<sup>-3</sup>) a colloid suspended in the organic phase formed. In this case, the phase separation became appreciably worse.

**Table 9.** Reductive stripping of <sup>238</sup>Pu from the irradiated solvent. Dose 1.4 × 10<sup>21</sup> eV cm<sup>-3</sup>; *n* = 1, *m* = 6; τ = 3 min. Initial <sup>238</sup>Pu concentration in the organic phase 2500 mg L<sup>-1</sup>. Stripping solution: 0.1 M Fe(NO<sub>3</sub>)<sub>2</sub> + 0.1 M N<sub>2</sub>H<sub>5</sub>NO<sub>3</sub> + 2 M HNO<sub>3</sub>

Run no.	<sup>238</sup> Pu concentration in the organic phase in indicated stripping step, mg L <sup>-1</sup>					
	1	2	3	4	5	6
1	1500	410	270	120	85	90
2	–	–	320	–	–	120

**Table 10.** Sequential stripping of <sup>238</sup>Pu from the irradiated solvent into 0.02 M HNO<sub>3</sub> and 0.5 M Na<sub>2</sub>CO<sub>3</sub>. Dose 1.4 × 10<sup>21</sup> eV cm<sup>-3</sup>; *n* = 1, *m* = 6; τ = 3 min. Initial <sup>238</sup>Pu concentration in the organic phase 2500 mg L<sup>-1</sup>

Stripping agent	<sup>238</sup> Pu concentration in the aqueous phase in indicated stripping step, mg L <sup>-1</sup>						ΣPu(aq)
	1	2	3	4	5	6	
HNO <sub>3</sub>	640	350	60	40	20	20	1130
Na <sub>2</sub> CO <sub>3</sub>	450	350	350	150	70	20	1390
Total							2520

Partial transfer of BHP to the organic phase was observed. However, these phenomena were not studied in detail.

#### *Stripping into Solutions of Complexing Agents and Sodium Carbonate*

We attempted to strip Pu that is retained in the irradiated solvent in the course of stripping into water or Fe(II) solution by using complexing agents. We tested the following stripping solutions: Na<sub>2</sub>EDTA in 0.02 M HNO<sub>3</sub>, 1 M CH<sub>3</sub>COOH in the presence of 0.1 M HNO<sub>3</sub>, and Fe(II) in 1 M CH<sub>3</sub>COOH with a small amount of HNO<sub>3</sub>. However, no appreciable positive effect was reached.

To ensure complete stripping of Pu from the irradiated solvent, we examined stripping into a 0.5 M Na<sub>2</sub>CO<sub>3</sub> solution. The results of one of such experiments are shown in Table 10. As can be seen, the stripping is not very efficient, although quantitative recovery of Pu is possible even at an irradiation dose of  $1.5 \times 10^{21}$  eV cm<sup>-3</sup>. Under these conditions, the solution becomes turbid and the phase separation becomes considerably worse, and at doses higher than  $1.5 \times 10^{21}$  eV cm<sup>-3</sup> (200 kGy) a white compact precipitate suspended in the organic phase is formed. In this case, gravity settling becomes virtually impossible. Similar phenomenon was observed with model solutions containing BHP and palmitic acid dissolved in 20% TBP in Sintin. After acidification, the precipitate dissolved in the organic phase. However, stripping from model solutions containing Pu and BHP without higher carboxylic acids occurs quantitatively with no complications in two steps. This fact suggests the decisive role of HCA sodium salts in this phenomenon.

#### *Pu(IV) Retention in the Course of Stripping and Aggregative Stability*

A spectrophotometric study shows that the oxidation state of Pu(IV) does not change in the course of irradiation of its solutions in TBP in a saturated hydrocarbon diluent, but the chemical form of Pu(IV) changes in the course of irradiation, apparently, because of the complexation with the accumulating BHP.

The known data on the Pu retention in the course of stripping, caused by complexation with BHP, contained no quantitative estimates. We have shown that, in stripping with 0.02 M HNO<sub>3</sub>, the ratio of BHP to the retained Pu is 2.2 molecules per atom. Apparently, Pu is retained by two HDBP molecules. H<sub>2</sub>MBP passes

into the aqueous phase to a noticeable extent and plays in this process less significant role requiring refinement.

Data obtained with the real  $\alpha$ -irradiated solvent showed that the Pu retention in stripping is larger than it follows from the above ratio, and BHP : Pu = 1.6. Additional experiments have shown that this retention is caused by HCA whose role was not examined. Apparently, additional Pu retention due to HCA can be excluded by increasing the acidity of the stripping solution (probably, to 0.1 M).

Carboxylic acids give rise to additional problems, preventing the carbonate stripping of Pu and strongly favoring emulsification with the precipitation at the phase boundary. On the whole, the Pu stripping into carbonate solutions is complicated, though still feasible. It should be noted that the presence of BHP alone in the model systems does not prevent the complexation of Pu with the carbonate ion, and the BHP themselves pass into the carbonate solution. The causes (thermodynamic and/or kinetic) of the preventing effect of carboxylic acids on the carbonate stripping of Pu are yet unclear and require a special study taking into account the already known data [5, 6, 17].

The reductive stripping of Pu into an Fe(II) solution from the irradiated solvent requires separate discussion. As already noted, such stripping occurs without complications only up to the BHP : Pu ratio of  $\sim 3.2$  (taking into account the content of dibasic H<sub>2</sub>MBP, the equivalent ratio is 4), after which the process is extremely slow. Because Pu(III) should not form stable complexes with BHP in acid solution, the Pu retention in the organic phase can be accounted for by slow phase-transfer reduction of the Pu(IV) BHP complex under the action of Fe(II), which is insoluble in the organic phase, and/or by slow accumulation of Fe(III), which forms stable complexes with BHP [30], the more so as an increase in the contact time leads to relatively minor recovery of Pu, tending to a certain limit, despite incomplete conversion of Fe(II). Indeed, introduction into the system of an extractable reductant, Np(IV), which efficiently reacts with BHP to displace Pu(III), gives a significant effect. The residual amount of Pu in the organic phase considerably decreases, and the efficiency of each step starting from the third step noticeably increases. The oxidized Np is reduced again with excess Fe(II).

It is interesting to compare the data obtained in this study on the yield of radiolysis products and on the Pu

stripping with the results of pilot reprocessing of irradiated Np using a solution of TBP in saturated hydrocarbons. As a criterion we can consider the residual amount of Pu that is not stripped into the reducing solution but passes into the sodium carbonate–peroxide solution in the course of solvent regeneration.

In the course of pilot operations, the dose of the solvent  $\alpha$ -irradiation in the extraction and scrubbing steps was  $2.6 \times 10^{19}$  eV cm<sup>-3</sup>, assuming that the irradiation occurred in 1.5 extraction steps and in all the 4 scrubbing steps (in proportion with the effective residence time of <sup>238</sup>Pu in the organic phase); the  $\beta$ - and  $\gamma$ -irradiation dose in eight extraction steps was  $1.3 \times 10^{18}$  eV cm<sup>-3</sup> in total. The solvent took up the total dose of  $3.8 \times 10^{19}$  eV cm<sup>-3</sup>, and, taking into account the dilution in the flowsheet,  $2.5 \times 10^{19}$  eV cm<sup>-3</sup>. In this case, the BHP concentration should be 0.2 mM, and the Pu retention in stripping into an Fe(II) solution in the presence of traces of Np, taking into account the phase ratio and contact time, should be 0.04–0.05 mM. In the sodium carbonate–peroxide scrubbing solution, the Pu concentration should be 4 times higher, i.e., 0.15–0.2 mM (35–45 mg L<sup>-1</sup>). According to the analysis data obtained in the course of the pilot reprocessing, it was 30–50 mg L<sup>-1</sup>, i.e., the data are in reasonable agreement.

## DISCUSSION

Analysis of the results obtained shows that, in the TBP–Sintin system in the presence of water and HNO<sub>3</sub>, there is no energy transfer between the organic products by any mechanism (molecular, radical, etc.), i.e., TBP and the diluent degrade directly. The proportional dependence of the BHP yield on the TBP concentration counts in favor of such conclusion. Simultaneously, as the BHP yield increases with increasing TBP concentration, the yield of nitro compounds and carboxylic acids linearly decreases (at a constant HNO<sub>3</sub> concentration) in accordance with a decrease in the concentration of hydrocarbons. This correlation is well followed at Sintin concentrations in the interval 90–25% (correspondingly, at TBP concentrations in the interval 10–75%). The same conclusion follows from the independence of the BHP yield from the HNO<sub>3</sub> concentration.

The radiation-chemical yields of HDBP and H<sub>2</sub>MBP in the above-indicated interval of TBP concentrations are 2 and 0.35 molecules, respectively, per 100 eV absorbed by TBP proper, and the total yield of

cleavage of the C–O–P bonds is 2.2. It should be noted that these data may differ from the data obtained upon longer irradiation or at a higher Pu concentration in the organic phase (at the expense of <sup>239</sup>Pu), because of possible catalytic hydrolysis of TBP, similar to that observed in the presence of zirconium nitrate [31].

The yield of radiolysis products formed from saturated hydrocarbons (Sintin) is determined by the reaction of hydrocarbon radicals with atmospheric oxygen, nitric acid, water, and products of their radiolysis. The prevalent oxidation products are HCA with the yield of up to 2 molecules/100 eV. Probably, 1.4 HCA molecules per 100 eV absorbed by hydrocarbons are formed via reactions with atmospheric oxygen and water. The remaining HCA amount is formed by the reaction with HNO<sub>3</sub> radiolysis products, as indicated by the linear dependence of the yield of these acids on the HNO<sub>3</sub> concentration in the organic phase, which, in turn, depends on the TBP concentration. The yield of nitro compounds also increases in proportion with the HNO<sub>3</sub> concentration, which suggests direct reaction of hydrocarbon radicals with the NO<sub>2</sub>· radical.

These data probably suggest large role of “direct” decomposition of HNO<sub>3</sub> into NO<sub>2</sub> and OH radicals. The reaction of the OH radical with oxygen under the conditions of  $\alpha$ -irradiation probably leads to the formation of the HO<sub>2</sub> radical and, in turn, to an increase in the yield of carboxylic acids. Comparison of the product yields shows that the direct decomposition of HNO<sub>3</sub> is not the only possible reaction leading to the formation of OH radicals and then of carboxylic acids.

The yield of carbonyl compounds is relatively low and virtually independent of the TBP : Sintin ratio and of the HNO<sub>3</sub> concentration. Probably, these compounds are formed with the participation of both the hydrocarbon radical and the butyl radical from the TBP decomposition. Their role as intermediate radiolysis products remains to be elucidated also.

Thus,  $\alpha$ -radiolysis of 20% TBP in Sintin, equilibrated with 3 M HNO<sub>3</sub>, yields the following products (per 100 eV): ~1.5 molecules of carboxylic acids, 0.2–0.3 molecule of carbonyl compounds, and similar amount of nitro compound. Counting on 100 eV absorbed by hydrocarbons, the total yield of products is about 2.8 molecules. The most significant effect on the radiolysis is exerted by the HNO<sub>3</sub> dissolved in the organic phase. To discuss the role of HNO<sub>3</sub> in more de-

**Table 11.** Initial yield of diluent radiolysis products ( $G$ , molecules/100 eV) in irradiation of 30% TBP in diluent in two-phase systems with 3 M HNO<sub>3</sub> with different kinds of radiation

Compound	$\gamma$ , 1.3 MeV ( <sup>60</sup> Co)							e, 7.5 MeV, solvent product [6]		$\alpha$ , 5.4 MeV, solvent product, Sintin (see above) <sup>d</sup>
	two-phase system, Sintin [32] <sup>a</sup>	two-phase system, air bubbling					C-13			
		Sintin [32, 33] <sup>b</sup>	[5, 23] <sup>c</sup>		[22]					
			RED-1	RZh-13	RED-2	C <sub>12</sub> H <sub>26</sub>		C-13		
HDBP	0.5	1.2	1.1–1.3	0.85	–	–	–	–	–	0.5
H <sub>2</sub> MBP	0.15	0.15	0.4–0.5	–	–	–	–	–	–	0.12
RNO <sub>2</sub>	0.4 → 1.6	0.2	2.0	3.0	2.4	1.1	1.0	2.1	1.8	0.17
RONO <sub>2</sub>	0.75	0.3	0.8	1.0	–	–	–	0.55	1.0	–
R <sub>2</sub> CO	1.2 → 0.7	1.2	2.5	1.5	2.2	0.91	0.93	<0.02	<0.02	0.28
RCOOH	–	–	0.1	0.15	–	–	–	0.1	0.18	1.4

<sup>a</sup> All the data for the two-phase system were obtained without stirring in air. <sup>b</sup> Oxygen bubbling (instead of air). <sup>c</sup> With vigorous mechanical stirring. <sup>d</sup>  $D(360\text{ nm}) = 105$ .

tail, it is necessary to make the nitrogen balance and, in particular, to determine organic nitrates and nitrites, which was not done in this step of the study.

Data on the UV absorption of the irradiated solvent show that the radiolysis results in the formation of an unidentified product with high extinction coefficient at  $\lambda \approx 360\text{ nm}$ .

Data on the radiolysis of 100% TBP are of much interest. In this system, the BHP yield counting on TBP remains equal to  $\sim 2.0$ , but the fraction of H<sub>2</sub>MBP increases from 0.22 to 0.33. In addition, carboxylic acids (yield 1.6–1.8 molecules/100 eV) and carbonyl compounds (yield about 0.3 molecule/100 eV) are detected. The total yield of these products approaches 2.3 molecules, i.e., the number of butyl radicals eliminated upon formation of BHP from TBP. Thus, in neat TBP, butyl radical is mainly oxidized to butyric acid, but its transformations in systems with the diluent in the presence of diluent degradation products are difficult to follow.

The data of this study on the  $\alpha$ -radiolysis of the TBP–hydrocarbons system are compared in Table 11 with published data on the  $\beta, \gamma$ -radiolysis, including the data obtained more recently [4–6, 22, 23].

According to [5], when 30% TBP in a mixture with a relatively narrow C<sub>13</sub> fraction of paraffin hydrocarbons (for composition, see [6]) is  $\gamma$ -irradiated with a <sup>60</sup>Co source on mixing with an aqueous 3 M HNO<sub>3</sub> solution, the BHP yield counting on TBP is 3.5 molecules per 100 eV, which is more than two times higher than in the settled system without stirring [33], for which the data coincide in this respect with the data on the  $\alpha$ -radiolysis; the degradation (evaluated by the

H<sub>2</sub>MBP yield) occurs to the same extent and is characterized by the HDBP : H<sub>2</sub>MBP ratio of  $\sim 4$ . On the other hand, with weak stirring by oxygen bubbling, this ratio is more than two times higher.

We cannot rule out the assumption that the increased yield of BHP and partial shift toward H<sub>2</sub>MBP formation in the stirred system are due to intense radiolysis of TBP dissolved in the aqueous phase, in which the radiation-chemical yield of HDBP is two times higher counting on the aqueous phase as a whole [34], with instantaneous extraction of HDBP, so that the calculation counting on the energy absorbed by TBP proper may be incorrect. Experiments on  $\gamma$ -irradiation in two-phase systems with oxygen or air bubbling give close values of  $G$  [33], falling in the interval 1–1.4 molecules/100 eV, characteristic, according to [7], of irradiation of two-phase systems with 30% TBP in alkanes. Unfortunately, for the system irradiated with accelerated electrons [6], and also in the majority of studies (in particular, [22]) on radiolysis of TBP diluents in the presence of TBP, data on the BHP yield are lacking.

Data on the formation of degradation products from the aliphatic diluent are less ample, and extensive review [35] contains no specific data. These data were actually systematized only in [4] and were partially known [32, 33] by the moment when this study on  $\alpha$ -radiolysis was started. The  $\gamma$ -irradiation of two-phase systems consisting of 30% TBP in alkanes and 3 M HNO<sub>3</sub> from a <sup>60</sup>Co source with vigorous stirring results in formation of the following radiolysis products (per 100 eV): 2–2.5 molecules of carbonyl compounds, 0.1–0.15 molecule of carboxylic acids, and 2–3 molecules of nitro compounds. According to the later data

of the same authors [22] and to the data of [32], in the two-phase system with air or oxygen bubbling the yields of nitration and oxidation products are more than two times lower. In this case, probably, the extraction of radiolysis products from the aqueous phase can play a significant role also, but here nitrogen oxides and peroxy compounds, which are capable to increase the concentration of active oxidants in the organic phase, are concerned.

A comparison shows that, as in the case of the BHP formation, in  $\alpha$ -radiolysis the process occurs more deeply, with oxidation to carboxylic acids prevailing, and at relatively low dose rate the oxygen supply due to diffusion appears to be sufficient. In irradiation with accelerated electrons at high dose rate, the radiolysis products contained no ketones, but these data were obtained without replacement of the aqueous phase (and, as a consequence, at decreasing HNO<sub>3</sub> amount) and at limited air access. Here, the yields of the radiolysis products are intermediate between those in  $\alpha$ - and  $\gamma$ -radiolysis, and the degradation of hydrocarbons and/or formation of unidentified intermediates, probably, plays here a more significant role. It seems that irradiation with accelerated electrons without phase mixing does not simulate to full extent the conditions of the real industrial process. Hence, performing comparative experiments under strictly standardized conditions becomes still more necessary.

On the whole, the study performed shows how strongly the effect of  $\alpha$ -radiation on the TBP-saturated hydrocarbons system differs from the effect of  $\gamma$ -radiation. For more serious comparison, it is necessary to perform a set of systematic studies to refine the role of the irradiation conditions and source.

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