Kinetics of Oxidation of 30% TBP Solutions in C13 Diluent with Nitric Acid: Effect of Temperature and γ-Irradiation

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Abstract—The behavior of the two-phase system consisting of a 30% solution of tri-*n*-butyl phosphate (TBP) in a paraffin diluent (C13) and a 12 M aqueous HNO_3 solution was studied in the temperature interval from 70 to 110°C. The parameters of thermolysis of TBP solutions in C13 in the reaction with HNO_3 in open vessels were determined with the aim of evaluating the explosion hazard of the system in the course of extraction reprocessing of high-level radioactive materials. Solutions of TBP in C13 in the two-phase systems are characterized in the examined temperature interval by more intense gas evolution compared to that from the single-phase systems.

Keywords: tributyl phosphate, C13 diluent, nitric acid, γ-irradiation, gas evolution, thermolysis

The regeneration of spent nuclear fuel from nuclear power plants (NPP SNF) is based on the PUREX process in which a solution of tributyl phosphate (TBP) in an inert diluent is used as solvent. Linear aliphatic hydrocarbons (dodecane, mixture of *n*-paraffins) and mixtures of isoparaffins (tetrapropylene) and of isoparaffins and naphthenes (dearomatized kerosene) are used as diluents [1]. Halogenated organic solvents, e.g., CCl_4 [2], are also used; the use of hexachlorobutadiene in high-level waste (HLW) partitioning has been reported [3].

Radiation-chemical actions cause degradation of the solvent and accumulation of compounds deteriorating its hydrodynamic properties and making the extraction less selective. Therefore, when performing extraction cycles, the solvent is constantly regenerated with a sodium carbonate solution, but some degradation products are not removed upon such treatment and are gradually accumulated in the solvent. The most harmful for the technology are degradation products of hydrocarbon diluents, among which nitration and oxidation products and mixed products of the reaction with TBP play the main negative role [4]. As a result, the thermal stability of the solvent decreases also [4–7]. Therefore, studying the effect of temperature and

ionizing radiation on the systems consisting of TBP in diluent and nitric acid is a very topical problem.

Previously we have studied a 30% TBP solution in a diluent based on *n*-tridecane, equilibrated with 12 M HNO_3 [8]. C13 is a light diluent consisting of a mixture of linear saturated hydrocarbons with 11 to 14 carbon atoms (72% *n*-tridecane) and containing various impurities. The weight fraction of *n*-alkanes in C13 is 99.7–99.9%, that of aromatic hydrocarbons, no more than 0.18%, and that of sulfur, less than 0.011%.

This study deals with the kinetics of the gas evolution in the course of thermal oxidation of TBP solutions in C13 at different temperatures in two-phase aqueous-organic systems, including those subjected to preliminary irradiation.

EXPERIMENTAL

Experiments were performed with a two-phase system consisting of a 30% solution of TBP in C13 and a 12 M aqueous HNO_3 solution. TBP was treated with an alkali solution containing 15 g L^{-1} $KMnO_4$, which was followed by oxalate washing in the presence of 0.3 M HNO_3 to remove MnO_2, treatment with a 10% alkali solution and repeated washing with water to neu-

tral reaction. The organic solutions were preliminarily equilibrated three times with a 12 M aqueous HNO_3 solution; the HNO_3 concentration in the unirradiated organic solutions after treatment with the aqueous HNO_3 solution before the thermolysis was 1.3 M. The organic solution saturated with HNO_3 was placed in a reaction vessel containing a fresh portion of a 12 M HNO_3 solution. The volume ratio of the organic and aqueous phases in all the operations was 1, and the total volume of the two-phase system was 60 mL.

Thermolysis experiments were performed in a glycerol thermostat without stirring. The temperature was maintained with an accuracy of ±1°C. The upper temperature boundary for the two-phase aqueous-organic systems studied is determined by the boiling point of the aqueous phase in open vessels, equal to 110–115°C for the HNO_3 solutions used. Therefore, the thermolysis was performed at 70, 90, and 110°C. The kinetic parameters of the reaction of HNO_3 with solution components were calculated from the gas evolution rate data, changes in the HNO_3 concentration, and accumulation of dibutyl hydrogen phosphate (HDBP) and monobutyl dihydrogen phosphate (H_2MBP) using the known procedures [1].

Irradiation of the acid-saturated solutions was performed on a GUG-120 γ-ray installation (Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences) equipped with a ^{60}Co source at a dose rate of 3.5 kGy h^{-1}. The 30% solutions of TBP in C13, irradiated to absorbed doses of 0.52, 1, and 2 MGy, were adjusted to the initial level of the HNO_3 concentration, 1.3 ± 0.1 M, by treatment with HNO_3, after which they were brought in contact in the reaction vessel with an equal volume of 12 M HNO_3. The gas evolution rate was determined volumetrically on a specially constructed installation [8].

The concentrations of HNO_3, HDBP, H_2MBP, and carboxylic acids (with possible titration of esters) were determined by potentiometric titration with an alcoholic solution of alkali on a Radiometer Type SBR 2c automatic titrator (Copenhagen) equipped with glass and calomel electrodes. The use of a differentiating solvent consisting of acetone and ethanol in a 3 : 1 ratio allowed separate determination of acid concentrations in the course of titration with an alcoholic 0.1 M NaOH solution. The uncertainty of the method does not exceed 10%. The concentration of carboxylic acids C_{10}–C_{12} (CA) was calculated as the difference between the total signal and the sum of the signals from HNO_3,

Table 1. Maximal specific gas evolution rate (W_{max}, min^{-1}) and time in which it is reached (τ_{max}, min) in the system consisting of 30% TBP in C13 and 12 M HNO_3 as functions of the γ-irradiation dose and temperature

Dose, MGy	70°C		90°C		110°C	
	W_{max}	τ_{max}	W_{max}	τ_{max}	W_{max}	τ_{max}
0	0.05	–	0.14	195	0.62	15
0.52	0.08	–	0.13	3	2.9	2.5
1	0.4	4.5	1.6	3.5	3.7	1.5
2	0.5	4	1.9	3	5.5	1.5

HDBP, and H_2MBP. pH of the first equivalence point (titration of HNO_3, e.p.1) is 3.3;

$$V_{titr}(HDBP) = V_{titr}(e.p.2) - V_{titr}(HNO_3), pH_{e.p.2} 6.7;$$
$$V_{titr}(H_2MBP) = V_{titr}(e.p.3) - V_{titr}(HDBP), pH_{e.p.3} 8.2;$$
$$V_{titr}(CA) = V_{titr}(e.p.4) - V_{titr}(H_2MBP), pH_{e.p.4} \sim 11.0.$$

RESULTS AND DISCUSSION

In unirradiated two-phase systems consisting of TBP in C13 and aqueous HNO_3 solution, no gas evolution is observed at HNO_3 concentrations in the aqueous phase lower than 8 M and temperatures lower than 90°C. For mixtures of the solvent with 12 M HNO_3, noticeable gas evolution started at 90°C after 1-h induction period (Fig. 1a).

The onset of the gas evolution is preceded by an induction period τ_{ind} whose length depends on the temperature. After the induction period, the gas evolution starts, and its rate after the time interval τ_{max} reaches the maximal value, W_{max}, also depending on the acid concentration and temperature. This is followed by a slow decrease in the gas evolution rate to a steady-state value, W_{st}, as shown in Fig. 1. Preliminary irradiation of the initial 30% solution of TBP in C13 decreases the gas evolution onset temperature to 70°C (Figs. 1b–1d), and no induction period is observed in this case.

The most important parameters of the gaseous product evolution in TBP/C13–HNO_3 two-phase systems with 12 M HNO_3 in the aqueous phase are given in Table 1. The maximal specific rate of gas evolution, $W_{max} = (V_G/V_L)/t$, increases by approximately an order of magnitude as the temperature of heating unirradiated samples is increased or as the irradiation dose is increased from 0 to 2 MGy at a fixed temperature. In the entire range of examined temperatures and irradiation doses, the gas evolution rate increases by more than 2 orders of magnitude: from 0.05 (without irradia-

Table 2. Temperature dependences of the induction period (τ_i), maximal gas evolution rate (W_{max}), time in which it is reached (τ_{max}), and steady-state gas evolution rate (W_{st}) in thermolysis of two-phase systems in open vessels

System	T, °C	τ_i, min	τ_{max}, min	W_{max}, min^{-1}	W_{st}, min^{-1}
TBP–12 M HNO$_3$	90	60	180	0.04	0.02
	110	10	30	0.50	0.16
30% TBP in C13–12 M HNO$_3$	70	–	–	0.05	
	90	60	195	0.14	
	110	6	15	0.62	
30% TBP in dodecane–12 M HNO$_3$ [4]	90	50	160	0.11	0.090
	110	10	30	0.7	0.250
30% TBP in HCBD–12 M HNO$_3$ [7]	90	240	270	0.0024	0.002
	100	60	220	0.028	0.020
	110	30	45	0.112	0.070
	115	20	45	0.165	0.140

tion, 70°C) to 5.5 min^{-1} (after irradiation to a dose of 2 MGy, 110°C).

As seen from Table 1, the time in which the maximal rate of gas evolution is reached decreases with an increase both in the temperature and in the preliminary irradiation dose.

Data for the unirradiated two-phase systems based on TBP solutions in different solvents in contact with 12 M HNO$_3$ are given in Table 2. At HNO$_3$ concentrations in the equilibrium aqueous phase of up to 12 M and temperatures of up to 100°C, there was virtually no gas evolution. In technical diluents such as RED-1 and especially RZh-3, the gas evolution was observed even at an HNO$_3$ concentration in the organic phase as low as 0.55 M [5]. The characteristics of the gas evolution from the unirradiated two-phase systems containing both neat TBP and TBP in such diluents as C13 and dodecane are very similar. Solutions of TBP in HCBD exhibit higher thermal stability compared to the systems with hydrocarbon diluents.

The differences in the gas evolution for the single- and two-phase systems are illustrated in Table 3 by the
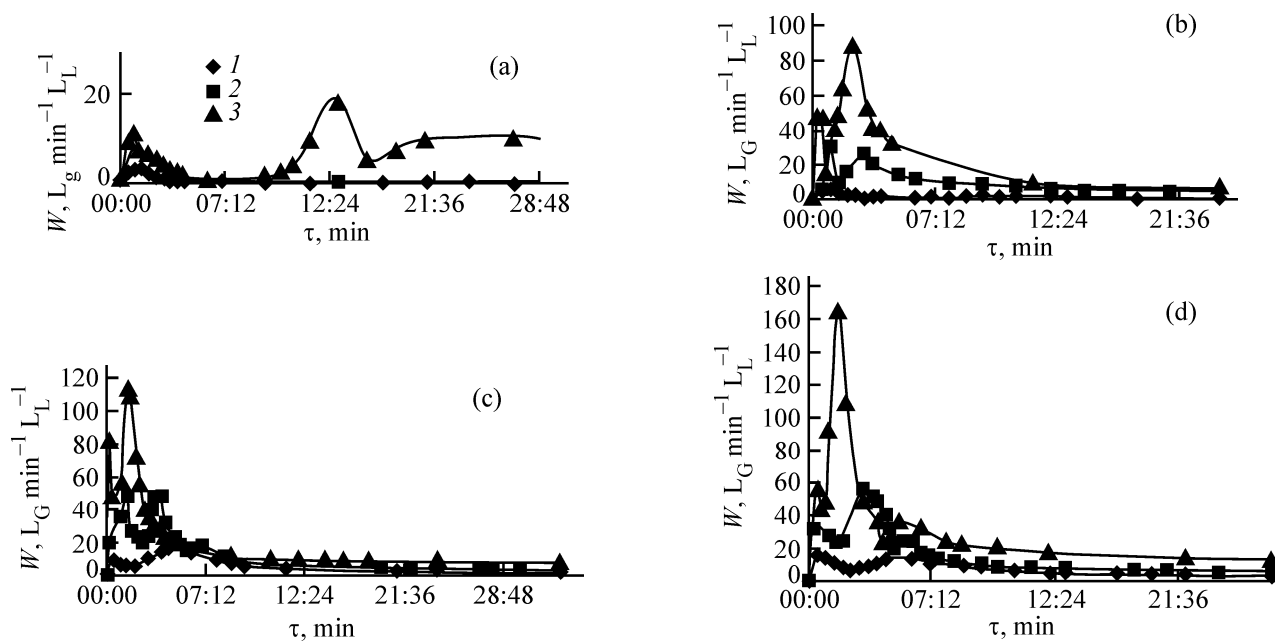

Fig. 1. Variation of the gas evolution rate in thermolysis of the two-phase system consisting of 30% TBP in C13 and a 12 M HNO$_3$ solution in the temperature interval 70–110°C depending on the irradiation dose (MGy): (a) 0 (no irradiation), (b) 0.52, (c) 1.0, and (d) 2.0. T, °C: (*1*) 70, (*2*) 90, and (*3*) 110.
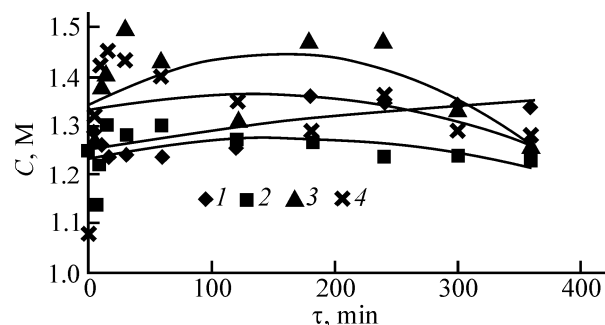
Table 3. Comparative characteristics of the gas evolution in single- and two-phase systems based on 30% TBP in C13 at 110°C

System type	τ_i, min	τ_{max}, min	W_{max}, min^{-1}	V_G/V_L
Single-phase [8]	8	11	0.26	5.1
Two-phase	6	15	0.62	7.5

Fig. 2. Variation of the HNO_3 concentration in the organic phase in thermolysis (110°C) of the two-phase system consisting of 30% TBP in C13 and a 12 M HNO_3 solution, depending on the irradiation dose. Dose, MGy: (*1*) 0 (no irradiation), (*2*) 0.52, (*3*) 1.0, and (*4*) 2.0; the same for Figs. 3–5.

Fig. 3. Kinetics of HDBP formation in the organic phase in the course of thermolysis (110°C) of the two-phase system consisting of 30% TBP in C13 and a 12 M HNO_3 solution, depending on the irradiation dose.

example of a system consisting of 30% TBP in C13 and aqueous 12 M HNO_3 solution at 110°C. In the two-phase system, the gas evolution starts earlier, but the maximal rate is reached in a longer time. On the other hand, the maximal gas evolution rate is two times higher than in the single-phase system. The total volume of the gases released from the two-phase systems is 1.5 times higher compared to the single-phase systems. The latter fact is due to the transfer of HNO_3 from the aqueous phase to the organic phase, compensating the oxidant consumption in the organic phase and contributing to the gas evolution. At temperatures lower than 90°C, the HNO_3 transfer from the aqueous phase to the organic phase compensates the acid consumption in oxidation processes. Above 110°C, the rate of these processes in the organic phase and the acid consumption exceed the rate of the acid transfer from the aqueous phase, which leads to a gradual decrease in the HNO_3 concentration in the organic phase and, as a consequence, to a decrease in the gas evolution. The HNO_3 boiling at temperatures higher than 110°C also leads to the heat loss.

At the examined temperatures, the HNO_3 concentration in the organic phase varies insignificantly, remaining close to the initial equilibrium concentration (1.3 M), which indicates that the HNO_3 mass exchange is efficient and compensates the HNO_3 loss for oxidation processes in the organic phase (Fig. 2).

The presence of HDBP in the unirradiated organic phase could be detected only after 3-h thermolysis at a temperature higher than 100°C. The maximal concentration of the accumulated HDBP in the organic phase in the course of thermolysis of a 30% TBP solution in C13 for 3 h at 110°C in the two-phase system is 0.1 M, which is lower than the value (0.16 M) reached in the single-phase system in 45 min [8]. The kinetics of the HDBP formation at 110°C depending on the preliminary irradiation dose is shown in Fig. 3. As the preliminary irradiation dose is increased, the HNO_3 concentration in the organic phase in the course of thermolysis performed for 300–350 min varies insignificantly. On the other hand, the HDBP concentration tends to a
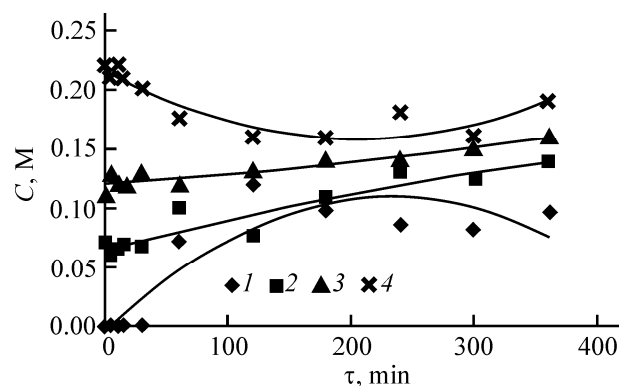
level of 0.11–0.15 M at the thermolysis time of 200–350 min and irradiation dose of 2 MGy.

Preliminary irradiation of the extraction system exerts a particularly strong effect on the H_2MBP formation. Figure 4 shows the data on the H_2MBP accumulation depending on the dose. In unirradiated systems, H_2MBP in the organic phase is not formed, but as the absorbed dose is increased to 2 MGy, the H_2MBP concentration reaches 0.11 M.

In thermolysis of unirradiated hydrocarbons, carboxylic acids are formed along with HDBP and H_2MBP by a two-step or more complex mechanism. Their concentration increases with an increase in the absorbed γ-radiation dose (Fig. 5).

Thus, when the extraction system consisting of 30% TBP in C13 and 12 M HNO_3 is heated in open
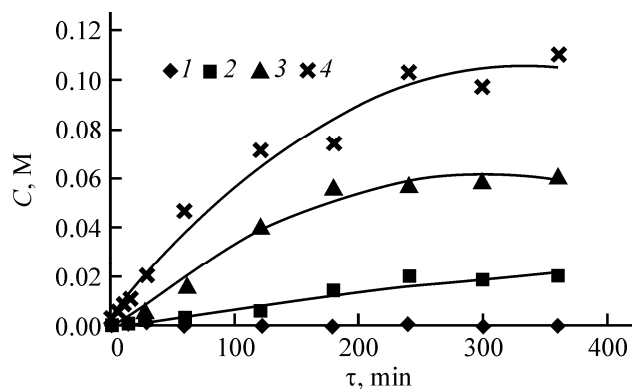
Fig. 4. Kinetics of H$_2$MBP formation in the organic phase in the course of thermolysis (110°C) of the two-phase system consisting of 30% TBP in C13 and a 12 M HNO$_3$ solution, depending on the irradiation dose.
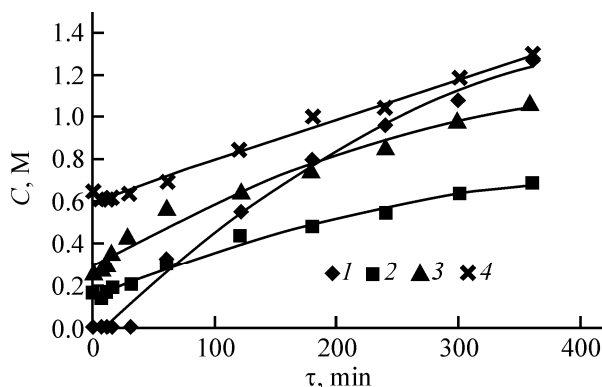

Fig. 5. Kinetics of the carboxylic acid formation in the organic phase in the course of thermolysis (110°C) of the two-phase system consisting of 30% TBP in C13 and a 12 M HNO$_3$ solution, depending on the irradiation dose.

vessels, despite high content of the oxidant, the conditions leading to the development of the autocatalytic oxidation are not created. Noticeable gas evolution starts at 90°C after 1-h induction period. In the two-phase systems, as in the single-phase systems, the gas evolution is preceded by an induction period whose duration depends on the temperature. The gas evolution rates after passing through a maximum decrease to steady-state values depending on the thermolysis temperature and considerably exceeding the values for single-phase systems. Upon γ-radiolysis of the two-phase systems consisting of TBP in C13 and 12 M HNO$_3$, the gas evolution onset temperature decreases to 70°C, and the induction period disappears. The

maximal gas evolution rates for the solutions irradiated to a dose of 2 MGy exceed, on the average, by an order of magnitude the values obtained for the unirradiated systems at the same temperatures (70–110°C). The volumes of the gaseous products released from the two-phase system irradiated to a dose of 2 MGy are relatively high and reach 7–9 L$_G$ L$_L^{-1}$. In heating of the preliminarily irradiated system, dibutyl hydrogen phosphate is formed in the highest yield, with monobutyl dihydrogen phosphate and carboxylic acids also formed.

For the commercial use of C13 diluent, it is necessary to perform additional studies on the development of a procedure for removing products of radiation-thermal degradation of the diluent from the irradiated organic solution.

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