Influence of γ-irradiation on the kinetics of heat release during the interaction of an aqueous solution of HNO_3 with aliphatic hydrocarbons

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The influence of preliminary γ-irradiation and γ-irradiation during the oxidation process on the kinetics of heat release in the systems *n*-decane—aqueous solution of HNO_3 and a solution of tributyl phosphate in a kerosene—aqueous solution of HNO_3 was studied. The preliminary γ-irradiation of the system at 43 °C increases the initial rate of the process (k_1). The increase is proportional to the irradiation dose at doses up to 150 kGy, then the increase in k_1 is retarded, and the further course of the process becomes practically independent of the irradiation dose. The effect of γ-irradiation during the oxidation depends on the temperature of the system: at temperatures lower than 80 °C, γ-irradiation increases the rate of heat release, whereas at higher temperatures, γ-irradiation decreases the rate of heat release. The effects observed were explained by the competition of NO_2 accumulation due to the radiolysis of nitric acid and processes of the addition of NO_2 to unsaturated hydrocarbons produced by the radiolysis of the organic phase.

Key words: *n*-decane, kerosene, tributyl phosphate, oxidation by nitric acid, kinetics, γ-irradiation, heat release.

We have previously studied[1,2] the kinetics of heat release in heterogeneous systems containing an aliphatic hydrocarbon from the kerosene fraction and an aqueous solution of HNO_3. The processes in these systems simulate extraction of uranium and plutonium during processing of heat-releasing elements (HRE) in atomic reactors. In these systems, the rate of heat release was established to be determined mainly by the rate of oxidation of hydrocarbons by the dissolved NO_2, and only at the very beginning of the process when NO_2 is absent is it determined by the rate of interaction of hydrocarbons with HNO_3. Nitrogen dioxide is formed in the interaction of the oxidation product (NO) with HNO_3; therefore, the reaction is autocatalytic. Its rate depends on the ratio of the organic and acid phases to the value of the free gas volume of the system. Since the volume of the system under study is small (the volume of the organic phase is less than 1 cm^3), NO diffuses from the organic phase to the boundary between the acid and organic phases, and NO_2 diffuses in the opposite direction sufficiently rapidly. The real concentrations of these oxides in both phases are close to the equilibrium values, which is confirmed by the quantitative description of the kinetic regularities of heat release using the thermodynamic equilibrium constants of the distribution of NO_2 between the phases and its dimerization.[1]

A 30% solution of tributyl phosphate (TBP) in kerosene[3] is used for extraction of uranium and plutonium from nitric acid solutions in processing of spent HRE. When the system contains dissolved salts of uranium, plutonium, and other radioactive products of nuclear fission, all phases undergo sufficiently strong irradiation. This can exert an effect on the rate and mechanisms of the processes occurring in the absence of ionizing radiation. Since very active radicals and radical ions are formed under the action of irradiation and their secondary reactions lead to the accumulation of sufficiently stable compounds capable of changing the rate of the process, it was necessary to study the effect of both the preliminary irradiation and irradiation performed directly during the oxidation on the kinetics of heat release in the systems *n*-decane—aqueous solution of HNO_3 and a solution of TBP in a kerosene—aqueous solution of HNO_3. Based on these data, we can estimate the possibility and conditions of the thermal stability loss in real extraction processes.

Evidently, uranium and plutonium ions can also exert a catalytic effect on the rates of oxidation reactions in the system studied, but this problem was not studied in this work.

Experimental

Preliminary irradiation of the systems I (decane—64.65% aqueous solution of HNO_3) and II (a 30.38% solution of TBP in kerosene—64.65% aqueous solution of HNO_3) sealed in glass ampules was performed on a Gamma-tok setup with the ^{60}Co γ-source with a power of 5 kGy h^{-1} at the equilibrium temperature of 43 °C inside the cobalt source.

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Kerosene was similar in composition to that used previously.[2] In irradiated samples, the overall content of nitrogen oxides was measured by the spectral Griess method and recalculated per NO_2. The rate of heat release was determined using a differential microcalorimeter[4] in the 60.0—100.5 °C temperature range. The kinetics of heat release in system II in the absence of irradiation was studied under similar conditions.

The effect of irradiation during the oxidation of *n*-decane was studied for system I. For this purpose, we specially designed a metallic thermostat that allowed a constant temperature to be maintained within 50—100 °C with the ±0.1 °C accuracy under irradiation conditions in the cobalt source. The ampules were filled with the mixture under study, sealed, placed in the thermostat, and kept at 70.2, 82.4, 90.5, and 95.0 °C for a specified time interval. Then the content of NO_2 was measured in the irradiated system, which reacted at a certain conversion, and the rate of heat release at the irradiation temperatures was determined.

Results and Discussion

In the real system of extraction of uranium and plutonium, the spectrum of various radiation sources and radiation types is very wide, but the ionization of the medium mainly determined by the absorption radiation energy referred to the mass unit of a substance (absorbed dose, *D*) is the primary process of the action of all sources. When the energy of ionizing particles is sufficiently high, this process depends slightly on the type of radiation. This fact makes it possible to simulate irradiation conditions using only one source, in the given case, the ^{60}Co γ-radiation source with a power of 5 kGy h^{-1}. According to the published data,[3] after storage for 150 days, the radiation power in the spent HRE based on UO_2 is ~22 W kg^{-1}, whereas 5 years after it is ~1 W kg^{-1}, which corresponds to the maximum possible radiation power within 4—8 to 0.2—0.4 kGy h^{-1}, respectively, at the concentration of these elements in solutions of HNO_3 of about 5—10 wt.%, *i.e.*, the power of the cobalt source is virtually equivalent to the maximum radiation power in the real extraction process.

The ionizing radiation affects both the acid and organic phases of the system. In the acid phase, NO_2, O_2, and H_2O are accumulated[5] at a sufficiently high concentration of HNO_3 when the formation of NO_2^- anions is difficult, and NO_2 mainly goes to the organic and gas phases according to the equilibrium considered previously.[1] No substantial accumulation of hydrogen should be observed, because the rate of the reaction $H + NO_2 \rightarrow HNO_2 \rightarrow H_2O + NO + NO_2$ is much higher than that of the reaction $H + H + M \rightarrow H_2 + M$ due to the high concentration of NO_2.

Only *n*-decane is present in the organic phase at the initial stage, while after the primary ionization the corresponding radicals are formed[6] due to the cleavage of C—H and C—C bonds. These radicals are very active and react rapidly with the components of the system. This results in the accumulation of hydrogen and hydrocarbons with different chain lengths both shorter and longer than that of the starting *n*-decane. Unsaturated hydrocarbons whose oxidation rate is substantially higher than that of saturated hydrocarbons compose about 20—30% of all radiolysis products. However, as nitrogen dioxide is formed in the acid phase and goes to the organic phase, NO_2 reacts more and more intensely with all hydrocarbon radicals to give the corresponding nitro compounds: $R^{\cdot} + NO_2 \rightarrow RNO_2$ ($R^{\cdot}$ is one of the possible aliphatic radicals in the mixture), $H + NO_2 \rightarrow HNO_2$; and the rate of accumulation of NO_2 should decrease. When the content of nitrogen dioxide in the organic phase is sufficiently high, almost all radicals formed in the organic phase react with NO_2, and the rate of consumption of NO_2 reaches a maximum and is determined by the overall radiation yield of all radicals.

The data on the effect of preliminary irradiation on the heat release kinetics in systems I and II are presented in Table 1 along with the results obtained for nonirradiated system II; similar data for system I have been determined previously.[1] The observed rate of heat release in system II, the value of the gas volume (V^g), and the number of moles of HNO_3 and H_2O (n^{ac}) were referred to 1 mole of a mixture of kerosene and TBP. The mass of the medium hydrocarbon of the kerosene fraction (dodecane) was accepted to be the molecular

Table 1. Experimental conditions and rate constants for the reactions of systems I and II with an aqueous solution of HNO_3 (64.62 wt.%) during preliminary irradiation

T /°C	*D* /kGy	V^g /L mol^{-1}	n^{ac} /$\frac{mol}{mol}$	$k_1 \cdot 10^4$ /$\frac{kcal}{mol\ s}$	$k \cdot 10^4$ /s^{-1}
System I					
75.0	70	10.3	588	3.1	—
82.4	0	10.8	581	1.4	8.0
82.4	5	12.5	379	1.7	11
82.4	30	11.0	603	2.7	8.4
82.4	70	12.3	589	6.1	8.6
82.4	150	11.0	611	11	7.6
82.4	360	13.2	596	12	9.1
90.5	70	8.0	577	12	20
95.0	70	9.5	583	16	32
100.5	70	6.7	593	23	61
System II					
48.4	0	3.2	187	0.93	0.23
55.0	0	2.6	253	0.98	0.68
60.8	0	3.2	167	1.5	1.4
67.8	0	3.6	178	2.8	3.9
74.4	0	3.1	188	3.5	7.8
80.2	0	11.5	763	2.31	5.4
93.0	0	3.0	198	19.0	48.7
60.0	70	11.2	809	0.89	0.4
80.2	70	11.4	785	6.6	—
80.2	100	12.3	776	7.9	4.5
80.2	150	13.8	775	10	5.2
80.2	252	14.0	766	14	4.9
80.2	360	11.5	786	18	4.9
90.4	70	10.2	790	15	14
100.5	70	12.3	796	36	40

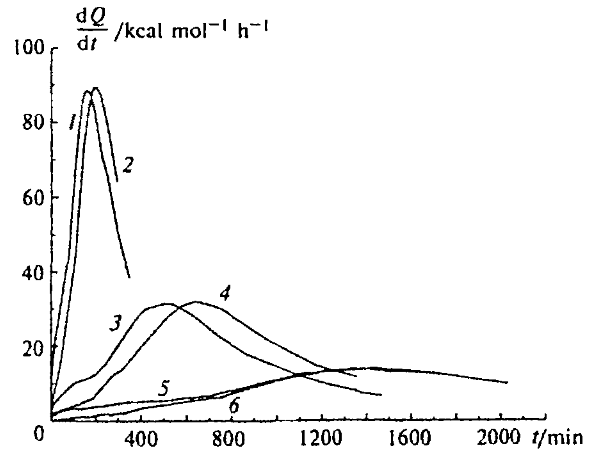

Fig. 1. Time dependences of the rate of heat release in irradiated (*1*, *3*, *5*) and nonirradiated (*2*, *4*, *6*) system I at different temperatures: T/°C = 100.5 (*1*, *2*); 90.5 (*3*, *4*); and 82.4 (*5*, *6*).

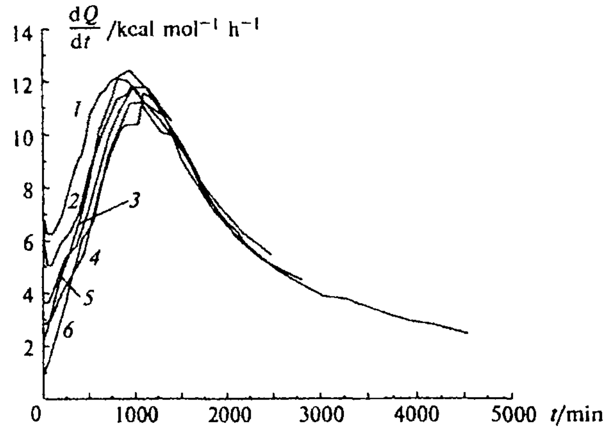

Fig. 2. Time dependences of the rate of heat release in system II at 80.2 °C and different doses of preliminary irradiation: D/kGy = 360 (*1*); 250 (*2*); 150 (*3*); 100 (*4*); 70 (*5*); and 0 (*6*).

mass of the kerosene. It has been shown that this approximation can introduce an error not greater than 2%.[2] Like system I, system II consists of one gas phase and two liquid phases. The kinetic regularities established for system I (the increase in the rate of the process in time related to the accumulation of NO_2 in the organic phase, the change in the concentration of NO_2 in the organic phase, and as a result, the dependence of the heat release rate on the value of V^g) are retained for system II.

The rate constants were calculated from the kinetic equations suggested[1] for the description of the heat release kinetics in system I. To determine the number of moles of NO_2 in the organic phase per mole of the kerosene—TBP mixture, we used the temperature dependences of Henry's constants for NO_2 and N_2O_4 and of the dissociation constants of N_2O_4 determined for system I.

If the system is pre-irradiated at 43 °C when the rate of oxidation of n-decane is very low, NO_2 and O_2 are accumulated due to the radiolysis of the system, and some changes in the hydrocarbon composition of the organic phase are observed. When the temperature of the pre-irradiated samples is subsequently increased to 70—100 °C (Figs. 1 and 2; Table 1), the reaction starts at a rate considerably higher than the rate of heat release in the nonirradiated system. At doses ≤150 kGy, the initial reaction rate increases linearly according to the equations $k_1 = 1.4 \cdot 10^{-4} + 6.4 \cdot 10^{-6}D$ (kcal mol^{-1} s^{-1}) for system I at 82.4 °C and $k_1 = 2.3 \cdot 10^{-4} + 7.3 \cdot 10^{-6}D$ (kcal mol^{-1} s^{-1}) for system II at 80.2 °C. At doses >150 kGy, further increase in the k_1 value is strongly retarded for both systems. At the same time, the overall number of NO_2 moles per 1 mole of the starting n-decane (β), which was accumulated in system I due to the radiolysis (Table 2), is proportional to the D value within the whole range of irradiation doses.

The nitrogen dioxide formed due to irradiation is distributed between the phases and is partially dimerized to N_2O_4; therefore, based on the formula obtained previously,[1] we calculated the content of NO_2 in the organic phase (see Table 2). The comparison of the k_1 values for the irradiated samples with the rate constants of heat release calculated from the equation for the heat release rate[1] at the corresponding values of $n^{org}_{NO_2}$ shows that in the whole range of doses, the initial rate is proportional to the $n^{org}_{NO_2}$ value (see Table 2).

Table 2. Experimental initial rates of heat release in system I during preliminary irradiation and calculated rates of heat release at the corresponding content of NO_2 in the organic phase at 82.4 °C

V^g /L mol^{-1}	n^{ac} /mol mol^{-1}	D /kGy	β (mol NO_2)	$n^{org}_{NO_2} \cdot 10^3$ (mol n-$C_{10}H_{22}$)$^{-1}$	$k_1^{exp} \cdot 10^4$ kcal mol^{-1} s^{-1}	$k_1^{calc} \cdot 10^4$ kcal mol^{-1} s^{-1}
9.3	583	5	0.029	5.2	1.4	1.1
7.6	594	10	0.051	10.0	1.4	2.1
8.4	596	20	0.157	27.1	5.0	5.9
11.0	603	30	0.186	26.2	5.5	5.6
12.3	589	70	0.228	29.3	6.1	6.3
11.0	611	150	0.321	42.6	10.8	9.1
13.2	596	360	0.507	55.4	11.9	11.9

Table 3. Accumulation of NO_2 in nonirradiated and irradiated system I at 70.2 °C

D/kGy	t/h	β /(mol NO_2) (mol n-$C_{10}H_{22}$)$^{-1}$
0	6	0.035
0	22.5	0.18
0	30	0.32
0	46.5	0.46
0	59.33	0.81
1.25	0.25	0.007
2.5	0.5	0.01
5	1	0.04
10	2	0.06
20	4	0.08
42.5	8.5	0.19
101.25	20.25	0.35
138.75	27.75	0.53

Therefore, the increase in the reaction rate after pre-irradiation is mainly related to the accumulation of NO_2 due to the radiolysis of the acid phase. The accumulation of the radiolysis products in the organic phase affect slightly the rate and heat of the process. The deviation of the dependence of k_1 on the irradiation dose from linearity is explained by the decrease in the relative fraction of NO_2 molecules in the organic phase mainly due to its dimerization to N_2O_4. In fact, the k_1 values for the irradiated samples correspond to the rate of reaction of NO_2 with hydrocarbons, which is determined by the second term in the equation used in our previous work,[1] but hereinafter we use the designation k_1 to retain the general form of the kinetic equation for the initial reaction rate of all samples. For the nonirradiated systems, the k_1 value corresponds to the rate constant of the reaction of hydrocarbons with nitric acid.

For nonirradiated system II, the temperature dependence of the initial reaction rate has the following form: $k_1 = 8.9 \cdot 10^8 \exp[-19.5 \cdot 10^3/(RT)]$ (kcal mol^{-1} s^{-1}). The value of k_1 is approximately 1.6-fold higher than that for neat hydrocarbons or their mixtures,[2] which can be associated with the fact that the kerosene contains ~2% nonparaffinic hydrocarbons increasing the initial oxidation rate.

We obtained the temperature dependences of the initial rates of heat release (k_1/kcal mol^{-1} s^{-1}) in systems I and II at the pre-irradiation dose of 70 kGy:

System I: $k_1 = 2.7 \cdot 10^9 \exp[-20.7 \cdot 10^3/(RT)]$;

System II: $k_1 = 6.4 \cdot 10^{10} \exp[-22.8 \cdot 10^3/(RT)]$.

The Arrhenius parameters k_1 for the irradiated systems are determined by a superposition of the temperature dependence of the rate constant of the reaction of NO_2 with hydrocarbons (k) and the temperature dependence of the relative amount of NO_2 in the organic phase. The $n^{org}_{NO_2}$ value decreases with a temperature increase, which results in a decrease in the activation energy for k_1 in the irradiated samples as compared to that for k. The k constants in systems I and II are independent of the irradiation dose and close to the corresponding values in the nonirradiated systems. For nonirradiated system II, we found the expression $k = 2.6 \cdot 10^{18} \exp[-35 \cdot 10^3/(RT)]$ (s^{-1}) for which the Arrhenius parameters almost virtually coincide with similar parameters for the rate constants of the reactions of NO_2 with individual hydrocarbons.[2]

The experimental results on the effect of irradiation during the oxidation are presented in Tables 3 and 4. At temperatures ≥70 °C, the radiolysis and oxidation of the components occur simultaneously with probable interactions of the products of both reactions. In principle, one could expect that the hydrocarbon radicals formed increase substantially the rate of the oxidation processes, because the majority of the oxidation reactions are branching chain processes. However, no noticeable increase in the reaction rate is observed in fact. In the presence of significant amounts of NO_2 in the organic phase, the major part of the radicals interact with NO_2 without development of the branching chain process to form different final products, first of all, due to the radical recombination:

$$R^{\cdot} + NO_2 = RNO_2.$$

Since NO is not formed, no increase in the content of NO_2 due to the reaction with nitric acid is observed.

Analysis of the data in Tables 3 and 4 shows that simultaneous radiolysis and oxidation lead to a certain

Table 4. Rates of heat release and accumulation of NO_2 in nonirradiated and irradiated system I at different temperatures and times corresponding to the 5% conversion of the reaction without irradiation

T/°C	D /kGy	t/h	dQ/d$t \cdot 10^3$ /kcal mol^{-1} s^{-1}	V^g /L mol^{-1}	n^{ac} /mol mol^{-1}	$n^{org}_{NO_2}$	β
						(mol NO_2)	(mol n-$C_{10}H_{22}$)$^{-1}$
82.4	0	9	1.3	10.8	581	0.071	0.58
	45	9	1.2	8.2	604	0.068	0.45
90.5	0	4.75	3.6	13.2	606	0.087	0.59
	23.75	4.75	2.1	8.4	590	0.068	0.51
95	0	3.33	4.3	12.3	596	0.044	0.45
	16.65	3.33	2.1	8.2	580	0.053	0.40

difference in the accumulation of NO_2 (*i.e.*, in β values) in the irradiated and nonirradiated systems. At low temperatures (43 °C or 70.2 °C), the β values for the irradiated system at the same times are greater than those for the nonirradiated system; this difference decreases with a temperature increase, and beginning from 82.4 °C, the β value for the irradiated system becomes lower than that for the nonirradiated one.

We compared the heat release rates referred to 1 mole of NO_2 in the organic phase per mole *n*-decane in the irradiated and nonirradiated phases in the 82.4—95.0 °C temperature range. In the system subjected to irradiation, the heat release rate was lower. The rate cannot decrease due to the increase in the conversion for the irradiated system at the moment of rate measurement, because further the reaction occurs with self-acceleration, and maximum rate and heat values close to the corresponding values for the nonirradiated system are achieved. We have no grounds to assume a decrease in the rate constant (k) of the reaction of NO_2 with *n*-decane in the irradiated system. The decrease in the β value and the decrease in the relative rate of heat release with a temperature increase can be explained by the occurrence of a parallel reaction proceeding at a sufficiently high rate with the activation energy higher than those for standard radical chemical reactions. This reaction is most likely the addition of NO_2 to unsaturated hydrocarbons (Eq. (1)), which are formed in considerable amounts during irradiation of aliphatic hydrocarbons.

$$C_nH_{2n} + 2\,NO_2 \rightarrow C_nH_{2n}(NO_2)_2 \qquad (1)$$

The rate of this process is sufficiently high,[7] and the heat of the nitration reaction is substantially lower (20—30 kcal per mole NO_2) than the heat of the oxidation reaction (80 kcal per mole NO_2); therefore, the consumption of NO_2 according to Eq. (1) decreases the observed rate of heat release. The scale of self-acceleration of the process also decreases, because NO_2 is consumed irreversibly in reaction (1) and no generation of new NO_2 molecules occurs. After the irradiation ceases and the unsaturated hydrocarbons in the mixture are consumed, the reaction develops with the same kinetic parameters as in the absence of irradiation.

Based on the results obtained, we can conclude that irradiation does not result in a substantial increase in the rate of heat release in the developed oxidation process; therefore, the critical conditions that characterize the loss of control of the process under irradiation change slightly. However, the irradiation increases strongly the initial reaction rate, and hence, the time of achievement of the critical conditions will be shortened.

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