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The effect of aliphatic alcohol additives on the radiolytic degradation of TODGA in Isopar-M

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Abstract
The radiolysis of solutions of TODGA (N,N,N′,N′-tetra-n-octylamide of diglycolic acid) in mixtures of Isopar-M (isoparaffins C_{13}–C_{14}) with n-nonanol or n-decanol at 500 kGy leads to predominant decomposition of TODGA. The radiation-chemical yield of this process is 0.4–0.5 µmol J^{-1}. The main products of the direct effect of ionizing radiation on TODGA are N,N-dioctylacetamide and 2-hydroxy-N,N-dioctylacetamide. The indirect effect of ionizing radiation is mainly due to reactions with alkoxy radicals and leads to the breaking of the C–N and C–C bonds in the α-position relative to the carbonyl group. An increase in the alcohol content in the solution results in the increase of the variety of radiolytic products, in the enhancement of gas evolution, and in the increase in the yield of TODGA decomposition. The replacement of n-decanol with n-nonanol does not significantly affect the radiolytic stability of the solutions.

Keywords TODGA extractant · n-alcohols · Radiolysis products · Radiation-chemical yield

Introduction

One of the critical characteristics of systems used to extract radionuclides from spent nuclear fuel is the radiolytic stability of the extractant and the whole system. Among the various extractants, diglycolamides [1–4], primarily TODGA—N,N,N′,N′-tetra-n-octylamide of diglycolic acid, are of the most significant practical interest considering high extraction ability and ease of utilization. TODGA solutions in mixtures of heavy paraffins with aliphatic alcohols, in particular in the mixture of iso-paraffins C_{13}–C_{14} (Isopar-M) with n-nonanol or n-decanol, are promising for practical use not only due to extraction efficiency and the possibility to regenerate the organic solutions but also due to their fire and explosion safety [5]. These mixtures are also promising for the extraction of An(III) and Ln(III) from solutions with a high concentration of nitric acid [6–8]. However, the optimal composition of the extraction systems must be determined based on the information, including their radiolytic stability. The radiolytic transformations of TODGA in hydrocarbon-alcohol solutions have not been previously experimentally studied. However, TODGA molecules' ability to serve as effective acceptors of excessive energy and charge in mixtures with dodecane was shown using pulsed radiolysis and stationary γ-radiolysis [9, 10].

The aim of this work is the analysis of key transformations and products of the radiolysis of TODGA solutions in a mixture of Isopar-M with n-decanol or n-nonanol under the effect of accelerated electrons.

Experimental

Extraction mixtures

The investigated extraction mixtures are based on TODGA (N,N,N′,N′-tetra-n-octylamide of diglycolic acid) in the complex diluent Isopar-M (a mixture of isoparaffins with a boiling point in the range of 208–257 °C) with aliphatic monohydric alcohols provided by JSC "V.G. Khlopin Radium Institute". The composition of the samples is shown in Table 1.

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Table 1 Names and compositions of the samples

Sample	Content of the components		
	TODGA, mol L^{-1}	n-decanol, vol.%	n-nonanol, vol.%
S1	0.15	6.0	–
S2		–	6.0
S3	0.20	20.0	–
S4		–	20.0

A source of ionizing radiation and radiolysis of the extraction mixtures

The extraction mixtures were irradiated in a cylindrical glass reactor with a water seal at an ambient temperature of 17 ± 2 °C using the UELV-10-10-S-70 linear accelerator with a scanning electron beam (energy of 8 MeV, pulse duration of 6 µs, a pulse repetition rate of 300 Hz, an average beam current of 700 µA, vertical scan frequency of 1 Hz, sweep width of 245 mm). Irradiation was performed in a pulsed mode: an irradiation interval to a dose of 10 kGy (dose rate 0.22 kGy s^{-1}) was followed by a cooling interval of the sample for 10 min. Phenazine dye-doped copolymer film standard reference material SO PD(F)R-5/50 [GSO (Certified Reference Material) No. 7875-2000] was used as a dosimeter.

Under real industrial conditions of the spent nuclear fuel reprocessing, the extractant receives a dose in the range of 0.1–1 W h L^{-1} (0.3–3 kGy) per cycle [11]. The average number of cycles for one extractant should be at least 100. Based on these assumptions, the maximum irradiation dose of the extraction mixture can be higher than 300 kGy. Thus, the total absorbed dose for each test sample was chosen equal to 500 kGy.

Chromatography

The samples were analyzed using a Thermo Scientific Trace 1310 gas–liquid chromatograph with an ISQ mass-spectrometer detector (ionization by electrons, 70 eV) and a Trace 1310 gas–liquid chromatograph with a flame ionization detector. The samples were dissolved in acetone for analysis. The flow segmentation mode was used (1:20 and 1:5). Helium was used as a carrier gas (flow rate 1.2 mL min^{-1}). Thermo columns with a polydiphenylsiloxane/polydimethylsiloxane ratio equal to 5:95 of 15 m (TG-5MS, 15 m × 0.25 mm) and 30 m long (TG-5MS, 30 m × 0.25 mm) were used for qualitative and quantitative analysis, respectively. Products were identified by their mass spectra and retention indices using the NIST-2017 database. According to the results of repeated experiments, the relative error of measurements did not exceed 10%.

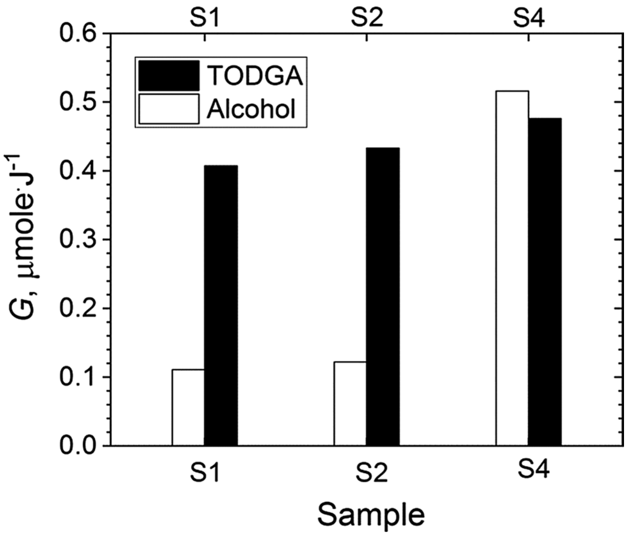


Fig. 1 The radiation-chemical yields *G* of decomposition of TODGA and alcohols for the samples S1, S2 and S4

Results and discussion

After irradiation of the samples S1 and S2 up to a dose of 500 kGy the alcohol content decreases by about 10%, while the TODGA content decreases by almost 4 times. Replacing n-decanol with n-nonanol (the difference between S1 and S2) has an insignificant effect on TODGA and alcohol's radiolytic stability. In the case of the samples S3 and S4 (with higher initial content of alcohol and TODGA), irradiation has an even greater effect on alcohol degradation than on the TODGA degradation. The corresponding radiation-chemical yields of the decomposition of alcohols and TODGA are shown in Fig. 1.

Chromatographic analysis of the irradiated samples does not reveal products heavier than TODGA. However, it reveals about 20 new peaks corresponding to alkylated nitrogen-containing products with a molecular weight higher than that of initial alcohols and iso-paraffins, but lower than that of TODGA (Fig. 2). This indicates that fragmentation of TODGA molecules is the dominant radiolytic process and, on the other hand, that intermediates of radiolysis of alcohols and/or iso-paraffins are significantly involved in the transformation of TODGA fragments. Simultaneously, the probability of the formation of stable products of radical attachment directly to the TODGA molecule is negligible.

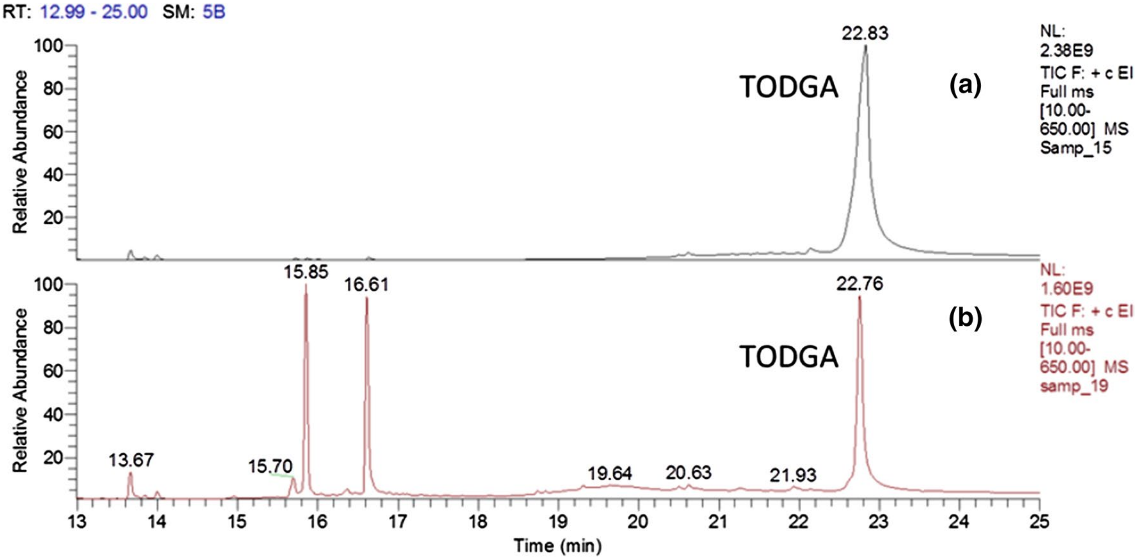


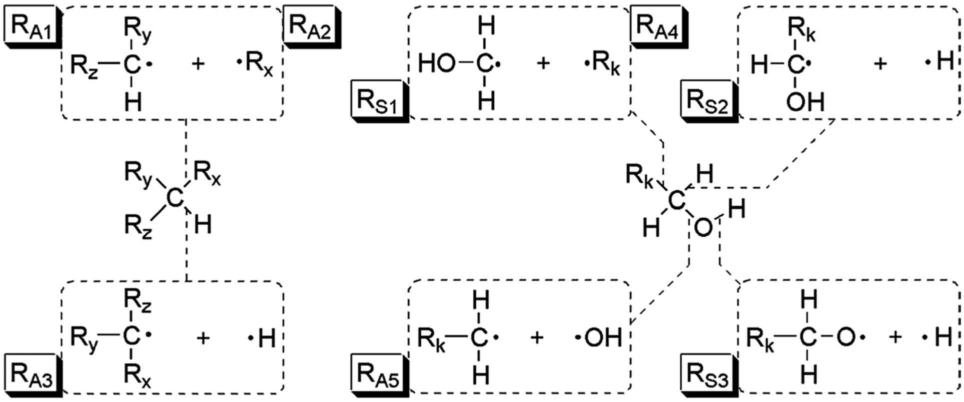
Fig. 2 Sections of chromatograms with components with a retention time of 13–25 min in the initial (**a**) and irradiated (**b**) sample S1

Usually, irradiation's direct effect on the components of a solution (ionization and excitation of molecules) is proportional to their weight fraction. Thus, iso-paraffins (Isopar-M) are primarily subjected to direct radiolytic damage because their fraction in the extraction mixture is the largest. Damage of the C–H and C–C bonds at the branching points of the carbon chain is the most typical effects at the stage of primary processes involving ions and excited molecules [12] (Fig. 3; the corresponding organic radicals are indicated in rectangular boxes). Thus, alkyl radicals (R_{A1}–R_{A3}) are formed along with H atoms. The variety of such radicals depends on the structure of the Isopar-M components.

Long-chain aliphatic alcohols slowly interact with the electron and are polar. Therefore, they can solvate electrons that are formed as a result of the ionization of any of the system's components. The alcohol content in the extraction system is less than iso-paraffins, but enough for a part of the alcohol molecules to be directly irradiated. Linear alcohols tend to form α-hydroxyalkyl radicals R_{S1} and R_{S2}, as well as the alkoxy radicals R_{S3} [13] (Fig. 3). The radiolysis of alcohols also leads to the formation of water molecules due to the breaking of the C-O bond and the subsequent capture of hydrogen atoms by OH radicals. Alkoxy radicals R_{S3}, like OH radicals, are highly reactive and can effectively capture hydrogen atoms and attach to double bonds. In addition, the breaking of C–C and C–O bonds results in the formation of alkyl radicals R_{A4} and R_{A5}. This leads to an increase in the variety of alkyl radicals in the system and those resulting from the Isopar-M decomposition. Large hydroxyalkyl and alkyl radicals disappear mainly in reactions of recombination and disproportionation with each other and other radicals. Particularly, a wide variety of branched alkenes and alkanes lighter than the Isopar-M components is observed in the irradiated solutions (Fig. 4).

TODGA transformations are caused by both direct and indirect effects of irradiation because of its high fraction

Fig. 3 The general scheme of the main channels of homolytic breaking of bonds in iso-paraffins and linear aliphatic alcohols



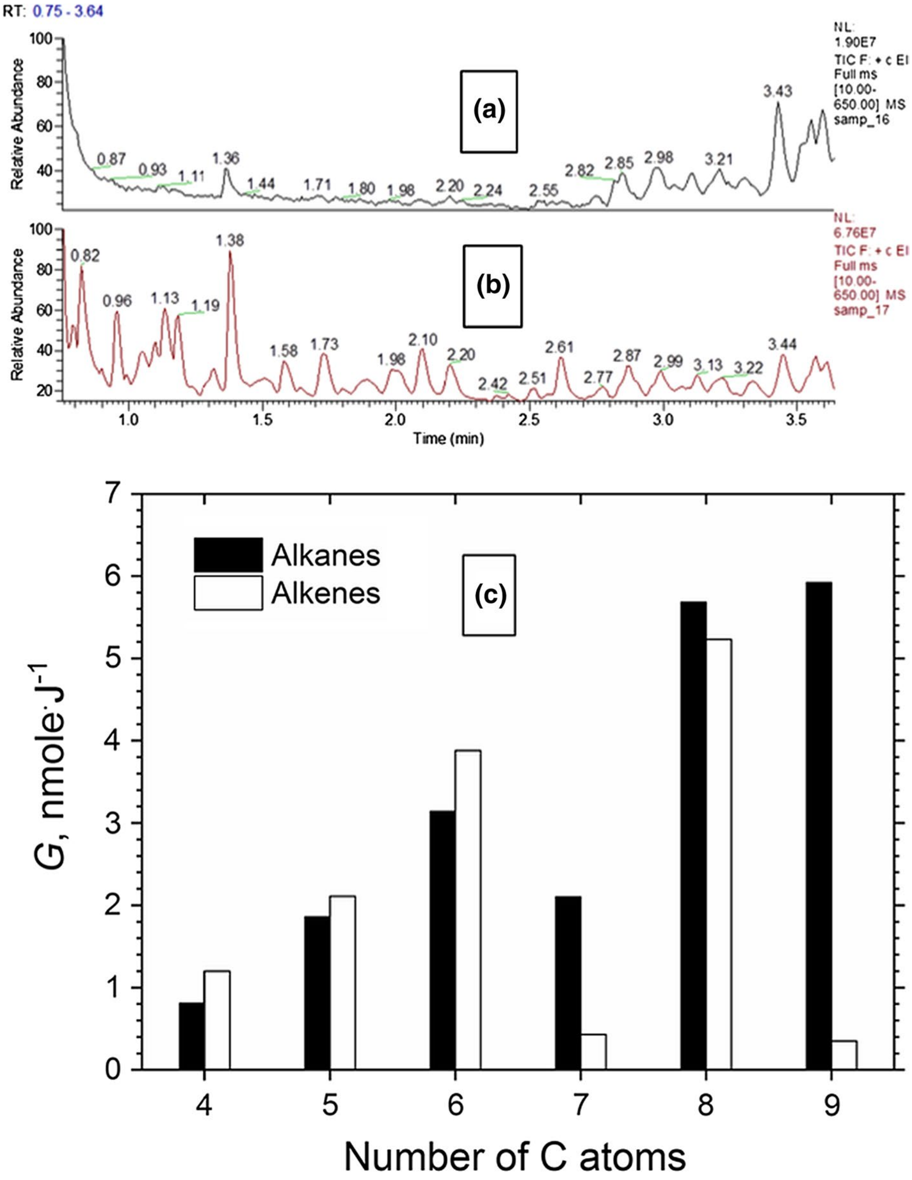


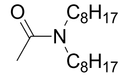
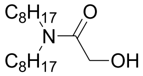
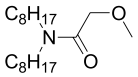
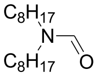
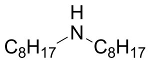
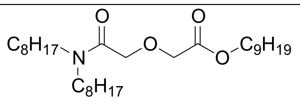
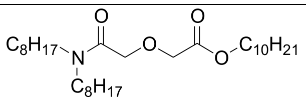
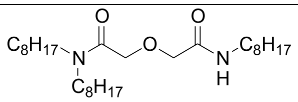
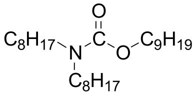
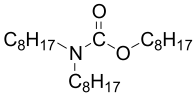
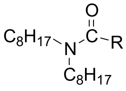
Fig. 4 Sections of chromatograms with peaks of light hydrocarbons in the initial (**a**) and irradiated (**b**) sample S2 and the corresponding calculated radiation-chemical yields of formation of C_4–C_9 hydrocarbons at an absorbed dose of 500 kGy (**c**)

in the extraction mixture. The observed radiation-chemical yields of TODGA decomposition in the samples S1-S4 are in the range 0.4–0.5 µmol J^{-1} (Fig. 1). These values are several times higher than the values expected based on the fraction of TODGA in the system, but about two times lower than the previously observed [9, 10] values for TODGA decomposition in dodecane (0.88 µmol J^{-1} [14]). On the one hand, high decomposition yields indicate a significant impact of the indirect effects of radiation on TODGA molecules, i.e., the active role of the intermediate products of the radiolysis of alcohols and iso-paraffins in the TODGA decomposition. On the other hand, the composition of the studied solutions is more favorable for the protection of TODGA molecules against decomposition than with the system studied in [14]. At the same time, as the absorbed dose increases, the solution is enriched in secondary products that are more reactive than TODGA. It also slows down the decomposition of TODGA at high doses.

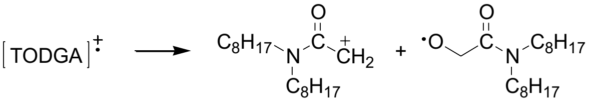
Table 2 presents the key radiolytic products that indicate the hierarchy of TODGA decomposition processes in the studied solutions. The numerous peaks of the Isopar-M components interfere with the detection and identification of some minor radiolytic products. However, most TODGA fragmentation products have been identified and are included in Table 2. Two categories of radiolytic products can be distinguished: products of direct TODGA decomposition and products of these fragments combination with alkyl and alkoxy radicals.

Ionization by low-energy electrons during mass-spectrometry analysis leads mainly to the breaking of C–C and C–N bonds near the carbonyl group of TODGA. In turn, the irradiation of the solutions by accelerated electrons results mainly in the breaking of the ether bond C–O in the center

Table 2 Key nitrogen-containing products of radiolysis of the mixtures of iso-paraffins, alcohols and TODGA (*M*—molecular weight, *G*—radiation-chemical formation yield)

	Product	*M*	Sample	*G*, nmol J^{-1}
P1		283	S1	190 ± 15
			S2	190 ± 18
			S4	150 ± 14
P2		299	S1	180 ± 19
			S2	190 ± 20
			S4	170 ± 18
P3		313	S1	3 ± 1
			S2	
			S4	
P4		269	S1	20 ± 3
			S2	19 ± 3
			S4	12 ± 2
P5	 $C_8H_{17}-\overset{H}{N}-C_8H_{17}$	241	S1	30 ± 4
			S2	32 ± 4
			S3	36 ± 4
			S4	
P6		483	S4	110 ± 10
P7		497	S3	112 ± 9
P8		468	S4	30 ± 3
P9	 $C_8H_{17}-\underset{C_8H_{17}}{N}-\overset{O}{\overset{\|}{C}}-O-C_9H_{19}$	411	S4	100 ± 13
P10	 $C_8H_{17}-\underset{C_8H_{17}}{N}-\overset{O}{\overset{\|}{C}}-O-C_8H_{17}$	397	S4	60 ± 7
P11	 $C_8H_{17}-\underset{C_8H_{17}}{N}-\overset{O}{\overset{\|}{C}}-R$, R–alkyl (C_7–C_{10})	367–409	S4	90 ± 10

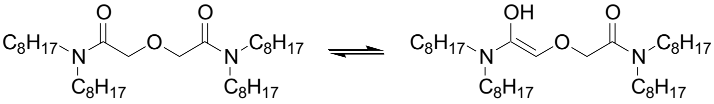
of the TODGA molecule. This is indicated by high yields of formation of of N,N-dioctylacetamide and 2-hydroxy-N,N-dioctylacetamide (products P1 and P2, Table 2). Fragmentation of the primary TODGA radical-cation consists in its separation into radical and ionic centers:



(1)

The rapid capture of a hydrogen atom from the nearest alkyl-containing molecule is typical for alkoxy radicals [15]. In the studied solutions, hydrogen atoms can be removed from paraffin or alcohol, resulting in the formation of P2 (Table 2). In turn, neutralization of the cation by electron or an anionic radical converts it into a radical center with the localized unpaired electron at the terminal CH_2-group. Subsequently, this radical disappears in the processes of disproportionation or combination with alkyl radicals resulting in the products P1 or P11, respectively.

Formation of N,N-dioctylglycolamide (P3) and N,N-dioctylformamide (P4) corresponds to the breaking of the C–C bond in the α-position relative to the carbonyl group of TODGA. The lower yields of the products P3 and P11 indicate a lower probability of such a bond break compared to the ether bond break. The relatively low probability of the α-C–C bond break can be explained, in particular, by the keto-enol tautomerism, which protects the α-C–C bond:

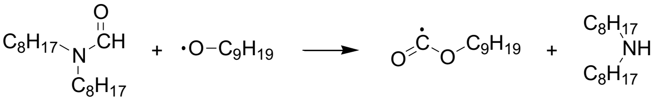


(2)

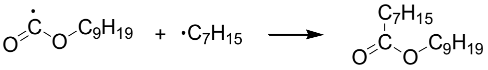
The cleavage of α-C-C and C–N bonds occurs mainly as a result of the indirect radiation processes. The main contributors in such processes are alkoxy radicals formed from alcohols: the higher alcohol content leads to a higher degree of TODGA decomposition. Alkoxy radicals are highly reactive in reactions of attachment to a carbonyl group. These processes predominantly relate to the type of dissociative attachment. A C–N bond often breaks in the resulting adduct leading to the formation of dioctylamine (P5) and n-decyl ester of N,N-di-n-octylamide of diglycolic acid (P7) in the solutions S1 and S3 or to the formation of P5 and P6 in the solutions S2 and S4.

On the other hand, some adducts undergo cleavage of the C–C bond in the α position relative to the carbonyl group with the formation of P9 and elimination of the terminal radical, which is subsequently involved in combination with alkyl radicals (giving P11). The cleavage of the C–N bond in the dioctylamide group is insignificant (forming P8) and it can result from the decomposition of excited TODGA molecules or the interaction of intermediates, one of which contains an imine group and the other contains an amide group. The radiolytic dealkylation of dioctylamine (P5) at high irradiation doses leads to the formation of imine [16] and subsequently to ammonia. These processes contribute significantly to the observed gas evolution in the irradiated solutions. Light radicals—H, CH_3, and C_2H_5—are also involved in the formation of gases. These radicals have a high ability to remove hydrogen atoms from alkyl groups by forming the corresponding gaseous products—H_2, CH_4, and C_2H_6. Experiments demonstrate that increasing alcohol and TODGA content leads to more intensive gas evolution.

The attachment of alcohol alkoxy radicals to both TODGA carbonyl groups becomes possible at high absorbed doses. In this case, breaking of C–N bonds leads to the formation of bis-decyl (in the solution S3) and bis-nonyl (in the solution S4) esters of diglycolic acid (Table 3, products P15 and P16). Alcohol alkoxy radicals are also involved in the formation of esters. For example, the attachment of an alcohol alkoxy radical to the carbonyl group of P4 can result in the elimination of P5 with the formation of a carbon-centered radical, which then disappears in combination with one of the alkyl radicals:



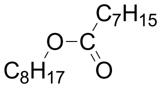
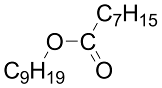
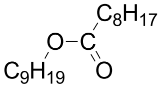
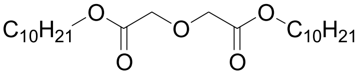
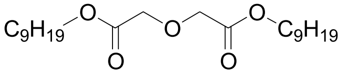
(3)

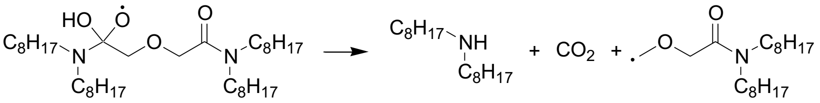


(4)

Such processes lead, in particular, to the formation of esters P13 and P14 (Table 3). Along with alkoxy radicals, alcohol also serves as a source of OH radicals [13, 16, 17]. For example, the yield of C–O bond break is in the range of 0.05–0.08 μmol J^{-1} for C_1–C_4 alcohols. The OH radical can attach to double bonds. In particular, the attachment of OH radical to the carbonyl groups of TODGA leads to the formation of CO_2.

Table 3 Characteristic esters without N atoms in the structure (*M*—molecular weight, *G*—radiation-chemical yield of formation)

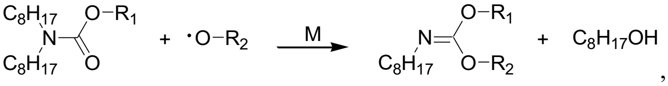
	Ester	*M*	Sample	*G*, nmol J^{-1}
P12		25,642	S4	50 ± 5
P13		27,045	S4	12 ± 2
P14		28,448	S4	8 ± 1
P15		41,462	S3	≤ 2
P16		38,657	S4	≤ 2



(5)

Due to these processes, the observed gas evolution under the irradiation of the investigated solutions increases with increasing the alcohol content. Similar processes of the formation of gaseous compounds can also result from the attachment of H and CH_3 radicals to the carbonyl group. Reactions of OH radicals with the alkenes mentioned above (Fig. 4), lead to the formation of hydroxyalkyl radicals, and subsequently to aldehydes via their disproportionation. The aldehydes can be converted to alkoxy radicals, particularly, upon attachment of H or CH_3 radicals to the carbonyl group. These alkoxy radicals compete with alcohol alkoxy radicals, leading to an increase in the variety of esters through reactions of the type (3). Figure 4 demonstrates that octenes are the main alkenes in irradiated solutions. Thus, they can serve as precursors of octoxy radicals and, as a result, lead to the formation of octyl ester of octanoic acid (P12) and similar esters.

High absorbed doses also favor the repeated reactions of alkoxy radicals with the same carbonyl group, resulting in the formation of amines and imines with two alkoxy substituents at the C atom, e.g.:



(6)

where R_1 and R_2—octyl, nonyl or decyl, depending on the initial alcohol; M—solvent. Masses of such products differ insignificantly from the products P9 and P10; so, their chromatographic peaks are probably superimposed on peaks P9 and P10.

It was previously shown [14] that TODGA cation-radicals are formed not only due to the direct effect of radiation, but also due to charge transfer from the dodecane cation-radical $RH^{\bullet+}$, which has a higher ionization potential:

$$RH^{\bullet+} + TODGA \longrightarrow [TODGA]^{\bullet+} + RH \tag{7}$$

The potentials of electronic activation (ionization and excitation) of iso-paraffins in Isopar-M are very close to the dodecane's corresponding values. Heavy alcohols, n-decanol and n-nonanol, also have similar values of electronic activation potentials. The formation of excited and overexcited molecules and ions of TODGA is possible due to the efficient transfer of charge and energy from iso-paraffins and alcohols to TODGA. These processes determine the higher yield of TODGA decomposition in comparison to other components of the studied solutions. In particular, the yield of radiolytic decomposition of alcohols in the solutions S1 and S2 is almost four times lower than the yield of TODGA decomposition.

Conclusions

In the studied solutions in Isopar-M and heavy aliphatic alcohols, TODGA has the highest sensitivity to ionizing radiation. Direct effects of radiation result mainly in the breaking of the ether bond with the formation of N,N-dioctylacetamide and 2-hydroxy-N,N-dioctylacetamide. TODGA also serves as an effective acceptor of radicals formed from alcohols and iso-paraffins. The most significant impact have alcohol alkoxy radicals, which attachment to the carbonyl group of TODGA leads to the formation of a decyl or nonyl esters with the parallel breaking of the neighboring C–C or C–N bonds.

A high absorbed dose, 500 kGy, results in the accumulation of various unsaturated compounds (mainly alkenes and aldehydes) in the solution. These compounds are involved in competitive radical capture reactions and, thereby, gradually reduce the impact of indirect radiolytic decomposition of TODGA molecules. Consequently, the observed set of radiolysis products varies as the absorbed dose increases. Gas evolution during the irradiation of the solutions is determined by the formation of hydrogen, light alkanes and alkenes, as well as the products of deep fragmentation of TODGA—NH_3 and CO_2.

The solutions containing 6 vol.% of alcohols are more radiolytically stable than the solutions with 20 vol.%. They exhibit a slightly smaller decomposition of TODGA and significantly lower gas evolution under irradiation. Moreover, the nature of the alcohol (n-decanol or n-nonanol) has no significant effect on the radiolytic stability of the solutions. A small difference in the case of lighter alcohol may be due to the greater mobility of the corresponding alcohol radicals and, probably, higher electronic activation (ionization and excitation) potentials, which result in more efficient transfer of energy and charge to TODGA molecules.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Informed consent This article does not contain any studies with human participants or animals performed by any of the authors.

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