

Influence of Boiling on the Radiolysis of Diglyme

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Abstract—The radiolysis of diethylene glycol dimethyl ether (diglyme) in a boiling state has been studied for the first time. Boiling facilitates the cleavage of internal C–O bonds, weakens the cage effect and diglyme regeneration processes, and facilitates the exchange and dimerization reactions of radicals. As compared with radiolysis at room temperature, the amount of unsaturated products of diglyme fragmentation formed during irradiation in the boiling state is smaller by a factor of 4, and the disproportionation products of heavy radicals are found in negligible amounts, if any. The yield of radiolytic decomposition of diglyme under boiling conditions is ~15 molecule/100 eV, which is higher than that at room temperature by a factor of almost 1.5.

Keywords: diglyme, electron accelerator, radiolysis, boiling, fragmentation, disproportionation, dimerization, radical exchange

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It is well known [1] that temperature substantially influences the radiolytic transformations of condensed substances, including polar liquids. Nucleate boiling is an extreme state of liquid when intense vaporization occurs both in the bulk of the liquid and on its surface. Boiling is accompanied by the mass transfer of vapor bubbles, which causes the effective mixing of the irradiated system. In this case, the state of boiling maximally frees molecules from intermolecular attracting forces. In the process of boiling, the molecules of liquid acquire the greatest mobility and elasticity. Under irradiation, the boiling substance is continuously depleted of the light products of radiolysis and, correspondingly, enriched in the heaviest products. All of these factors can be responsible for an essential difference between the radiolysis of a boiling liquid and its radiolysis at room temperature or with insufficient heating.

In this work, we studied the radiolysis of boiling diglyme—diethylene glycol dimethyl ether or 1-methoxy-2-(2-methoxyethoxy)ethane (Fig. 1). Its molecule contains three ether bridges; this fact is of fundamental interest from the point of view of the analysis of the radiation resistance of C–O bonds depending on both their position in the molecule and irradiation conditions.

Diglyme is a popular inert aprotic high-boiling solvent and extractant. It is characterized by high thermal resistance and stability at high values of pH. Diglyme is also considered as a promising component of environmentally appropriate alternative fuels [2]. In particular, diglyme exhibits spontaneous ignition (cetane number, >125), and it is suitable for diesel engines.

The radiolysis of diglyme at room temperature and in a boiling state can be considered as a model for the production of composite fuel with the extended fractional composition of glymes.

In terms of inertness, diglyme is a typical representative of the group of symmetrical diethylene glycol ethers. The molar mass, density, and boiling point of diglyme are 134.18 g/mol, 949.8 kg/dm³, and 163.0°C,

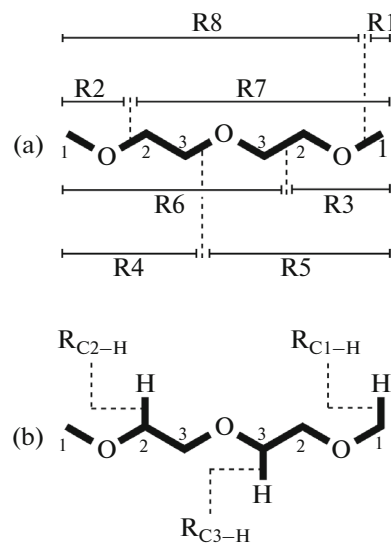


Fig. 1. Structure of diglyme and designation of structure-forming radicals, which correspond to (a) the homolytic cleavage of skeletal C–C and C–O bonds and (b) the rupture of C–H bonds.

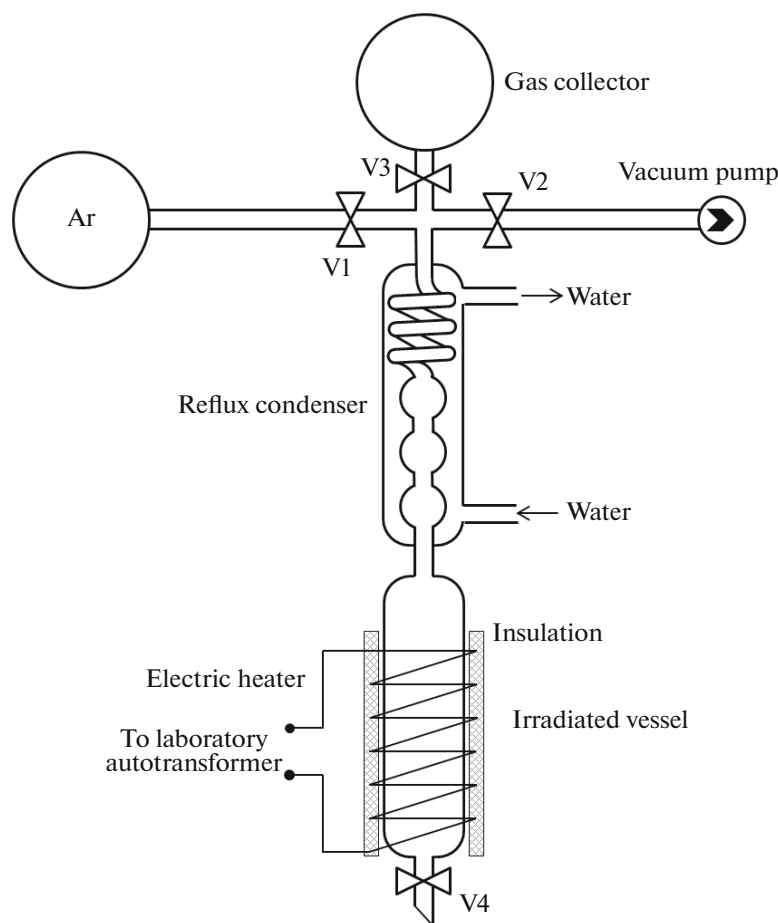


Fig. 2. Laboratory setup for the irradiation of diglyme (the accelerator it is not shown).

respectively [2]. Building blocks for the synthesis of glymes ($-\text{CH}_2-\text{CH}_2-\text{O}-$) can be obtained from almost any renewable biomass, in particular, by radiolysis [3].

The radiolysis of ethers was investigated by many researchers using as an example the simplest acyclic ethers, where one ether bridge connects two alkyl groups (for example, see [4–8]). The radiolysis of ethers with the alternation of the $-\text{CH}_2-\text{CH}_2-\text{O}-$ groups typical of glymes was mainly studied with the use of cyclic ethers as an example [9–13]. It was found that the products of C–O bond cleavage were formed with the highest yields from all of the test ethers, and the H atom was detached from the C atom nearest to the oxygen atom. The mechanism of diglyme radiolysis was not studied in detail; however, it was shown that the yield and properties of solvated electrons in irradiated diglyme are consistent with the general regularities typical of the radiolysis of other ethers [14].

In this work, we analyzed the radiolysis of diglyme at room temperature and under boiling conditions.

EXPERIMENTAL

Diethylene glycol dimethyl ether (99%, Acros) was used after double distillation. The concentration of organic impurities in the purified diglyme did not exceed 0.2 wt %, and their composition and content remained unchanged during irradiation. Deaerated samples were irradiated with fast electrons using a UELV-10-10T linear accelerator (energy, 8 MeV; pulse duration, 6 μs ; pulse repetition frequency, 300 Hz; average beam current, $\leq 800 \mu\text{A}$; sweep width, 245 mm; and sweep frequency, 1 Hz). The following two modes of irradiation were used: the CI mode at an ambient air temperature of $16 \pm 2^\circ\text{C}$ and the BI mode under boiling conditions at 163°C . The radiolysis of boiling samples was carried out on a laboratory setup shown in Fig. 2.

The setup included a heat-resistant glass reaction vessel, a water-cooled reflux condenser, and a collector of gaseous products. A rubber bladder with a volume of 2 dm^3 served as a collector. The rubber collector also served as a damper to impede an excessive increase in pressure in the course of the irradiation of boiling diglyme. The reaction vessel was equipped with asbestos heat insulation and a Nichrome heating

coil, which was connected to a laboratory autotransformer. Diglyme was placed in the reaction vessel together with short glass capillaries as boiling sticks. The reaction vessel was filled by about 60% (35–40 mL). The assembled setup was evacuated to a residual pressure of 20 torr with the aid of a vacuum pump. Evacuation was performed for the removal of dissolved gases from the test diglyme and the elements of the setup. The evacuation of gases was continued for 30 min. Then, argon was let into the setup to balance pressures inside and outside the setup. The procedure of evacuation (at a shorter term evacuation) and filling with argon was repeated three times. Next, the setup was placed in front of the accelerator outlet port. The reflux condenser was cooled with tap water at $16 \pm 2^\circ\text{C}$. Valves V1–V4 served for switching between the evacuation, argon supply, and sampling regimes.

Immediately before irradiation in the BI mode, diglyme was heated to steady-state nucleate boiling. A phenazine dye-doped copolymer standard reference material SO PD(F)R-5/50 (GSO [Certified Reference Material] 7865-2000) was used for dosimetry. The irradiation was performed at an absorbed dose rate of 10–14 kGy/min. The maximum absorbed dose was 215 kGy. Each of the test samples was analyzed immediately after cessation of irradiation. The quantitative analysis of the compositions of initial and irradiated test samples was carried out with the use of an Agilent 5977EMSD/7820AGC gas chromatography–mass spectrometry instrument (carrier gas, helium; glass capillary column of 60 m in length and an inner diameter of 0.25 μm) and the NIST library of mass spectra.

RESULTS

The initial (extrapolated to zero dose) radiation-chemical yield of diglyme decomposition $G(-\text{diglyme})$ at 16°C was 10.4 ± 0.9 molecule/100 eV, whereas it increased to 15.5 ± 1.1 molecule/100 eV in the BI mode (1.08 and 1.61 $\mu\text{mol/J}$, respectively). In irradiated diglyme, to 120 radiolytic products were detected, the majority of which are heavier than the parent diglyme. The yield of H_2 formation in the BI mode did not exceed 3 molecule/100 eV, whereas it was higher by about a third in the CI mode. Figure 3 shows the radiation-chemical yields of light products (LPs)—compounds that can be considered as the primary products of the disproportionation of radicals and their reactions with diglyme—in both of the irradiation modes. In the case of irradiation in the CI mode, the yields of the unsaturated products methoxyethylene and (2-methoxyethoxy)ethylene were noticeably higher than those of methoxyethane and 2,5-dioxahexane, similar saturated compounds. In turn, in the BI mode, unsaturated compounds were formed with smaller yields. The total yields of the LP fraction in the CI and BI modes were about 4.3 and 7.0 molecule/100 eV, respectively.

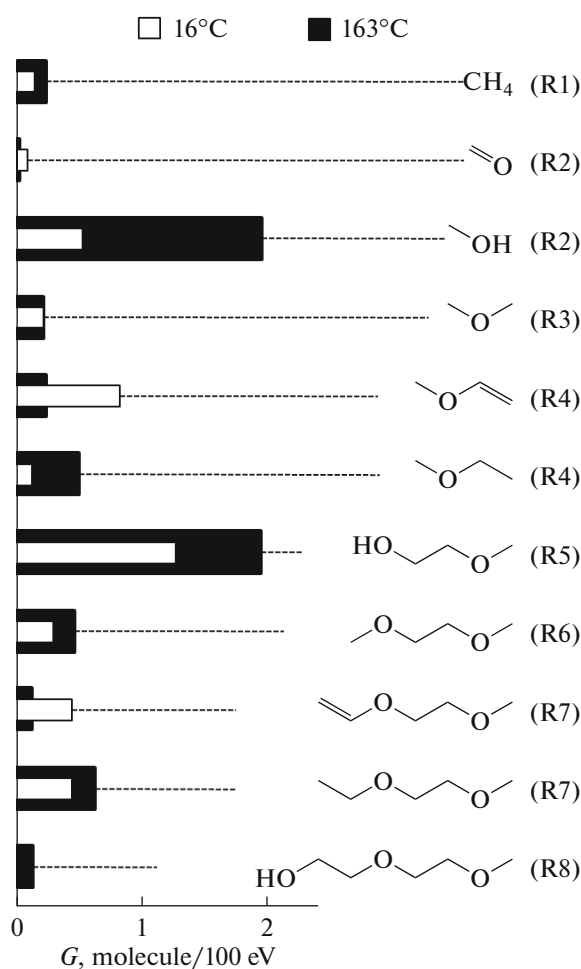


Fig. 3. Radiation-chemical yields of the formation of radical disproportionation products and radical reactions with diglyme at room temperature (16°C) and under boiling conditions of (163°C). The radicals whose reactions lead to the specified products are given in parentheses.

The following products, which can be due to the combination reactions of small radicals, were also present among the LP fraction: ethylene glycol, methyl propyl ether, dimethoxypropane, dimethoxybutane, 3-methoxy-1-propanol, 1-methoxy-2-propanol, 3-methoxy-1,2-propanediol, 1,3-dimethoxy-2-propanol, 1-propoxy-2-methoxyethane, and 1-ethoxy-2-methoxyethane. However, these compounds are minor products: in the BI mode, the yield of each of these products varied from 0.03 to 0.09 molecule/100 eV, whereas the yields of formation of these compounds were several times lower in the CI mode.

There are two compounds that can appear as a result of combination of the methoxy radical with R3 and R6 radicals: dimethoxymethane and 2,4,7-trioxa-octane. The yields of these compounds in the BI or CI mode were 0.03 and 0.05 or 0.01 and 0.05 molecule/100 eV, respectively.

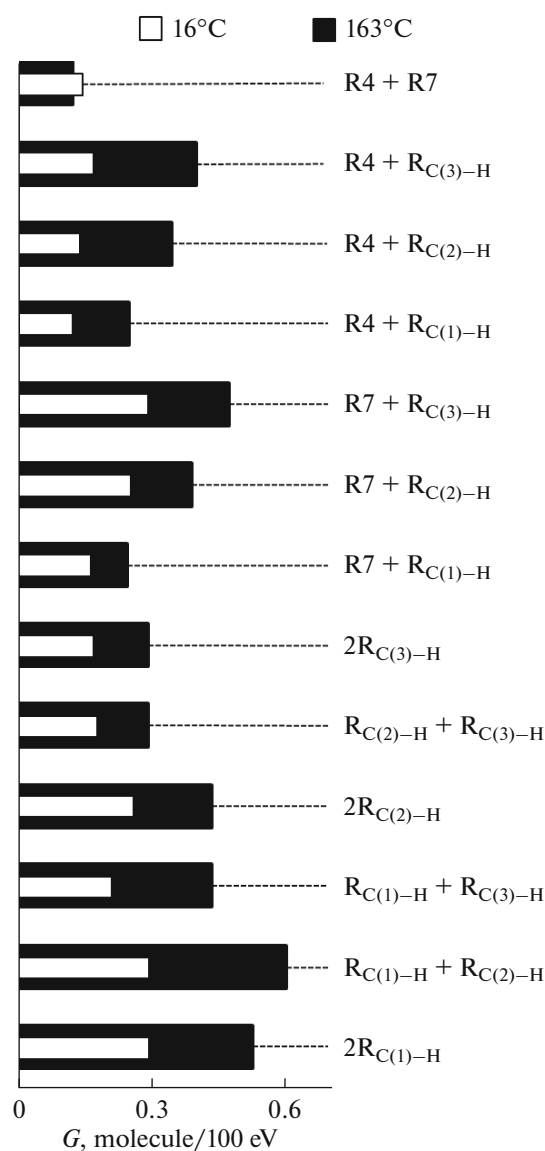


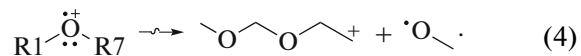
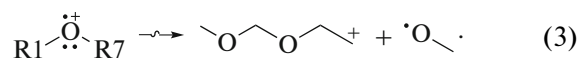
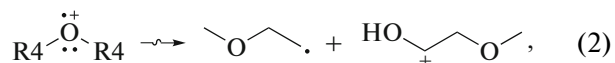
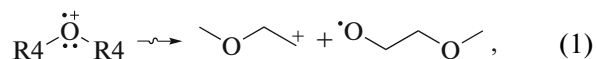
Fig. 4. Radiation-chemical yields of some primary products of radical dimerization at room temperature (16°C) and under boiling conditions (163°C).

Compounds that can be the products of the combination of bulky radicals and whose molar mass is greater than that of diglyme were formed with the highest yields (Fig. 4). The total yields of these heavy products in the CI and BI modes were ~6.2 and ~8.5 molecule/100 eV, respectively.

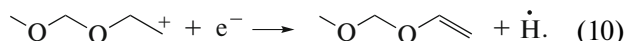
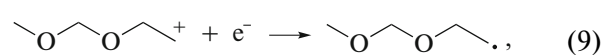
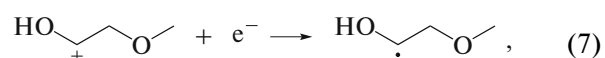
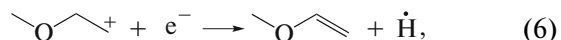
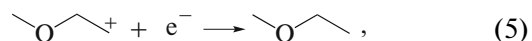
DISCUSSION

Figure 3 shows that light molecular products include a wide range of compounds formed as a result of the rupture of all skeletal bonds. In both of the irradiation modes, the products of C(2)–O and C(3)–O bond rupture, in particular, methanol and

methoxyethanol, respectively, were formed with the highest yields. The R2 and R5 radicals, which are produced via the homolytic decomposition of diglyme molecules or by the fragmentation of primary radical cations, can serve as precursors of these alcohols. Depending on the configuration of the ionized molecule, the energy acquired by it, and the ionization site, the degradation of radical cations can follow various routes [15], for example:



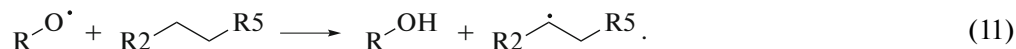
Correspondingly, a portion of radical and molecular products is formed via the neutralization of fragment cations and radical cations:



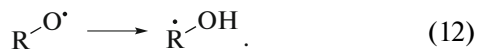
Undoubtedly, the irradiation of boiling diglyme is different from radiolysis in the CI mode. Differences manifest themselves in both the composition and yield of the radiolysis products (Figs. 3, 4). In the BI mode, the total yield of the products of skeletal bond cleavage was much higher than that in the CI mode. Simultaneously, the higher yields of the heavy products of radical combination were observed in the BI mode. The relative yield of unsaturated compounds in the CI mode was much higher. In this case, the products of C(2)–O and C(3)–O bond scission were accumulated in comparable quantities in the BI mode, whereas the products of C(3)–O bond scission were formed with the greatest yields in the CI mode.

An important similarity between the radiolysis of diglyme in the CI and BI modes is a very small yield of the disproportionation products of R2, R5, and R8 radicals. The corresponding aldehydes and alcohols could be expected products of their disproportionation. The observed deficiency of aldehydes indicates that a portion of alcohols can be formed by a molecular mechanism in primary processes like reaction (8), and the R2, R5, and R8 radicals are predominantly

formed in the alkoxy form. The alkoxy radicals are characterized by rapid conversion into an alcohol by

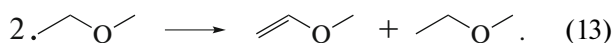


Reaction (11) prevents the conversion of R2, R5, and R8 into less reactive α -hydroxyalkyl radicals, which are more prone to disproportionation

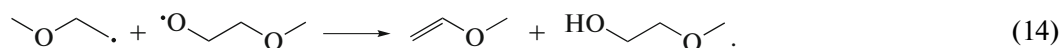


Nonetheless, a small quantity of α -hydroxyalkyl radicals was formed either in reaction (12) or in primary processes like reaction (7). This can be evidenced by the following combination products of α -hydroxyalkyl radicals: ethylene glycol ($G = 0.01$), 3-methoxy-1-propanol (0.10), 1-methoxy-2-propanol (0.01), 3-methoxy-1,2-propanediol (0.02), and 1,3-dimethoxy-2-propanol (0.04). At the same time, dimethoxymethane (0.03) and 2,4,7-trioxaoctane (0.05) were detected simultaneously; they resulted from the combination of the R2 methoxy radical with the R3 and R6 radicals, respectively. However, it is likely that a large portion of the R2, R5, and R8 radicals in an alkoxy form manages to react with diglyme (like reaction (11)); therefore, they almost did not afford the unsaturated products of disproportionation. The total yield of corresponding aldehydes in the BI mode was no higher than 0.01, whereas their yield in the CI mode was close to 0.06 molecule/100 eV.

Note a large difference between the yields of methoxyethylene and methoxyethane in the CI mode. It might be assumed that both of these compounds are formed predominantly by the disproportionation of the R4 radicals



However, reaction (13) would ensure the formation of methoxyethane and methoxyethylene in equal quantities. The additional formation of methoxyethane as a result of the combination of R1



The homolytic cleavage of the C(1)-O, C(2)-O, and C(2)-C(3) skeletal bonds gives rise to radical pairs in which a smaller and, correspondingly, more mobile radical ($\cdot\text{CH}_3$, $\text{CH}_3\text{O}\cdot$, or $\cdot\text{CH}_2\text{OCH}_3$) occurs together with a bulky radical. These small radicals more easily leave the cage; therefore, a rearrangement like reaction (14) in the CI mode is less probable for them. The BI mode weakens the cage effect and increases the mobility of any radical and molecule;

hydrogen atom abstraction from surrounding molecules [1, 6, 7], for example,

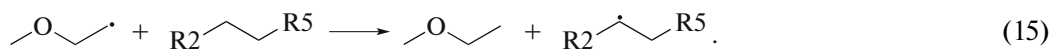
and R3 radicals is highly improbable because methyl radicals R1, as a rule, rapidly abstract hydrogen from surrounding molecules to give methane [1, 16]. At the same time, it can be assumed that the observed yield of methoxyethylene could be somewhat lower because of its partial consumption in the processes of radical addition to a double bond. However, a deficiency of methoxyethane and, correspondingly, an excess of methoxyethylene were actually observed. This could be explained by the fact that methoxyethylene is formed not only via reaction (13) but also as a result of the disproportionation of R4 with smaller R1-R3 radicals. However, the mobile radicals R1-R3 are more prone to the abstraction of H from solvent molecules than to disproportionation [1, 16].

The formation of some amount of methoxyethylene can be due to primary processes like reactions (3) and (6). However, an additional pathway of methoxyethylene formation can be considered. The homolytic dissociation of the C(3)-O bond simultaneously gives rise to large radicals R4 and R5. This radical pair and surrounding diglyme molecules are rather bulky. The viscosity and density of diglyme (1.15 mm²/s and 0.95 kg/m³, respectively) are considerably higher than those of the lighter ethers investigated earlier. Correspondingly, the radical pair R4 + R5 in diglyme can be more strongly influenced by the cage effect, which hampers the diffusion of radicals from the site of their formation but facilitates the reproduction of excited diglyme or a rearrangement of the radicals. In particular, this rearrangement and the disintegration of the excited diglyme molecule can consist in the simultaneous formation of methoxyethanol and methoxyethylene

therefore, the excessive formation of methoxyethylene was not observed.

In the case of BI mode, there is a considerable deficiency of the unsaturated products of the disproportionation of alkyl radicals R3, R4, and R7, where the unpaired electron is located at the terminal methyl or ethyl group. The structure of R3 radicals hampers their disproportionation. However, the R4 and R7 radicals can undergo disproportionation, as in the case

of CI mode. Usually, a lighter radical is converted into a saturated product upon disproportionation. Correspondingly, the R4 radical could give methoxyethane upon cross recombination with heavier radicals. However, among the heavier products (Fig. 3), there was



It is likely that the reactions of hydrogen abstraction by light and heavy radicals are substantially facilitated in boiling diglyme. Accordingly, the majority of R7 radicals can disappear in a similar manner. The detachment of H atoms from diglyme molecules in reactions like (11) and (15) leads to the formation of radicals $\text{R}_{\text{C}1-\text{H}}$, $\text{R}_{\text{C}2-\text{H}}$, or $\text{R}_{\text{C}3-\text{H}}$. Thus, the effective exchange of radicals occurs: small radicals are replaced by bulkier ones. Obviously, this process plays

a more significant role in the BI mode. As a consequence, the yield of the heavy products of radical dimerization and the total yield of diglyme decomposition $G(-\text{diglyme})$ in the BI mode are higher by a factor of almost 1.5 than those in the CI mode (see Fig. 5). In the total set of radiolytic products, the fraction of products heavier than diglyme is about 80 wt %. In addition to a large contribution of radical exchange reactions, the higher value of $G(-\text{diglyme})$ in the BI mode can also be due to factors, such as the aforementioned weakening of the cage effect (weakening of diglyme regeneration) and a certain increase in the yield of fragmentation of primary radical cations. Figure 5 shows that the fraction of radiolytic scissions of the C(2)–O and C(3)–O bonds in a boiling state increased by a factor of 1.5–2, whereas the extent of C(2)–C(3) and C(1)–O bond scissions in the CI mode was somewhat higher than that in the BI mode. The latter effect in the CI mode can be caused, in particular, by the cage effect, which exerts an insignificant influence on the yield of the lightest and mobile radicals but partially prevents the separation of heavy radical pairs.

In both of the diglyme irradiation modes (see Fig. 5), the detachment of H proceeds with almost equal probabilities from any of the C atoms. It is likely that primary processes of the type of reactions (6), (10), and (16)



are responsible for the preferred detachment of H from central C atoms; however, the subsequent distribution of H detachments is leveled off as a result of the aforementioned exchange reactions of types (11) and (15). This leveling in diglyme occurs very effectively because of a high proportion of alkoxy radicals, which rapidly react with the surrounding diglyme molecules.

The recombination of $\text{R}_{\text{C}1-\text{H}}$, $\text{R}_{\text{C}2-\text{H}}$, and $\text{R}_{\text{C}3-\text{H}}$ radicals occurs in different ways. The dimerization of the terminal radicals $\text{R}_{\text{C}1-\text{H}}$ leads to the formation of linear pentaglyme. In other combination processes of heavy radicals $\text{R}_{\text{C}-\text{H}}$, the isomers of pentaglyme with disrupted regularity in the alternation of ether bridges are formed. Figure 4 shows that $\text{R}_{\text{C}3-\text{H}}$ radicals interact with each other to form a smaller amount of dimers than in the case of other radicals; this can be caused by steric hindrances. However, these hindrances are not manifested in the combination of $\text{R}_{\text{C}3-\text{H}}$ with shorter

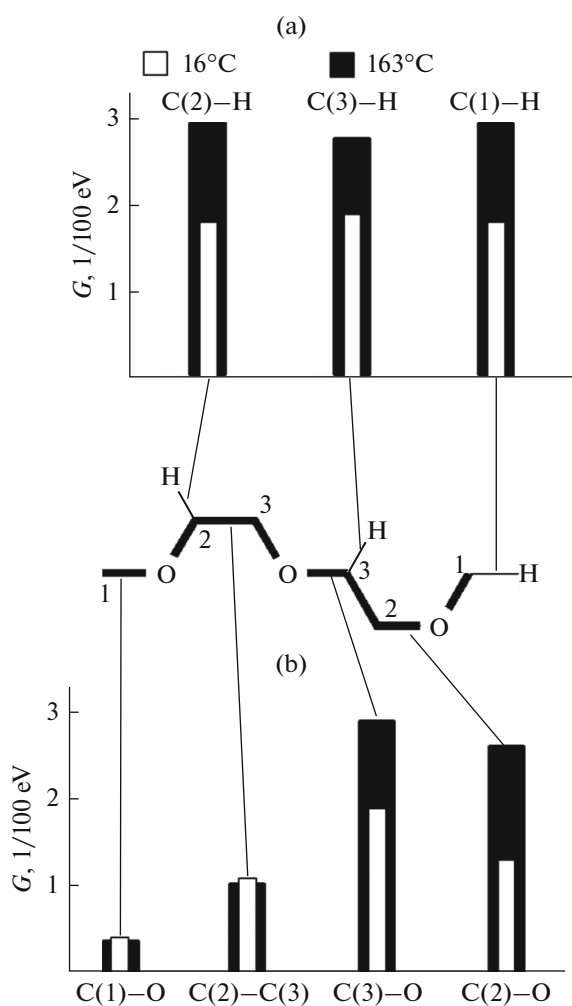


Fig. 5. Radiation-chemical yields of the rupture of (a) C–H bonds and (b) skeletal C–C and C–O bonds in diglyme at a temperature of 16°C and under the conditions of boiling at 163°C. Dotted lines indicate the corresponding bonds.

terminal radicals. Moreover, the unsaturated products of disproportionation are almost not formed in the BI mode. In turn, the total yield of unsaturated diglyme derivatives in the CI mode does not exceed ~1 molecule/100 eV. The low proportion of the unsaturated compounds may be due to the fact that radicals with the unpaired electron on the terminal atom (R1–R8), for which dimerization rather than disproportionation is more typical, participate in the majority of recombination processes [16]. Second, the products of the combination of bulky radicals R_{C-H} with similar and shorter radicals are stable because of the possibility of rapid excess energy dissipation over the polyatomic skeleton.

The low yield of unsaturated compounds in the BI mode does not leave a lot of room for polymerization processes. In turn, in the CI mode, the formation of oligomeric products heavier than pentaglyme is observed with a yield of about 1 molecule/100 eV.

CONCLUSIONS

In comparison with the CI mode, the radiolysis of diglyme in a boiling state gives a yield of molecular products higher by a factor of almost 1.5; about 80 wt % of these products are condensation products; that is, they are heavier than diglyme. The irradiation of boiling diglyme leads to the cleavage of C(2)–O and C(3)–O skeletal bonds with similar efficiencies with the preferred formation of the alcohols methanol and methoxyethanol. In turn, in the CI mode, the C(3)–O bond is predominantly cleaved. The regime of boiling prevents the formation of unsaturated products, in particular, due to an increase in the role of radical reactions with the solvent (hydrogen atom abstraction from the solvent) and radical combination (dimerization) reactions, as compared with the disproportionation reactions of radicals. The predominance of the reactions of hydrogen detachment from molecules of the irradiated medium leads to the effective replacement of small radicals by large ones and, as a result, to the high yields of the heavy products of radical combination. It is likely that the higher mobility and elasticity of radicals in boiling diglyme in dimerization processes facilitates the more rapid achievement of a stable configuration of transition complexes in the form of dimers, whereas the higher viscosity of the medium and the smaller mobility of radicals at a low temperature decelerate the development of a stable configuration; as a result, disproportionation plays a more significant role. Along with radical exchange reactions, the high yield of the radiolytic decomposition of boiling diglyme is due to the weakening of its regeneration processes and to an

increase in the yield of fragmentation of the primary radical cations and excited molecules.

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