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Boiling-induced changes in the mechanism of diglyme radiolysis

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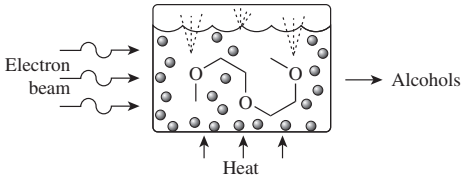
Boiling intensifies the radiolytic conversion of diglyme since it stimulates the cleavage of the C–O bonds in the excited molecules and the primary radical cations, enhances the radical exchange reactions, and weakens the diglyme regeneration reactions.



The molecule of diglyme (diethylene glycol dimethyl ether) **1** containing three ethereal bridges in the linear chain is of fundamental interest from the standpoint of comparing the radiation resistance of C–O bonds, depending on their position and irradiation conditions. In turn, radiolysis can be intensified by heating. Bubble boiling is the extreme state of the liquid being heated. Boiling is accompanied by intensive mass transfer, maximum increase in mobility and elasticity of molecules, as well as weakening of intermolecular interaction. In addition, bubble boiling promotes the disengagement of light and heavy radiolytic products, changing their exposure time in the irradiated volume. Accordingly, irradiation of diglyme in a boiling state is attractive for obtaining new information on the mechanism of fragmentation and synthesis in linear ethers containing several ether bridges.

In practice, diglyme **1** is used as an inert aprotic high-boiling solvent and extragent which has high heat resistance and pH-stability, and is considered as a promising component of environmentally friendly alternative fuels.[2] In particular, it has good autoignition (cetane number > 125) and is suitable for diesel engines. Radiolysis of diglyme can serve as a model for the synthesis of composite fuels with an expanded fractional composition from glymes. Unlike radiolysis of linear ethers containing one oxygen bridge,[3–5] and cyclic ethers,[6–8] radiolysis of glymes has not been previously studied. In the present work, radiolysis of diglyme at room temperature and under boiling conditions was examined.†

In irradiated samples, up to 85 molecular radiolytic products of the first generation are observed, about 80 wt% of them being heavier than the original diglyme **1**. Figure 1 represents the

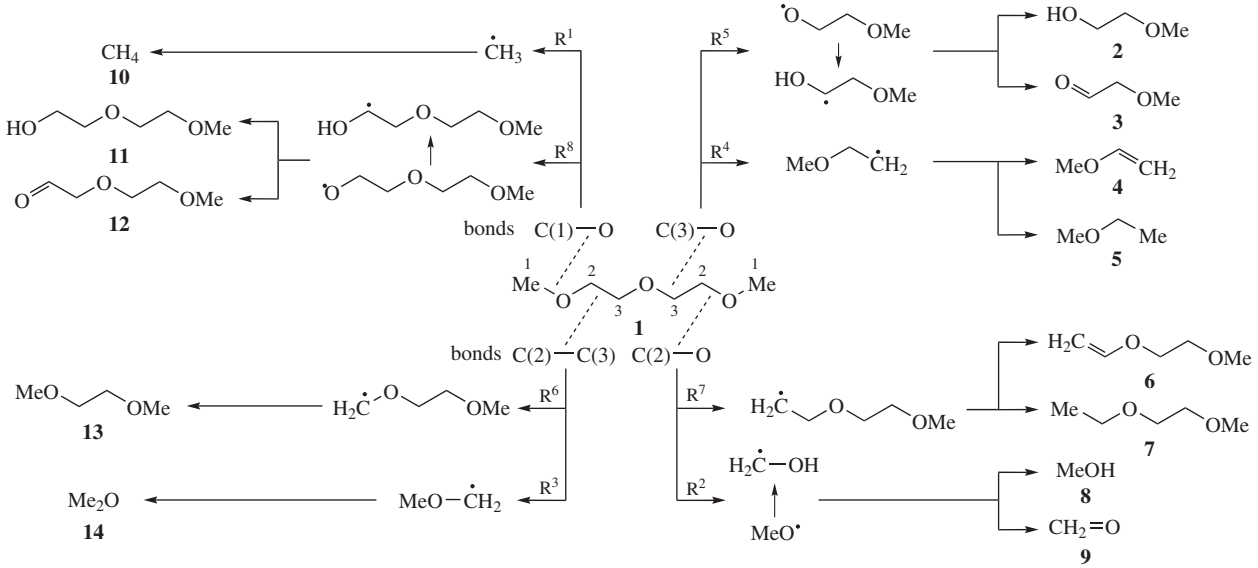


Figure 1 Possible pathways of diglyme **1** transformations in the course of radiolysis *via* homolytic cleavage of C–O and C–C bonds. Symbols from R^1 to R^8 stand for species containing accordingly from 1 to 8 non-hydrogen atoms, namely, C and/or O.

† Diglyme **1** (99%, ACROS) after double distillation was used in the experiments. The molar mass, density and boiling point of diglyme are 134.18 g mol^{-1}, 949.8 kg m^{-3} and 163.0 °C, respectively.[2] Samples were irradiated with accelerated electrons (UEVK-10-10T linear accelerator; energy, 8 MeV; average beam current, ⩽500 μA; beam scanning; scan frequency, 1 Hz). Two irradiation modes were used: at 16±2 °C (AR mode) and under boiling conditions at 163 °C (BR mode). The irradiation was carried out in argon at atmospheric pressure in a closed installation consisting of a reaction vessel, a reflux condenser and a rubber reservoir that acted as a collector of gaseous products. Phenazine dye-doped copolymer film standard reference material SO PD(F)R-5/50 [GSO (Certified Reference Material) no. 7875-2000] was used as dosimeter.

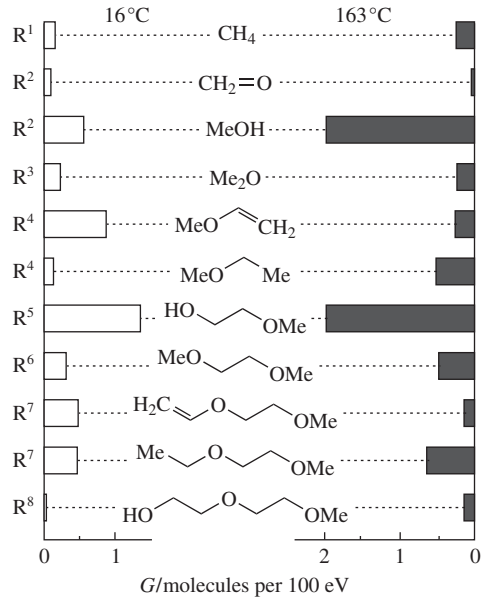
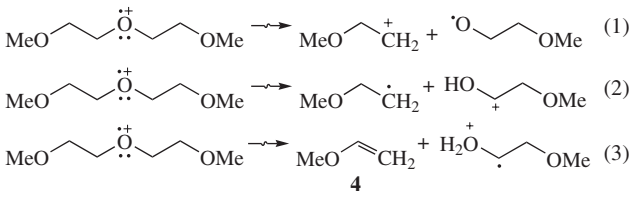


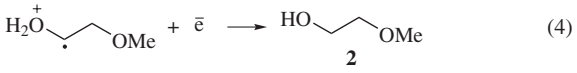
Figure 2 Product distribution of diglyme radiolysis at 16 and 163 °C. On the left the radicals are indicated (see Figure 1) whose reactions lead to these products.

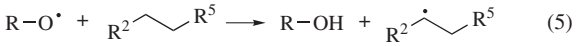
structure of diglyme **1** and the scheme for the formation of primary radicals R^1–R^8 and molecular products **2**–**14** *via* the cleavage of skeletal C–O and C–C bonds. There are several key differences of diglyme radiolysis in BR (boiling at 163 °C) and AR (16±2 °C) modes. First of all, boiling increases the diglyme decomposition yield from 10.4±0.9 to 15.0±1.1 molecules per 100 eV (1.08 and 1.55 μmol J^{-1}, respectively). Boiling levels the probability of C(2)–O and C(3)–O bonds cleavage, prevents the formation of unsaturated compounds, but enhances the reactions of radicals with diglyme.

Figure 2 shows the observed radiation-chemical yields of light compounds which can be attributed to the products of R^1–R^8 disproportionation and the reactions of these radicals with diglyme. Comparison of Figures 1 and 2 indicates that the products of all skeletal bonds cleavage are present in the light fraction. However, the highest yields correspond to 2-methoxyethanol **2** and methanol **8** which are the products of C^3–O and C^2–O bonds cleavage. Undoubtedly, the R^5 and R^2 radicals can be the predecessors of the above-mentioned dominant alcohols. The formation of R^5 and R^2 is due to the fragmentation of excited molecules or primary radical cations of diglyme **1**. For example, in boiling diglyme, depending on the absorbed energy, ionization location and configuration of a molecule undergoing ionization, the R^5 radical can appear along with other ions and radicals in competing processes[9] [equations (1)–(3)].



A very low yield of aldehydes indicates a small role of radical disproportionation reactions in the formation of alcohols. Apparently, alcohols are formed due to the hydrogen abstraction directly in neutralization reactions as well as *via* interaction of alkoxy radicals with diglyme[1,4] [equations (4) and (5)].

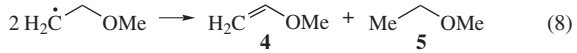




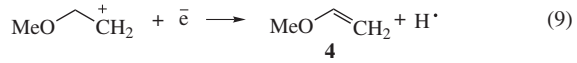
Reactions similar to that outlined in equation (5) prevent the conversion of the R^2, R^5 and R^8 alkoxy radicals to less reactive α-hydroxyalkyl ones [equation (6)] which in turn tend to disproportionation to a higher extent. Nevertheless, a small amount of α-hydroxyalkyl radicals is formed either according to equation (6) or in primary processes similar to that shown in equation (7).

The total yield of the corresponding unsaturated products of α-hydroxyalkyl radicals disproportionation in BR mode does not exceed 0.01, whereas in AR mode their yield is about 0.06 molecules per 100 eV.

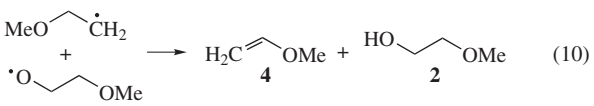
The proportions between the yields of congruent unsaturated and saturated ethers **4**–**7**, **13**, **14** derived from R^3, R^4, R^6 and R^7 oxaalkyl radicals differ significantly in the AR and BR modes, which indicates a disparity in the mechanism of their formation. The imbalance of the yields of methoxyethylene **4** and methoxyethane **5** in the AR mode indicates the small contribution of the process shown in equation (8) in their formation.



Small R^1–R^3 radicals cannot form additional methoxyethylene **4** *via* disproportionation with R^4, since R^1–R^3 are more prone to the abstraction of hydrogen from solvent molecules.[1,10] Accordingly, a more significant source of methoxyethylene formation is provided by primary processes [equations (3) and (9)].



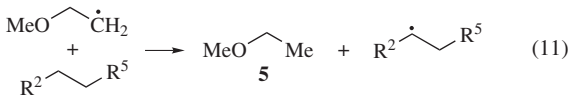
At the same time, one more way of methoxyethylene **4** formation can be assumed. The homolytic cleavage of the C^3–O bond generates simultaneously R^4 and R^5 large radicals. This radical pair and the surrounding diglyme molecules are rather bulky. The viscosity and density of diglyme (1.15 mm^2 s^{-1} and 950 kg m^{-3})[2] are much higher than the corresponding parameters of the lighter ethers studied previously. Accordingly, R^4 + R^5 radical pair can be subject to the cage effect. This effect hinders the migration of radicals from the place of their formation, but promotes the reproduction of excited diglyme or the rearrangement of radicals. In particular, such a rearrangement, as well as the decay of an excited diglyme molecule, can involve the simultaneous formation of methoxyethylene **4** and 2-methoxyethanol **2** [equation (10)].



Homolytic cleavage of C^1–O, C^2–O or C^2–C^3 skeletal bonds gives a radical pair where the large radical is adjacent to the smaller and, therefore, more mobile radical (Me•, MeO• or $MeOCH_2$•). Such small radicals leave the cage more easily and, thus, the rearrangement of type (10) in AR mode is less likely for them. The BR mode weakens the cage effect and increases the mobility of any radicals and molecules and, accordingly, excess methoxyethylene formation is not observed.

Dose rate was 10–14 kGy min^{-1}, and the maximum absorbed dose was 215 kGy. After irradiation was completed, quantitative analysis of the initial and irradiated samples was immediately carried out using gas chromatograph and mass spectrometer (Agilent 5977EMSD/7820AGC, helium, 60 m glass capillary column with 0.25 μm internal diameter, NIST library).

The apparent deficit of unsaturated disproportionation products (see Figure 2) indicates that methoxyethane **5** under boiling conditions, most likely, arises from R^4 radicals *via* the abstraction of hydrogen atoms from surrounding molecules [equation (11)]. Apparently, boiling significantly helps small and larger radicals (like R^4 and R^7) to abstract hydrogen atom from diglyme **1** molecules.



(11)

The abstraction of H atoms from diglyme in reactions outlined in equations (5) and (11) leads to formation of the heaviest radicals, whose subsequent combination with similar and smaller radicals generates products heavier than diglyme. The total yield of such heavy products in AR and BR modes is ~6.2 and ~8.0 molecules per 100 eV, respectively. All the fragmentary radicals in boiling diglyme are capable of abstracting hydrogen atoms from surrounding molecules. This phenomenon underlies the effective exchange of radicals and gives an important difference to BR mode from AR mode. The enhanced exchange of small radicals into larger radicals is one of the most important reasons for a 1.5-fold increase in the diglyme decomposition yield in the boiling state.

Figure 3 summarizes the experimental data on the yields of radiolytic fragmentation of C–O, C–C and C–H bonds in diglyme **1**. As seen, the realization of the radiolytic cleavages of C^2–O and C^3–O bonds increases by a factor of 1.5–2 due to boiling,

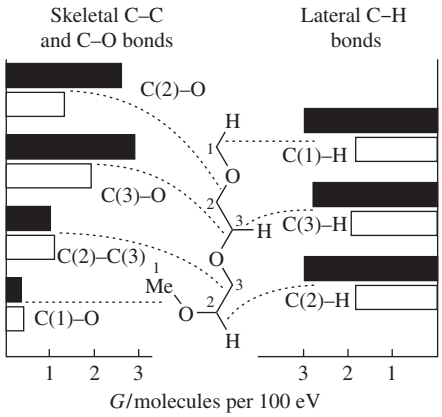


Figure 3 Radiation-chemical yields of the cleavage of lateral C–H bonds and skeletal C–C and C–O bonds in diglyme at (□) 16 and (■) 163 °C. Dotted lines indicate the corresponding bonds.

whereas in the AR mode, cleavages of the C^2–C^3 and C^1–O bonds are realized somewhat more frequently than in the BR mode. In particular, the latter phenomenon in AR mode may be due to the cage effect, which hardly influences the yield of the lightest and mobile radicals, but partially prevents the separation of heavy radical pairs. The realization of the cleavages of CH bonds does not depend much on their position in the molecule, which is undoubtedly caused by the exchange of radicals and a large fraction of the reactive alkoxy radicals participating in this exchange.

In conclusion, in comparison with the AR mode, the radiolytic decomposition of boiling diglyme **1** occurs 1.5 times more efficiently. Boiling intensifies the fragmentation of primary cation-radicals and excited molecules. In this case, the main contribution to the decomposition is made by the cleavages of the skeletal C^2–O and C^3–O bonds, approximately equal in efficiency. Boiling eliminates the cage effect, enhances both the reactions of radicals with the solvent and the formation of dimers and, thereby, prevents the regeneration of diglyme and the formation of unsaturated products of radical disproportionation.

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