



Radiation-chemical transformations of diethylene glycol dimethyl ether at room temperature and at boiling point

A.V. Ponomarev*, S.I. Vlasov, E.M. Kholodkova

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Prospect, 31, Moscow 119071, Russia

ARTICLE INFO

Keywords:

Diglyme
Radiolysis
Electron accelerator
Boiling point
Radical recombination
Radical exchange

ABSTRACT

Diethylene glycol dimethyl ether (diglyme) is interesting as a representative of ethers with several oxygen bridges in the molecule and as a model alternative fuel. A comparative study of the diglyme radiolysis at room temperature and at the boiling point was carried out. Boiling facilitates the cleavage of internal C–O bonds, weakens the cage effect and diglyme regeneration processes, and also favors radical exchange and dimerization reactions. Unlike radiolysis at room temperature, irradiation at the boiling point generates four times less unsaturated fragmentation products and practically does not give disproportionation products of heavy radicals. The yield of radiolytic decomposition of boiling diglyme reaches 15.5 molecules/100 eV, which is almost 1.5 times higher than at room temperature.

1. Introduction

Heating is an important factor that intensifies radiolytic transformations of condensed organic substances (Woods and Pikaev, 1994), including polar liquids. Bubble boiling when intense vaporization takes place both in the bulk and on the surface of the liquid is one of the extreme states. Boiling is accompanied by a mass transfer of vapor bubbles which provides a fairly effective mixing of the system being irradiated. At the same time, the boiling state maximally weakens the intermolecular interaction. Molecules of boiling liquid become the most mobile and elastic. Under irradiation, boiling matter is continuously impoverished by light radiolytic products and, accordingly, is enriched with the heaviest products. All these factors can significantly change the radiolysis of the boiling liquid compared to that at room temperature or with insufficient heating.

In the present work the radiolysis of boiling diglyme (Fig. 1) - diethylene glycol dimethyl ether or 1-methoxy-2-(2-methoxyethoxy)ethane - has been investigated. Its molecule contains three ether bridges and therefore diglyme is of fundamental interest in order to compare the radiation resistance of C–O bonds depending on their position in the molecule and the irradiation conditions. Fig. 1 represents a scheme for the formation of primary radicals and molecular products via homolytic cleavage of skeletal bonds. Radicals formed via the cleavage of C–H bonds are shown in Fig. 2.

Diglyme is popular as an inert aprotic high-boiling solvent and extractant which has high heat resistance and pH-stability. Diglyme is also considered as a promising component of environmentally friendly

alternative fuels (Grekhov and Markov, 2010). In particular, diglyme has good autoignition (cetane number > 125) and is suitable for diesel engines. Radiolysis of diglyme at room temperature and in the boiling state can be considered as a model for the synthesis of composite fuels with an expanded fractional composition from glymes.

By its inertness, diglyme is a typical representative of the group of symmetric ethers of diethylene glycol. The molar mass, density and boiling point of diglyme are 134.18 g/mol, 949.8 kg/dm³ and 163.0 °C, respectively (Grekhov and Markov, 2010). Building blocks (-CH₂-CH₂-O-) for glymes synthesis can be obtained virtually from any renewable biomass, including by radiolysis (Ponomarev et al., 2012).

Radiolysis of acyclic ethers whose molecules contain one oxygen bridge has been investigated by many authors (see, for example, Cooper et al., 2003; Wu et al., 2002; Vermeer and Freeman, 1974; Ng and Freeman, 1965; Newton, 1957). Radiolytic transformations of ethers containing alternating (-CH₂-CH₂-O-) groups have been studied mainly on the example of cyclic compounds (see, for example, Kiss and Teplý, 1971; Baxendale and Rodgers, 1967; Kuruc and Šeršeň, 1990; Nesterov, 1998; Von Sonntag and Schuchmann, 2010). As has been shown in all the ethers studied, the products of C–O bond cleavage are formed with the greatest yields, and the H abstraction occurs from the C atom closest to the O atom. A detailed study of the diglyme radiolysis mechanism was not carried out however it was shown that the yield and properties of solvated electrons in irradiated diglyme agree with the general patterns characteristic of the radiolysis of other ethers (Jou and Dorfman, 1973).

In the present work, radiolysis of diglyme was analyzed at room

* Corresponding author.

E-mail address: ponomarev@ipc.rssi.ru (A.V. Ponomarev).

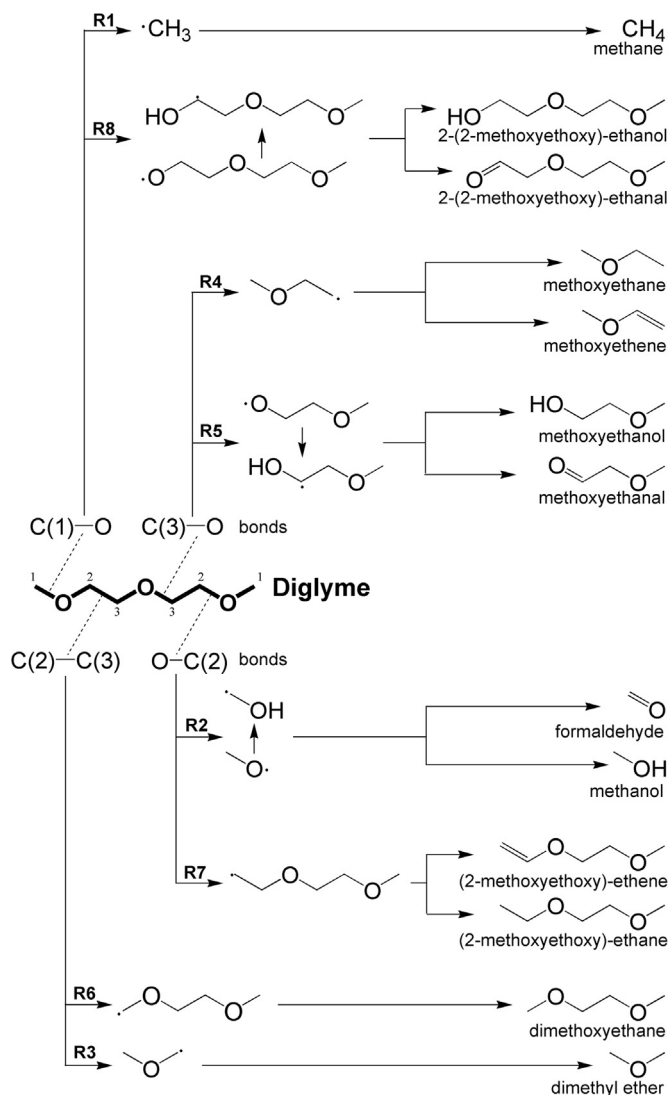


Fig. 1. Structure of diglyme and scheme of product formation via homolytic cleavage of C–O and C–C skeletal bonds.

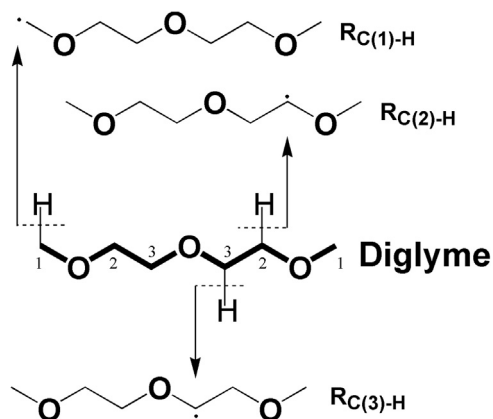


Fig. 2. The designation of radicals formed by H abstraction.

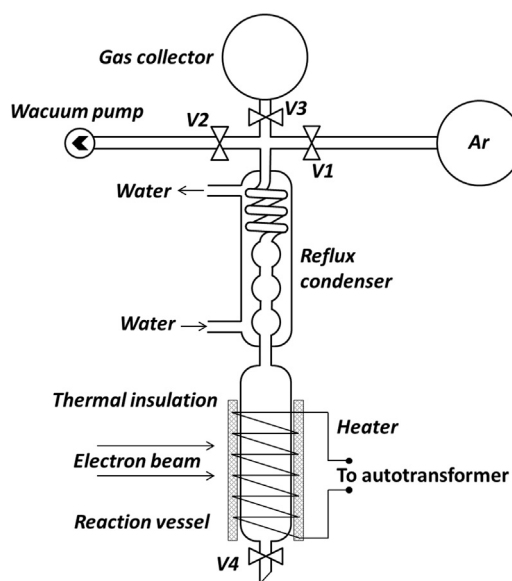


Fig. 3. Laboratory installation for irradiation.

distillation was used in the experiments. The content of organic impurities in purified diglyme was less than 0.2 wt%, and their composition and concentration did not change during irradiation. Deaerated samples were irradiated with accelerated electrons (UEVK-10-10T linear accelerator; energy, 8 MeV; average beam current, $\leq 500 \mu\text{A}$; beam scanning; scan frequency, 1 Hz). Two irradiation modes were used: at $16 \pm 2^\circ\text{C}$ ambient temperature (CI mode) and under boiling conditions at 163°C (BI mode). The equipment for the samples radiolysis is shown in Fig. 3.

The laboratory installation contained a reaction vessel made of heat-resistant glass, a water-cooled reflux condenser and a collector of gaseous products. A 4-dm³ rubber chamber served as a gas collector. The rubber collector also functioned as a damper preventing excessive pressure buildup in the installation during the irradiation of boiling diglyme. The reaction vessel was equipped with asbestos thermal insulation and a nichrome heater connected to a laboratory auto-transformer. Diglyme (35–40 ml, $\approx 60 \text{ vol}\%$) was placed in a reaction vessel together with short glass capillaries that stimulate boiling. The assembled installation together with the sample was degassed to 20 Torr residual pressure by a vacuum pump. Following a 20-min evacuation the installation was filled with argon until the pressure was equalized inside and outside the installation. The procedure of evacuation (with a shorter pumping-off time) and filling with argon was repeated three times. Then the installation was placed in front of the accelerator beam window. The reflux condenser was cooled with tap water at $16 \pm 2^\circ\text{C}$. V1–V4 valves served to switch between the modes of evacuation, supply of argon and sampling.

Immediately before irradiation in BI mode the diglyme was heated to a stable bubble boiling. 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. Dose rate was 10–14 kGy/min, and the maximum absorbed dose was 215 kGy. Each sample was analyzed immediately after irradiation was completed. Quantitative analysis of the composition of the initial and irradiated samples was carried out using gas chromatograph and mass spectrometer (Agilent 5977EMSD / 7820AGC, helium, column-glass capillary 60 m long with an internal diameter of 0.25 μm , NIST mass spectra library).

temperature and under boiling conditions.

2. Experimental

Diethylene glycol dimethyl ether (99%, ACROS) after double

3. Results and discussion

Up to 120 molecular radiolytic products, most of which are heavier

Download English Version:

<https://daneshyari.com/en/article/8251139>

Download Persian Version:

<https://daneshyari.com/article/8251139>

[Daneshyari.com](https://daneshyari.com)