Chemistry

DETERMINATION OF THE REACTION RATE CONSTANT FOR THE INTERACTION OF DIETHYL SULFOXIDE WITH THE HYDROXYL RADICAL ON THE BASIS OF COMPETITIVE KINETICS

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In the paper, radical scavenging property of diethyl sulfoxide towards hydroxyl radical with the use of competitive reaction kinetics has been investigated. The obtained results confirm that diethyl sulfoxide compared with dimethyl sulfoxide has a greater ability to capture OH radical.

Keywords: diethyl sulfoxide, dimethyl sulfoxide, hydroxyl radical, UV radiation, 4,4-dimethyl-4-nitrosoaniline, rate constant.

Introduction. In our earlier works, it was shown that diethyl sulfoxide (DESO) like dimethyl sulfoxide (DMSO) has unique physicochemical properties and can find biomedical applications [1–3]. Particularly, DESO compared with DMSO is more effective for preservation of the membrane potential after freezing-thawing. DESO–water mixtures form an amorphous glassy state and exhibit cryoprotective abilities [2]. On the other hand, it is well known that DMSO acts as radical scavenger and radioprotectant. DMSO can capture the hydroxyl radical to form methane sulfuric acid (CH_3SOOH). The rate constant for this reaction in neutral media is $4.2 \cdot 10^9 \ M^{-1}s^{-1}$.

As DMSO has low toxicity, it has been suggested as a molecular probe for detection and quantitation of hydroxyl radicals in biological systems [4].
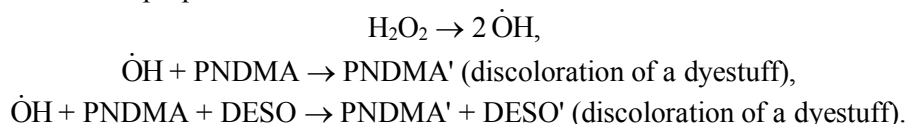
In this work, radical scavenging ability of DESO towards hydroxyl radical with the use of competitive reaction kinetics has been investigated.

Materials and Methods. DESO was synthesized and purified according to the procedure in [5]. Tested by gas chromatography purity was greater than 99.5 mass %, the water content, after drying on molecular sieves, was lower than 0.01 mass %. DMSO (99.9% purity) and dyestuff 4,4-dimethyl-4-nitrosoaniline (PNDMA) were purchased from "Aldrich Chemical Co" and used without further purification. A photolytic equipment with mercury lamp was used as a source of UV radiation. A dyestuff PNDMA was used for its competitive oxidation with hydroxyl radical. In [6, 7], to reveal, the reaction ability of some organic compounds towards hydroxyl radical a competitive kinetics approach was suggested [8]. According to this approach to generate hydroxyl radicals a photolysis (λ=313 *nm*) of hydrogen

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peroxide solution (10^{-3} *M*) has been done. The UV-vis spectrophotometric measurements were carried out using Specord 50PC spectrophotometer in the wavelength range from 400 to 800 *nm*.

Results and Discussion. For the above mentioned reactions the following scheme can be proposed:

$$H_2O_2 \rightarrow 2\,\dot{O}H,$$

$$\dot{O}H + PNDMA \rightarrow PNDMA' \text{ (discoloration of a dyestuff)},$$

$$\dot{O}H + PNDMA + DESO \rightarrow PNDMA' + DESO' \text{ (discoloration of a dyestuff)}.$$

Concentration decrease of PNDMA was monitoring photometrically at $\lambda=440$ *nm* according to the Lambert-Beer law. The dependences of PNDMA absorbance (*A*) on UV radiation time (*t*) in the presence of various concentration of DESO are shown in Fig. 1. From these dependences the slopes (tg α), which are directly compared with the rate of reaction, have been calculated.
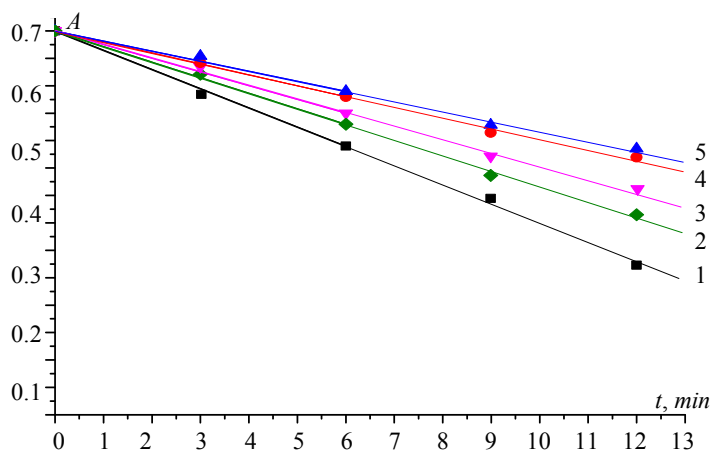

Fig. 1. The dependence of PNDMA absorbance on UV radiation ($\lambda=313$ *nm*) time in the presence of DESO with following concentrations, 10^{-5} *M*: 1 – 0; 2 – 2.82; 3 – 5.64; 4 – 7.05; 5 – 8.46.

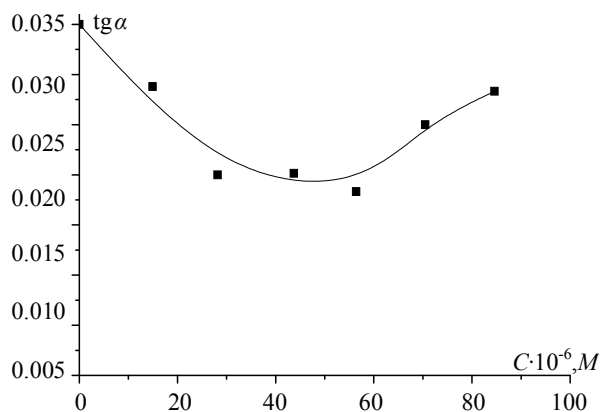The plot of the dependence of the reaction rate on the concentration of DESO is shown on Fig. 2.

Fig. 2. The dependence of tg α on DESO concentration.

To determine the rate constant for the reaction of OH radical with DESO the following general equation has been used [7, 9]:

$$k_{\dot{O}H+DESO} = 1.25 \cdot 10^{10} \frac{[PNDMA]}{[DESO]} \cdot \left(\frac{W_1}{W_2} - 1 \right) \ (M^{-1}s^{-1}),$$

where $1.25 \cdot 10^{10}$ is the rate constant of the reaction $PNDMA + \dot{O}H$; W_1 and W_2 are the rates of reactions in the presence and absence of DESO. From the analysis of kinetic data the value of rate constant for the reaction of DESO with hydroxyl radical was determined: $k_{\dot{O}H+DESO} = 7.5 \cdot 10^9 \ M^{-1}s^{-1}$. It should be noted that for the reaction of DMSO with hydroxyl radical the rate constant obtained on the basis of above mentioned competitive kinetics is in good agreement with literature data: $k_{\dot{O}H+DESO} = 4.2 \cdot 10^9 \ M^{-1}s^{-1}$ [6].

Thus, the obtained results confirm that DESO has ability to capture OH radical and this property is somewhat more in comparison with DMSO.

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