

## Spontaneous Oligomerization of Epibromohydrine With Benzimidazole

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### Abstract

*In this paper, we have synthesized oligomers of epibromohydrine (EBG) with benzimidazole (BIZ) for the first time. According to spectroscopic studies and the dependence of the reaction rate on the ratio of the starting materials, the temperature the mechanism and kinetics of the objective laws of synthesis processes were established. It was established for the first time that in the interaction of EBG with BIZ spontaneous polymerization process proceeds with the formation of soluble oligomeric products containing quaternary ammonium groups. Zwitter-ionic reaction mechanism of interaction EBG with BIZ was proposed. A series of new metal-containing oligomers based on the products of interaction EBG with BIZ with the salts of divalent metals - copper and cobalt that has stabilizing properties has been synthesized and studied.*

**Keywords:** oligomerization, zwitter-ionic mechanism, quaternary ammonium groups.

### Introduction

Studies on synthesis and study of properties of oligomers containing active groups with reaction ability represent definite theoretical interest<sup>[1,2]</sup>. The most common methods of synthesis of oligomers with reaction ability are ion and radical oligomerization of reactive monomers, the method of chemical transformation and others. As it is known, these methods differ with multistage complexity of oligomerization and are often accompanied by side reactions<sup>[3,4]</sup>.

In this aspect a particular interest represents obtaining reactive oligomers by spontaneous oligomerization at relatively low temperatures (room and above) and in the absence of initiator<sup>[5-8]</sup>. For example, based on the products of spontaneous oligomerization of EBG with BIZ can be synthesized oligomers with reaction ability having improved colloid-chemical, physico-chemical and physico-mechanical properties.

The choice of EBG nitrogen-containing heterocyclic as starting reagents for the synthesis of reactive oligomers: BIZ is perspective as EBG, being relatively accessible polyfunctional monomer, due to the presence of functionally active groups as the epoxy group and a bromine atom readily undergoes a variety of chemical reactions under specific conditions, and these studies allow to reveal the influence of the heterocyclic nature and presence of BIZ amino group in spontaneous oligomerization process, allowing to obtain the products with complex forming properties with the salts of divalent metals having effective stabilizing properties.

In literature there is very little information on the synthesis and systematic studies of such reactions, and found reports basically have the character of a patent. No information concerning to the possibility of obtaining reactive oligomers by spontaneous oligomerization under interaction of EBG with BIZ, therefore the study of the kinetics and mechanism of the respective oligomerization process is very important.

## Materials and Methods

Epibromohydrine, benzimidazole, oligomer, the salts of divalent metals - copper, cobalt.

**Methods** IR-, PMR-, EPR-spectroscopy.

## Result and Discussion

We have found that in the interaction of EBG with BIZ spontaneous oligomerization process proceeds. The study of kinetics of the objective laws of spontaneous oligomerization of EBG with BIZ in initial stage of conversion with different molar ratios of components showed that the highest yield of the oligomer is achieved in an equimolar ratio of starting monomers.

The reaction rate in the steady period is proportional to the concentration of EBG in degree 1,12 and benzimidazole in degree 0,97. According to the results of kinetic studies, the overall rate of spontaneous oligomerization of EBG with BIZ is described by the equation:  $V=K[EBG]^{1,12} \cdot [BIZ]^{0,97}$

The results indicate that the reaction of spontaneous oligomerization, apparently mainly come involved in quaternization reaction of amino compounds of EBG molecules.

In order to find optimal conditions for obtaining oligomers based on EBG with BIZ an oligomerization was conducted in the medium of solvents with different dielectric permeability (ethanol, tetrahydrofuran and water). It was experimentally established that the rate of spontaneous oligomerization proceeding in the interaction of EBG with BIZ depends on medium occurring rather easily in water and in polar organic media.

Increasing the polarity of the medium promotes acceleration of the process of spontaneous oligomerization, and in all cases, the greatest rate is observed in aqueous medium. Increasing the rate of the process of spontaneous oligomerization with increase of the medium polarity in the interaction of EBG with BIZ, apparently, can be explained by the acceleration of the Menshutkin reaction, being limiting stage of the spontaneous oligomerization process. In the interaction of EBG with BIZ due to the high reactivity of the bromine atom EBG and nucleophilicity of nitrogen-containing compounds have the quaternization of amino compounds in the intermediate product which enhances the activity of the functional groups, which in its turn increases the rate of spontaneous oligomerization.

In order to determine the dependence of the spontaneous oligomerization rate proceeding in the interaction of EBG with BIZ in temperature a series of experiments was carried out in ethanol at 298-313 K, that the conversion rate of the initial monomers into oligomer increases with the increase of the temperature and its dependence on the reverse values of the temperature in the range 298- 313 K obeys the Arrhenius equation. The overall activation energy, determined from the angle tangent of the slope of the curve defined in Arrhenius coordinates makes 30,1 kDj/mol, which is close to the activation energy of the Menshutkin reactions. It should be noted that during the spontaneous oligomerization of EBG with BIZ at 313K the yield of the oligomer EBG with BIZ in equimolar ratio of the starting components reached 94-95%.

To elucidate the nature of the interaction reaction of EBG with BIZ were recorded by PMR- and IR-spectra of the initial components, as well as the final product at room temperature. Oligomerization of EBG with BIZ was studied by very sensitive method PMR-high resolution spectroscopy, where EBG is characterized by two multiple signals at 2,5 and 2,75 centered at 2,65 m.f. inherent protons of the methylene group of the epoxide ring, and multiple signal relatively with weak intensity at 3,1 m.f. refers to a proton of methylene group of epoxide ring. This assignment is supported by the fact that the form of these signals identical to the corresponding signals in the spectrum of propylene oxide. The multiple signal, located in weaker fields at 3,45 m.f. refers to two ducts of methylene group bonded to bromine atom.

Data of PMR spectrum show that the protons signals of the aromatic rings BIZ appear in 7,5-7,9 m.f. and the protons signals of NH-groups are observed at 4.4 m.f.

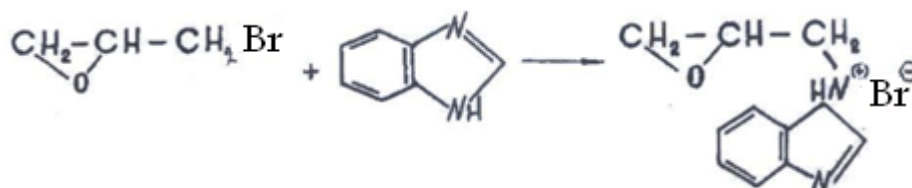
In the PMR spectrum of the oligomer synthesized on the basis of EBG with BIZ, appear protons signals of aromatic rings BIZ in multiple form centered 7,6 m.f., protons of methylene  $N^+CH_2$  appear as multiplets in the region 5,2 m.f. Downfield shift of  $N^+CH_2$  signal is due to obviously formation of quaternary ammonium group. In this case is also formed multiple signals of protons of the methylene group of the cycle in 3,76 m.f., indicating that the detection of the epoxy group of EBG in the process of spontaneous oligomerization.

The IR spectrum of the oligomer has an absorption band  $1630\text{ cm}^{-1}$  related to the valent vibrations of C = N bonds,  $1600-1500\text{ cm}^{-1}$  due to valent vibrations of aromatic ring. Valent vibrations of C-Br bond ( $720-750\text{ cm}^{-1}$ ) belonging to  $CH_2Br$  group of EBG, as well as the deformation vibration of NH group ( $1545\text{ cm}^{-1}$ ) completely disappear due to the formation of new quaternary ammonium groups in the region of  $2200-2500\text{ cm}^{-1}$ . It also formed new intensive absorption bands in the region of  $1050-1100\text{ cm}^{-1}$  belonging to asymmetric valent vibrations of ether (-C-O-C-) bond by opening the epoxy groups ( $1260, 930-855\text{ cm}^{-1}$ ) EBG in spontaneous oligomerization process of EBG with BIZ.

It was experimentally found that usual inhibitors of radical oligomerization (difenilpikrilhidrazine, 2,2,6,6-tetramethylpiperidyl-1-oxyl, hydroquinone, and air oxygen) on spontaneous oligomerization process of EBG with BIZ exercise no significant effect, indicating non-radical nature of oligomerization process.

On the basis of kinetic studies and data of PMR- and IR-spectroscopic studies is supposed an oligomerization mechanism of interaction of EBG with BIZ, in which the first stage of the process is salt formation:

#### I. Salt formation



The rate of this stage can be expressed in terms of molar concentrations of reactants:

$$V_1 = K_1 [EBG] \cdot [BIZ] \quad (1)$$

Where  $K_1$  - the salt formation reaction rate constant;  $[EBG]$  - molar concentration of EBG;  $[BIZ]$  - Molar concentration of BIZ.

In salt formation reaction EBG reacts with BIZ in an equimolar ratio, then

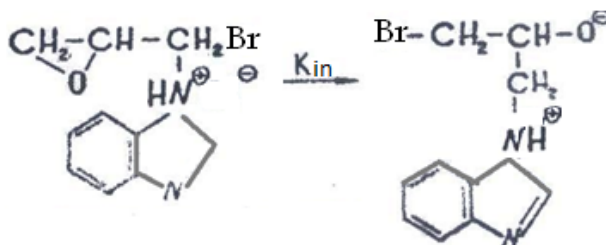
$[EBG] = [BIZ] = [M]$  and equation (1) has the form:

$$V_1 = K_1 [M]^2 \quad (2) \text{ or } -dM/dt = K_1 [M]^2$$

where:  $-dM/dt$  - defines the true reaction rate at the moment as the concentration of the derivative in time (a symbol minus indicates decrease of the initial concentrations of the reactants in time).

After the salt formation reaction is supposed opening of epoxy group with the formation of zwitter-ion, which is the active center, i.e. initiation stage.

#### II. Initiation

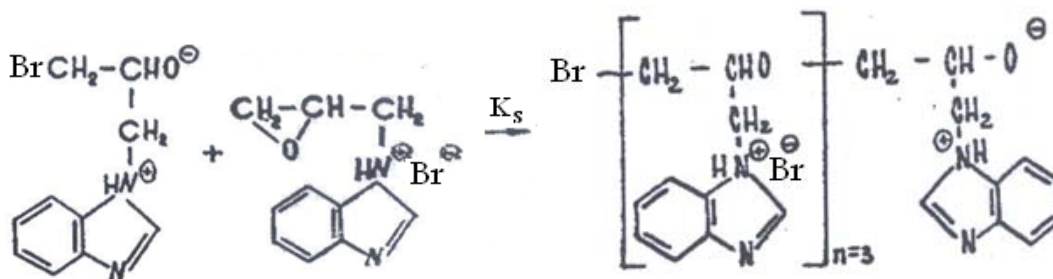


$$\text{Rate of the initiation stage can be expressed as: } V_2 = K_{in} [M'] \quad (3)$$

Where  $[M']$  - molar concentration of salt.

The resulting zwitter-ion by connecting monomeric salt the chain growth starts in usual scheme of anionic oligomerization:

## III. Chain growth

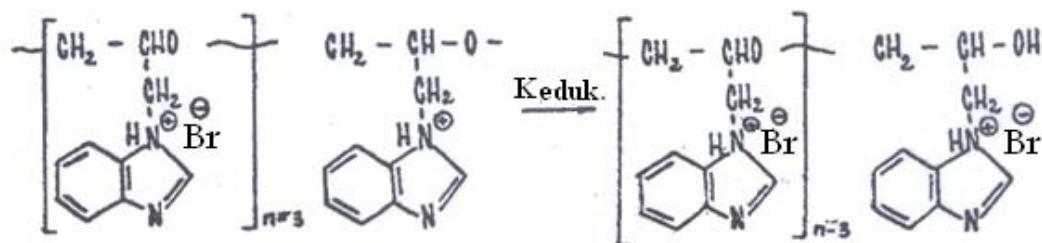


The rate of the chain growth is expressed by the equation:  $V_s = K_s[A][M]$

Where  $[A]$  –molar concentration of active centers.

The chain termination in all probability occurs due to the interaction of the growing macro-zwitter with low molecular HOH on the scheme:

## IV. Chain termination:



Here the rate of chain termination is expressed:  $V_{\text{term.}} = K_{\text{term.}} [A] [X]$

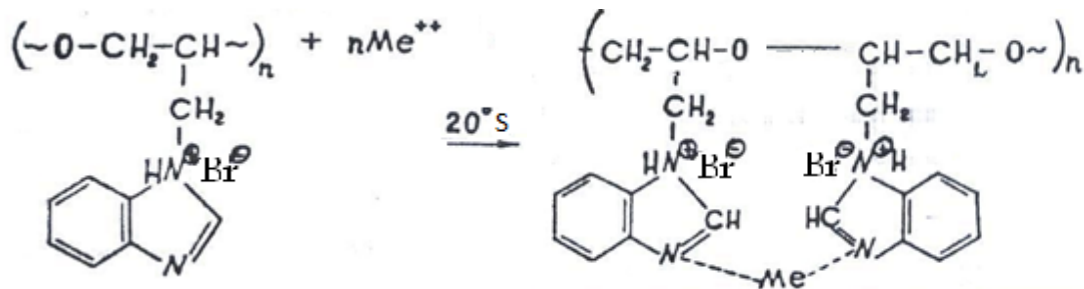
Where,  $[X]$  -molar concentration of HOH.

Indeed, when adding a small amount of HOH to the system a reduction in viscosity of the resulting oligomer is observed.

Synthesized by us ammonium oligomers based on the products of spontaneous oligomerization of EBG with BIZ because of containing an electron donor atom of nitrogen in its structure can form intermolecular compounds with the salts of divalent metals ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ). Oligomeric complexes have been prepared by direct reacting ammonium oligomers with a calculated amount of the salts of divalent metals at room temperature in alcohol.

EPR spectra indicate the formation of intermolecular compounds of metals with nitrogen atoms in the oligomer both with a copper salt and with a cobalt salt. For the complex of EBG with BIZ copper salt anisotropic singlet with average value of the g factor equals to 2,0733; line width at a height  $\Delta H = 97,4$  gf, and for the complex of EBG with BIZ with cobalt salt singlet signal with  $g = 2,1533$  and the line width (between the points of maximum slope)  $\Delta H = 1262$  gf.

Complex formation reactions on the example of the oligomer EBG with BIZ with the salts of divalent metals can be represented as follows:



Synthesized oligomeric metal containing complexes are amorphous powders, soluble in water and ethanol.

### Conclusions

New oligomers were synthesized by reacting EBG with BIZ. By spectroscopic and kinetic studies was determined the mechanism of interaction, reaction order on components, the dependence of the chemical structure of the oligomer on the composition of the initial mixture. It was established that the process is carried out by reacting nitrogen and bromine ion and due to opening epoxy group of EBG.

In the interaction of the products of spontaneous oligomerization of EBG with BIZ with the salts of divalent metals (copper and cobalt) oligomeric metal containing complexes were synthesized.

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