UDC 66-92 92 **DOI:10.30724/1998-9903-2019-21-3-4-3-6**

THERMOGRAPHIC STUDY OF DIBUTYL SULFIDE OXIDATION BY CONCENTRATED HYDROGEN PEROXIDE SOLUTION

L.R. Gaynullina, V.P. Tutubalina

Kazan State Power Engineering University, Kazan, Russia
gainullina7819@mail.ru

Abstract: *We used the thermographic method to study reaction of oxidation of dibutyl sulfide in n-octane concentrated by 95,6 % solution of hydrogen peroxide in a mixing reactor with propeller mixer.*

It was established that dibutyl sulfide oxidation by hydrogen peroxide in an equimolar ratio of 1:1 at a temperature of 80 °C proceeds to formation of dibutyl sulfoxide, and at a ratio of 1:2 and at a temperature of 100 °C it proceeds to formation of dibutyl sulfone.

The increase in amount of hydrogen peroxide and rise of temperature leads to formation of sour products: the sulfonium and sulfonic acids.

Gas-liquid chromatography was used to prove that during oxidation of dibutyl sulfide by hydrogen peroxide it does not destruct.

Keywords: *transformer oil, dibutyl sulfide, oxidation, hydrogen peroxide, thermogram.*

For citation: Gaynullina L.R., Tutubalina V.P. Dibutylsulfide oxidation research the concentrated hydrogen peroxide solution by means of thermograms. *Proceedings of the higher educational institutions. ENERGY SECTOR PROBLEMS.* 2019; 21(3-4):3-6. (In Russ). doi:10.30724/1998-9903-2019-21-3-4-3-6.

Introduction

At present, the chemistry of bivalent sulfur compounds faced the appearance of new substances with unique properties. It is known that organic sulfur compounds are widely used as inhibitors of oxidative conversion of hydrocarbons of oil fractions (T_{boil}=300–400°C) and transformer oils, improving their physical-chemical and operational characteristics [1, 2].

The researchers attention is attracted to organic sulfoxides and sulfones, which are formed during thermal and oxidative transformations of organic sulfur compounds [3–8].

Sulfides and oxidized organic sulfur compounds inhibit the oxidation of oil hydrocarbons, increasing their thermal stability, due to their ability to destroy hydroperoxides, which stimulate the auto-oxidation of hydrocarbons in the chain-oxidative process [1].

Experimental part

This research work is devoted to study the nature of interaction between individual sulfide (dibutyl sulfide) with hydrogen peroxide. To understand the mechanism of reaction of oxidative transformation of dibutyl sulfide, it is necessary to have reliable information about the products formed during the oxidation of dibutyl sulfide by hydrogen peroxide. In order to determine the reaction products and the influence of temperature on the course of the reaction, we used chromatographic analysis and thermographic studies. The concentration of dibutyl sulfide in terms of total sulfur was 0,5 % and remained constant in all experiments in order to obtain comparable experimental data. It is known [1], that this concentration of sulphides is optimal.

The reaction of dibutyl sulfide oxidation by hydrogen peroxide was carried out in n-octane medium, taken in amount of 100 cm^3, in the thermostate mixing device equipped with a propeller stirrer. In all experiments, the number of revolutions of mechanical mixer was 800 rpm, which is optimal for obtaining sulfoxides and sulfones.

Hydrogen peroxide of 95,6 % concentration was used as the oxidizing agent. The amount of hydrogen peroxide in the reaction of oxidation of dibutyl sulfide varied with a ratio of dibutyl sulfide: hydrogen peroxide in the range of 1:1,1:2 and higher.

It is known [9] that when the ratio of dibutyl sulfide: hydrogen peroxide is 1:1, sulfoxides are formed, and at a ratio of 1:2 sulfones are formed.

Preparation of model mixtures of *n*-octane-dibutyl sulfide and sampling from them were carried out in accordance with the Russian State Standard GOST R 52714-2007.

The concentration of total sulfur in model mixtures was found according to the Russian State Standard GOST R 51859-2002. The concentration of sulfide and sulfoxide sulfur was evaluated according to the method described in [10].

The concentration and composition of products formed during the oxidative transformation of dibutyl sulfide under the action of hydrogen peroxide were investigated using the Crystallux 4000 M chromatograph equipped with a thermal conductivity detector and having a sensitivity of 1500 MV·cm^3/mg. The gas chromatography column has a form of helix made from stainless steel, its inner diameter is 3 mm, its length is 2,5 m. Molecular NaX sieves with particle sizes of 0,2–0,4 mm were used as a sorbent. Silica gel KSM No. 5 was used as a desiccant, the particle sizes of which were 0,4–0,8 mm (GOST 3956-76). As a carrier gas we used helium (TU 51-689-75), medical or technical oxygen (GOST 5583-78). The reducer for oxygen supply was DKP-1-65 (TU 26-05-463-76). The relative error in determining the concentration of reaction products did not exceed 0,5 %.

In order to identify the sequence of dibutyl sulfide transformation, when interacting with hydrogen peroxide, thermograms of reactions were recorded using the TQ 170 thermograph in the temperature range of 30–130 °C with a measurement error of ±1,0 °C. The obtained thermograms are shown in the figure.

Results and discussion

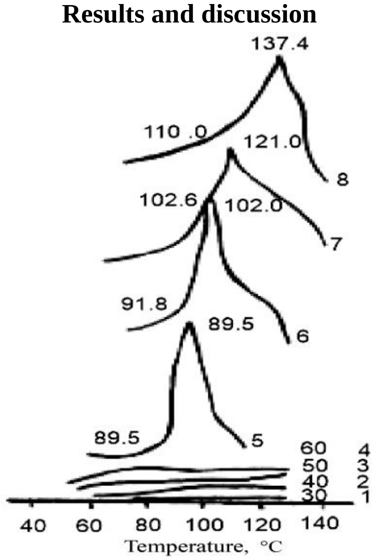

Fig. Thermograms of interaction of dibutyl sulfide with hydrogen peroxide at temperatures: *1, 2, 3, 4* – respectively 30, 40, 50 and 60 °C; *5* – 80 °C; *6* – 100 °C; *7*–120 °C; *8* – 130 °C

The experimental data presented in the figure shows that oxidation of dibutyl sulfide by hydrogen peroxide practically does not proceed at temperatures of 30, 40, 50 and 60 °C. Oxidation reactions proceed very slowly without formation of a thermal effect, as evidenced by the curves *1*, *2*, *3* and *4*.

Intensive interaction of dibutyl sulfide with hydrogen peroxide begins at a temperature of 80 °C. In the figure, this is expressed by curve 5, which can be characterized by a narrow and high exo-effect. The resulting exo-effect is characterized by a 9,5 °C rise in temperature.

When concentration of hydrogen peroxide in dibutyl sulfide oxidation reaction is increased to a dibutyl sulfide: hydrogen peroxide ratio of 1:2, a slight shift of the exo-effect to high temperatures is observed (curve 2). In this case, hydrogen peroxide is completely consumed for oxidation of dibutyl sulfide to the corresponding sulfone. At the same time, the exo-effect of the reaction is 12,5 °C (curve 5).

Analysis of the resulting products of oxidation of dibutyl sulfide by a concentrated solution of hydrogen peroxide showed that when the ratio dibutyl sulfide: hydrogen peroxide is 1:1, the oxidation proceeds with the predominant formation of sulfoxide for temperatures up to 89,5 °C.

The output of sulfoxide is 98,7 %. At higher temperature and ratio of dibutyl sulfide: hydrogen peroxide, equal to 1:2, the formation of dibutyl sulfone is observed with a yield of 97,9 % (curve 6).

With an increase in the reaction temperature and the amount of hydrogen peroxide supplied, dibutyl sulfide is oxidized by hydrogen peroxide to form sulfinic and sulfonic acids and the exo-effect shifts to higher temperatures (curves 7 and 8).

The obtained experimental data show that oxidation of dibutyl sulfide by hydrogen peroxide proceeds with formation of sulfoxides and sulfones only in the temperature range of 80–100 °C and for dibutyl sulfide: hydrogen peroxide ratio of 1:1 and 1:2. The temperature rising up to 120 and 130 °C and increasing the amount of hydrogen peroxide is accompanied by formation of acidic products, as evidenced by low pH values of the reaction mass: 5 and 6, respectively. The exo-effect of the reaction increases, respectively, by 19 and 16,4 °C.

Therefore, the oxidation of dibutyl sulfide by hydrogen peroxide can be represented as the following scheme:

$$RSR \xrightarrow{H_2O} RSOR \xrightarrow{H_2O} RSO_2R \xrightarrow{t} RSO_2H \xrightarrow{t} RSO_3H.$$

In accordance with the proposed scheme, the oxidation of dibutyl sulfide by concentrated solution of hydrogen peroxide can proceed with formation of acidic compounds at high temperatures and increased amounts of hydrogen peroxide.

According to the thermogram shown in the figure, oxidation of dibutyl sulfide by hydrogen peroxide proceeds without destruction of its molecule. By varying the temperature and the amount of hydrogen peroxide, the dibutyl sulfide oxidation reaction can be purposefully turned towards formation of sulfoxides and sulfones.

Analysis of the reaction mixtures by gas liquid chromatography showed that the main product of the dibutyl sulfide oxidation reaction by hydrogen peroxide is water. No decomposition of dibutyl sulfide was detected, since no evolution of gases, including hydrogen sulfide, was observed.

Thus, oxidation of dibutyl sulfide by concentrated 95,6 % hydrogen peroxide solution purposefully proceeds with formation of dibutyl sulfoxide and dibutyl sulfone for dibutyl sulfide: hydrogen peroxide ratios, respectively, equal to 1:1 and 1:2, and temperatures of 80 and 100°C.

Conclusions

1. It was shown that an increase in the amount of hydrogen peroxide fed to the reaction system over the dibutyl sulfide-hydrogen peroxide ratio of 1:2 results in a shift of exo-effect towards high temperatures, and formation of acidic products.

2. Gas-liquid chromatography was used to prove that during dibutyl sulfide oxidation by hydrogen peroxide dibutyl sulfide is not destroyed and the main products of reaction are sulfoxides, sulfones and water.

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Authors of the publication

Leysan R.Gaynullina – PhD in Engineering sciences, Associate Professor of the Department of Power Supply of Enterprises and Energy Resource-Saving Technologies of Kazan State Power Engineering University. E-mail: gainullina7819@mail.ru.

Valeria P. Tutubalina – Grand PhD in Engineering sciences, Professor, Chief Researcher, Kazan State Power Engineering University.

Received ***February, 18 2019***