

## Oxidation of Condensed Thiophene Derivatives with Brønsted Acidic Ionic Liquid

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**Abstract**—A catalyst based on ionic liquid consisting of a pyridinium cation having Brønsted acidity and a molybdenum anion (1-butyl-3-carboxypyridinium molybdate) is obtained. Its catalytic activity in the oxidation of sulfur-containing compounds is studied. The influence of the oxidation's duration, temperature, and the quantity of the oxidation agent and catalyst on the conversion of dibenzothiophene (DBT) is also considered. The conversion of DBT is 100% in the presence of the catalyst under the following conditions: molar ratio H<sub>2</sub>O<sub>2</sub> : S = 10 : 1, catalyst mass 0.02 g, reaction temperature 50°C, and duration 120 min.

**Keywords:** ionic liquid, Brønsted acid center, molybdenum-containing catalysts, hydrogen peroxide, oxidative desulfurization

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Currently, the problem to decrease the total amount of sulfur in oil fractions is attracting a great deal of attention [1].

Often crude oil with a high amount of sulfur is being processed. The high degree of corrosivity of oil is because of this toxic component. Sulfur is a poison for refining processes; thus, developing methods for removing sulfur-containing components from oil is important problem. Hydrotreatment is the conventional technology used to remove sulfur and is based on processing raw materials under the pressure of hydrogen at a high temperature in the presence of catalysts [2]. The introduction of stringent environmental regulations for fuels poses a challenge for researchers to search for new technological solutions to remove sulfur compounds from oil fractions [3], especially oxidative desulfurization [4]. The method implies the oxidation of sulfur-containing compounds with the subsequent removal of sulfoxides and sulfones from the hydrocarbon medium by extraction or adsorption. The advantages of oxidative desulfurization are the relatively mild conditions for the oxidation process (not more than 80°C) and the use of environmentally friendly and safe oxidation agents.

Hydrogen peroxide used independently and also with homogeneous and heterogeneous catalysts is the most common, commercially available, and environmentally friendly oxidation agent for the desulfurization of oil fractions [5]. During the oxidation with hydrogen peroxide and homogeneous catalysts, among which acids are often used, peroxyacids, which are much stronger oxidation agents that effectively

oxidize the sulfur compounds, appear [6]. The use of acids, however, lead to side effects of the oxidation of hydrocarbon components of fuels and an increase in the corrosive activity of the oil fractions. Homogeneous catalysts based on transition metal salts leading to active peroxide complexes allow oxidation under significantly milder conditions and with greater selectivity compared to that of acids [7].

The problem on mass transfer in the oxidative desulfurization process is key, because the oxidation agent and the catalyst are in an aqueous phase, whereas the substrate is in an organic one. Solving the problem of mass transfer will significantly soften the conditions for the oxidation process, which will increase the selectivity of the oxidation of organosulfur substrates. The well-known publications indicate that interphase carriers based on ammonium, pyridinium, and imidazolium salts are widely used. Quaternary ammonium salts [Bu<sub>4</sub>N<sup>+</sup>RCOOO<sup>-</sup>], consisting of the oxidation anion [RCOOO<sup>-</sup>] and ammonium salt cation [Bu<sub>4</sub>N<sup>+</sup>], are used as interphase carriers in a two-phase hydrocarbon/water system. This pair participates in the oxidation of sulfur-containing compounds due to the transition from the polar phase to the nonpolar one [8]. The oxidative desulfurization was performed in the presence of hydrogen peroxide, phosphorotungsten acid, and tetraoctylammonium bromide as an interphase carrier [9, 10]. A quaternary ammonium salt, which acts as an interphase carrier, is used together with amphiphilic phosphorotungsten acid, which makes it possible to stabilize the emulsion and to decrease the quantity of sulfur, when 98% of the

hydrogen peroxide in diesel fuel is used as an oxidation agent. The ionic liquids were recently used as phase transfer catalysts [11]. The degree of desulfurization for a model mixture of dibenzothiophene (DBT) in *n*-octane is 94%, and the ionic liquid may be repeatedly used without regeneration and loss of activity.

In this work, the catalytic properties of an ionic liquid that acts as an interphase carrier bearing a Brønsted acidic center and a molybdenum atom in the anion to form peroxo complexes in the presence of hydrogen peroxide is studied during the oxidative desulfurization of a model mixture containing dibenzothiophene. This method allows combining the catalytic properties of both organic acids and transition metal compounds during the oxidation process to minimize phase restrictions.

## EXPERIMENTAL

Nicotinic acid (99%, Chemical Line), bromobutane (99%, Sigma Aldrich), ethyl alcohol (96%), chemically pure dimethyl sulfoxide (DMSO, Khimmed), sodium molybdate  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (99%, Sigma Aldrich), and butyl methylimidazolium chloride (BMIMCl, 99%, Sigma Aldrich) were used for the synthesis of ionic liquid. Benzothiophene (BT, 98%, Sigma Aldrich), dibenzothiophene (DBT, 98%, Sigma Aldrich), 4-methyl-dibenzothiophene (MeDBT, 96%, Sigma Aldrich), and dodecane (99%, Sigma Aldrich) as a solvent were used to prepare the model mixture. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 37%, Prime Chemicals Group) was used as an oxidation agent for the catalytic reactions.

The structure of the compounds was elucidated with  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, ESI-MS mass spectrometry, and elemental analysis.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were acquired on a Varian-XR-400 spectrometer with an operating frequency of 400 MHz. Also, 2% solutions of the samples in deuterated dimethyl sulfoxide and water were used. Chemical shifts are given in parts per million (ppm) relative to hexamethyldisiloxane as the internal standard.

ESI-MS spectra were recorded on a Dionex Ultimate 3000 spectrometer equipped with an AB Sciex 3200 Qtrap tandem quadrupole mass-spectrometric detector during the electrospray ionization (ESI) in the positive ion mode. A 0.1% aqueous solution of formic acid and acetonitrile were used as a mobile phase in chromatography. The samples were prepared in deionized water, and the mass fraction of the substance was 2%. The sample was introduced with an autosampler through a zero volume connector directly into the mass spectrometer. The flow rate of the mobile phase was 0.3 mL/min. Mass-spectrometric detection was performed in the scanning mode within  $m/z = 80\text{--}500$  Da. Mass-spectra of the product ions were obtained within 50–143 Da.

Elemental analysis of the ionic liquid was performed to find the quantity of metal on an ARL Per-

form'X X-ray fluorescence wave spectrometer (Thermo Fisher Scientific, New Wave). The samples were prepared according to the following procedure: the powder samples were pressed into tablets on a boric acid substrate and covered with a lavesan film, which was pressed to the cell with a ring-shaped rim. Liquid samples were placed in a cuvette, covered with a lavesan film, and pressed with its frame.

The composition of the reaction products and the purity of the starting materials were monitored via gas chromatography on a Kristall 2000 M chromatograph equipped with a flame ionization detector. A Zebron column ( $l = 30$  m,  $d = 0.32$  mm, and ZB-1 liquid phase) was used; the temperature was programmed from 100 to 250°C. The chromatograms were recorded and analyzed on a computer with the Khromatek Analytik 1.5 software.

The conditions for the analysis of the reaction mixture before and after oxidation were as follows: the carrier gas was nitrogen ( $p = 200$  kPa), the volumetric flow rate was 30 mL/min, the initial temperature of the column was 100°C, the temperature of the injector was 150°C, the temperature of the detector was 250°C, and the heating rate of the column was 20°C/min.

The ionic liquid was synthesized as follows. Nicotinic acid (1.23 g) was dissolved in DMSO, and a stoichiometrical amount of 1-bromobutane (0.01 mol) was added. The mixture was refluxed for 24 h, the reaction mixture was cooled, the liquid part was decanted, and the solvent was distilled off in vacuo. The obtained ionic liquid N-1 was analyzed with  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and ESI-MS: N-1: 1-butyl-3-carboxypyridinium bromide.  $^1\text{H}$  NMR spectrum (DMSO, 400 MHz): 0.86–0.9 (s, 3H), 1.26–1.32 (s, 2H), 1.85–1.91 (s, 2H), 4.7–4.74 (s, 2H), 8.25–8.29 (t, 1H), 8.93–8.95 (d, 1H), 9.33–9.35 (d, 1H), and 9.59 (s, 1H).  $^{13}\text{C}$  NMR: 165.1, 149.3, 148.4, 146.7, 128.2, 126.7, 63.6, 30.3, 19.5, and 12.9 ppm. ESI-MS:  $m/z$  [ $\text{M}^+$ ] = 180.

An ion exchange reaction was performed to obtain the molybdate of the corresponding ionic liquid (N-1). Saturated aqueous solutions of sodium molybdate and the ionic liquid were prepared in a molar ratio of the ionic liquid to molybdate of 2 : 1. The ionic liquid solution was poured dropwise into the molybdate solution and stirred for 1 h. The precipitate formed was centrifuged, washed with water (210 mL) and ethyl alcohol (210 mL), and dried at room temperature for a day. The product was analyzed for its molybdenum content with XRD. The quantity of molybdenum in the ionic liquid synthesized was 19.31 wt %.

The organosulfur compound (BT, DBT or MeDBT) was dissolved in 5 mL of dodecane to prepare a model mixture with a total sulfur amount of 500 ppm. Then, 1.5 mL of acetonitrile was added to the resulting model mixture and then to the oxidation-catalytic mixture consisting of hydrogen peroxide and ionic liquid. This mixture was prepared by adding an N-2 ionic liquid

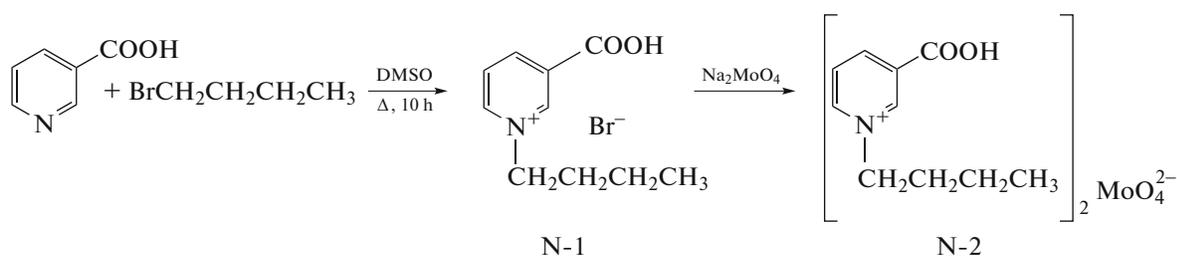


Fig. 1. Synthesis of N-2 ionic liquid.

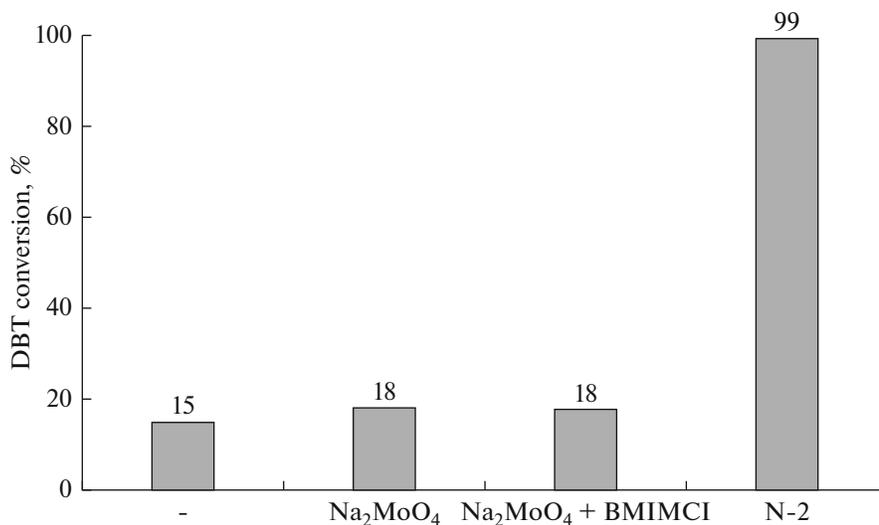


Fig. 2. The activity of various catalytic systems for the conversion of DBT ( $\text{H}_2\text{O}_2 : \text{S} = 10 : 1$ ,  $\text{Mo} : \text{S} = 1 : 2.5$ ,  $T = 50^\circ\text{C}$ ,  $t = 30 \text{ min}$ , and 1.5 mL of  $\text{CH}_3\text{CN}$ ).

(the ratio of molybdenum to sulfur ranges from 1.0 : 2.5 to 1 : 50) to a 37% hydrogen peroxide solution (the amount of hydrogen peroxide is calculated from the molar ratio of hydrogen peroxide and sulfur ranging from 2 : 1 to 10 : 1). When the molybdenum/sulfur ratio is 1 : 50, the ionic liquid completely dissolves in hydrogen peroxide, whereas when it is 1.0 : 2.5, a suspension forms, which then completely dissolves in the lower phase consisting of acetonitrile. The oxidation reactions of model mixtures were carried out at 20–70°C for 0.5–2 h. After the termination of the reaction, the mixture was cooled to room temperature and analyzed by gas chromatography.

## RESULTS AND DISCUSSION

In order to obtain an ionic liquid consisting of a pyridinium cation with Brønsted acidity and a molybdenum atom in the anion, a synthesis was performed according to the scheme of the reaction of pyridine alkylation with alkyl halides in the presence of a bipolar aprotic solvent (DMSO) and the subsequent ion exchange reaction. Figure 1 shows the synthesis scheme.

We studied a model mixture consisting of a DBT solution in dodecane, in which the total amount of sulfur was 500 ppm, to assess the catalytic activity of the N-2 ionic liquid with Brønsted acidity in the cation. The introduction of a molybdenum atom in the anion of an ionic liquid makes it possible to form a peroxocomplex together with an acid center in the presence of hydrogen peroxide, which enhances the catalytic activity of such a system. The activity of oxidation systems was comparatively assessed by the simple addition of sodium molybdate to the reaction mixture in the presence of an ionic liquid with a chlorine anion and the synthesized N-2 ionic liquid (Fig. 2). In this work, acetonitrile ( $\text{CH}_3\text{CN}$ ) was used as an extractant of oxidation products of sulfur compounds [12]. Single experiments on the extraction of unoxidized DBT with acetonitrile reduced the amount of DBT in the model mixture by 10%.

It should be noted that acetonitrile also acts as a solvent for peroxo complexes in this method. Considering that the ionic liquid is almost insoluble in water and poorly soluble in hydrogen peroxide solution, the addition of acetonitrile allows oxidation in a two-phase system, whereas hydrogen peroxide and the cat-

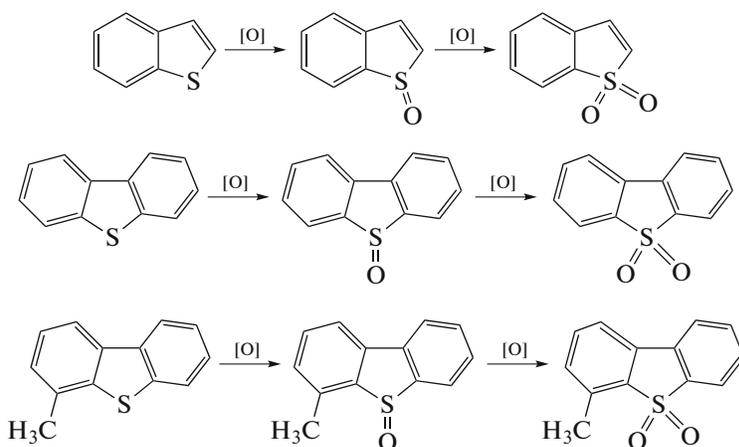


Fig. 3. Oxidation reactions of sulfur-containing compounds.

alyst are dissolved in acetonitrile and the substrate is dissolved in a hydrocarbon medium. If there is no acetonitrile, three phases appear: the hydrocarbon phase, the aqueous hydrogen peroxide solution, and the solid catalyst precipitate. Such an experiment leads to a significant increase in phase limitations, which does not allow us to assess the catalyst's efficiency in comparison with systems based on water-soluble molybdates. Figure 3 shows the oxidation scheme of sulfur-containing compounds.

The experimental results show that the N-2 ionic liquid, which has Brønsted acidity and contains a molybdenum atom in the anion, possesses a greater catalytic activity in the oxidation reactions of heterocyclic sulfur compounds than that of the oxidation system obtained by the simple addition of sodium molybdate and 1-butyl-3-methylimidazolium chloride (BMIMCl) used as an interphase carrier (Fig. 2). The conversion of DBT in such systems is low (18%),

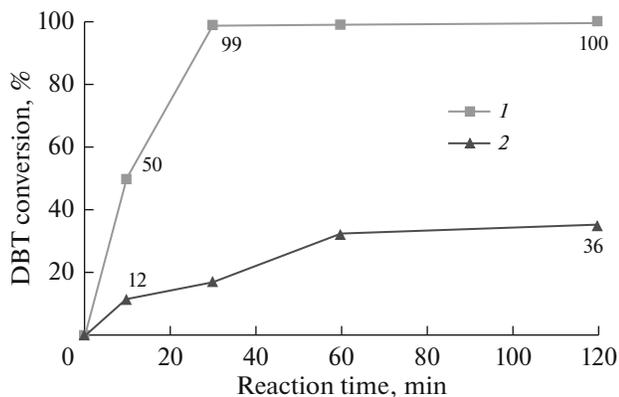


Fig. 4. The influence of duration of oxidation on DBT conversion in the presence of (1) N-2 and (2)  $\text{Na}_2\text{MoO}_4 + \text{BMIMCl}$  ( $\text{H}_2\text{O}_2 : \text{S} = 10 : 1$ ,  $\text{Mo} : \text{S} = 1 : 2.5$ ,  $T = 50^\circ\text{C}$ , and 1.5 mL of  $\text{CH}_3\text{CN}$ ).

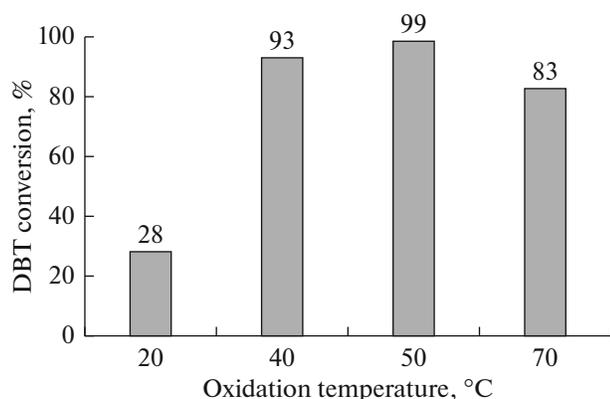
which is because of the instability of the peroxy complex formed [13]. The high degree of catalytic activity of the N-2 catalyst indicates that the formation of a molybdenum peroxy complex is stabilized with a carboxyl group included in the ionic liquid; in addition, the catalyst is concentrated at the phase boundary due to the hydrophobicity of the cation, which should make a significant contribution to the oxidation process of sulfur compounds. It should be noted that acid additives in equimolar ratios of organic acid and sulfur (1 : 1) were also used in previous works [3], where sodium molybdate was used at molar ratios of molybdenum and sulfur of 1 : 100. The use of sodium molybdate without an acid additive is impractical and does not lead to the oxidation of sulfur compounds under the conditions even with a molar ratio of molybdenum and sulfur equal to 1 : 1 (in this case, a high degree of DBT conversion can be achieved only in the presence of an ionic liquid without additives).

The relationship between DBT oxidation and time was studied under the action of hydrogen peroxide and a temperature of  $50^\circ\text{C}$  (Fig. 4).

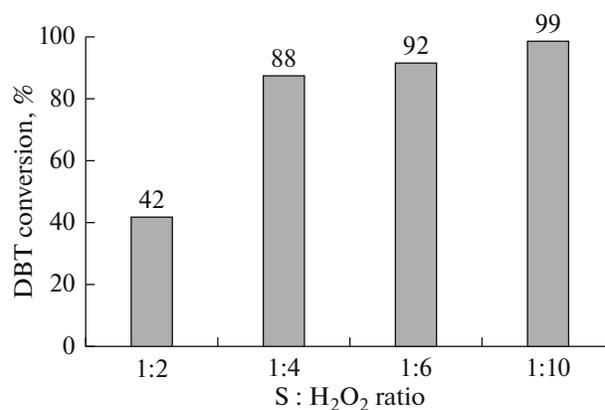
The catalytic activity of the N-2 ionic liquid and the system obtained by simply mixing sodium molybdate and 1-butyl-3-methylimidazolium chloride (BMIMCl) were compared for a long time. Figure 4 indicates that the conversion of DBT in the presence of a simple mixture of sodium molybdate and BMIMCl is low and is not more than 36% after 2 h. The conversion of DBT in the presence of the N-2 catalyst having Brønsted acidity increases with the duration of the oxidation reaction, being 50% after 10 min and 100% after 2 h.

The process was performed at different temperatures and for a fixed reaction time to study the influence of the temperature of the oxidation reaction on the DBT conversion. Figure 5 shows the experimental results.

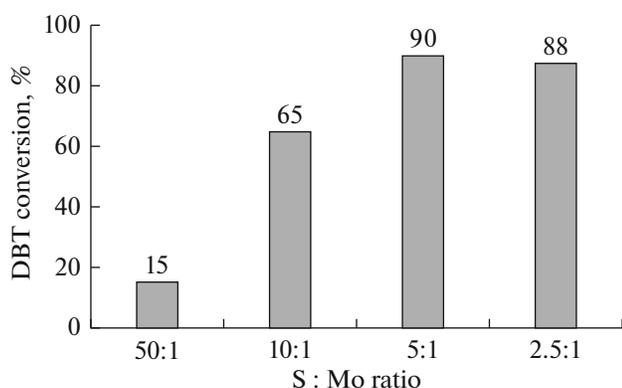
An increase in the temperature of the process, on the one hand, leads to an increase in the activity of the



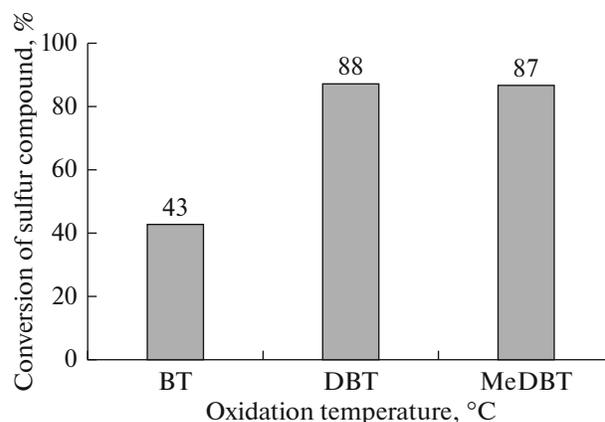
**Fig. 5.** Temperature dependence of DBT oxidation in the presence of N-2 ( $\text{H}_2\text{O}_2$  : S = 10 : 1, Mo : S = 1 : 2.5,  $t$  = 30 min, and 1.5 mL of  $\text{CH}_3\text{CN}$ ).



**Fig. 6.** The influence of amount of oxidation agent on DBT conversion in the presence of N-2 (Mo : S = 1 : 2.5,  $T$  = 50°C,  $t$  = 30 min, and 1.5 mL of  $\text{CH}_3\text{CN}$ ).



**Fig. 7.** The relationship between amount of catalyst and DBT conversion in the presence of N-3 ( $\text{H}_2\text{O}_2$  : S = 4 : 1,  $T$  = 50°C,  $t$  = 30 min, and 1.5 mL of  $\text{CH}_3\text{CN}$ ).



**Fig. 8.** The oxidation of BT derivatives ( $\text{H}_2\text{O}_2$  : S = 4 : 1, Mo : S = 1 : 5,  $T$  = 50°C,  $t$  = 30 min, and 0.5 mL of  $\text{CH}_3\text{CN}$ ).

catalyst, which directly affects the DBT conversion, and, on the other hand, it accelerates the decomposition of hydrogen peroxide. As a result, it is undesirable to increase the temperature by more than 50°C (Fig. 5). The highest DBT conversion is observed at 50°C being 99%.

The influence of the molar ratio of hydrogen peroxide and sulfur at a fixed quantity of the catalyst was studied at 50°C in the presence of N-2 (Fig. 6). The experiments showed that an increase in the amount of the oxidation agent leads to an increase in the DBT conversion. Figure 6, however, shows that there is a threshold value of the amount of the oxidation agent, after which the influence of hydrogen peroxide becomes weaker. The ratio of hydrogen peroxide and sulfur (4 : 1) is optimal from the point of view of oxidizer consumption, whereas the DBT conversion is 88%.

The results of studies on the effect of the amount of N-2 catalyst on the oxidation of DBT (Fig. 7) show that an increase in the mass of the catalyst leads to an increase in the DBT conversion. The introduction of the catalyst into the catalytic system in a molar ratio of

molybdenum and sulfur of 1 : 50 leads to a decrease in the rate of the oxidation reaction and allows us to achieve a 15% removal of DBT within 30 min. The further increase in the molar ratio (to more than 1 : 2.5) is impossible because of the limited solubility of the catalyst in hydrogen peroxide.

It should be noted that DBT conversion (Fig. 7) decreases slightly up to 65% with a decrease in the amount of ionic liquid to a ratio of molybdenum and sulfur of 1 : 10, which indicates that a decreased amount of the catalyst continues to work. The molar ratio of molybdenum and sulfur of 1 : 2.5 is due to the fact that it allows achievement of the high degree of DBT conversion with a shorter reaction time (30 min) compared to previous studies, in which oxidation was carried out for 2–6 h [3, 4]. Benzothiophene is the least active among the compounds used as oxidation substrates (benzothiophene, dibenzothiophene, and 4-methyldibenzothiophene), which is in good agreement with the published data on the oxidation of these compounds in other oxidative systems (Fig. 8) [14].

## CONCLUSIONS

The catalyst for the oxidation of condensed thiophene derivatives with hydrogen peroxide was synthesized based on an ionic liquid consisting of a pyridinium cation with Brønsted acidity and a molybdenum atom in the anion. The catalytic activity of 1-butyl-3-carboxypyridinium molybdate in the oxidation reactions of various sulfur-containing compounds was studied. The influence of the duration of the reaction, temperature, amount of the oxidation agent, and catalyst on the DBT conversion was studied. The optimum conditions for the DBT oxidation, which provide 100% conversion in the presence of a catalyst, were as follows: molar ratio  $\text{H}_2\text{O}_2 : \text{S} = 10 : 1$ ,  $\text{Mo} : \text{S} = 1 : 2.5$ , reaction temperature  $50^\circ\text{C}$ , and reaction time 120 min.

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## CONFLICT OF INTEREST

The authors declare they have no conflict of interest.

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