ISSN 1070-4272, Russian Journal of Applied Chemistry, 2019, Vol. 92, No. 4, pp. 569–575. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Zhurnal Prikladnoi Khimii, 2019, Vol. 92, No. 4, pp. 531–537.

Catalytic Activity of Polyfunctional Ionic Liquids in Oxidation of Model Sulfur Organic Compounds

A. V. Akopyan[a],*, E. A. Eseva[a], P. D. Polikarpova[a], T. M. Baigil'diev[a], I. A. Rodin[a], and A. V. Anisimov[a]

[a] *Chemical Faculty, Lomonosov Moscow State University, Moscow, 119234 Russia*
**e-mail: arvchem@yandex.ru*

Received October 8, 2018; revised December 14, 2018; accepted January 28, 2019

Abstract—Ionic liquids based on 1-methylimidazole were synthesized. The liquids contain Brønsted acid centers in the cation and a transition metal atom in the anion. The polyfunctional ionic liquids synthesized in the study are effective catalysts for the oxidative desulfurization process. The conditions are found for reaching the 100% conversion of methyl phenyl sulfide under mild conditions in the presence of the catalysts, ionic liquids [ionic liquid: 3-(carboxymethyl)-1-methyl-1*H*-imidazol-3-ium molybdate with S : Mo molar ratio = 24 : 1, 2 h, 40°C, H_2O_2 : S molar ratio = 12 : 1].

Keywords: ionic liquids, oxidative desulfurization, 1-methylimidazole, peroxo complexes, molybdenum, hydrogen peroxide.

DOI: 10.1134/S1070427219040141

Because of the introduction of severe ecological requirements to fuels, the demand increases for a search to find new solutions for purification of oil fractions to remove sulfurous compounds [1, 2]. The most widely used desulfurization method, hydrodesulfurization, requires a gross capital and energy expenditure in its implementation, and the increase in the content of sulfur in hydrocarbon raw materials results in that the conditions of this process become more severe, which requires that the already existing catalysts should be improved and reactors be made larger [3]. Because of the rising cost of the hydrodesulfurization process, hydrogen-free desulfurization method find steadily increasing application, the most promising of which is the oxidative desulfurization [4, 5]. The method is based on the oxidation of organosulfur compounds, with their subsequent extraction with a polar solvent or adsorbent from the hydrocarbon medium [6]. One of the main advantages of the oxidative desulfurization is constituted by the mild oxidation conditions (temperatures of up to 80°C and atmospheric pressure). A promising oxidizing agent is hydrogen peroxide, and it is an ecologically safe solvent yielding water as product of its reduction.

The most widely used catalytic systems for oxidative desulfurization contain compounds of transition metals, such as molybdenum, tungsten, or vanadium, which can form peroxo complexes in the presence of hydrogen peroxide or alkyl peroxides [4–9]. However, application of these systems is associated with phase constraints because sulfurous compounds are in the organic phase, and the catalyst and oxidizing agent, in the aqueous phase. This constraint can be diminished by using ionic liquids (IL), which can serves as interphase transfer agents in the course of oxidation [10–12].

The application of Brønsted acids as catalysts for oxidation of sulfurous compounds is extensively described in the literature (inorganic acids: sulfuric, phosphoric; organic acids: formic, acetic, trifluoroacetic, etc.) [13–15]. Examples are known of using ionic liquids with Brønsted acid centers as catalysts for oxidation of sulfurous compounds [16–18]. However, systems of this kind are inferior in efficiency to catalysts based on salts of molybdenum or tungsten [19–21]. In the present study, we used polyfunctional ionic liquids composed of imidazolium cation with a carboxy group and anion containing molybdenum, tungsten, or vanadium. An important advantage of this approach is that a catalyst combines a high catalytic activity inherent in transition metal compounds and acids with functions of an interphase transfer.

EXPERIMENTAL

The ionic liquids were synthesized from chloroacetic acid (97.6%, RusKhim), ethanol (96%), 1-methylimidazole (99%, Lanster), sulfuric acid (95%, Komponent-Reaktiv), and hydrochloric acid (37%, Sigma-Tek).

The model mixture was composed of methyl phenyl sulfide (MeSPh, 99%, Acros Organics) dissolved in dodecane (99%, Sigma Aldrich). The initial content of the total sulfur in the system was 1000 ppm. Mixtures of dibenzyl sulfide (Bn_2S, 98%, Sigma Aldrich), benzothiophene (BT, 98%), and dibenzothiophene (DBT, 98%, Sigmal Adrich) were prepared in a similar way. The oxidizing-catalytic mixtures were synthesized from sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$, 99%, Sigma Aldrich), sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, 99%, Sigma Aldrich) sodium vanadate ($NaVO_3$, 99%, Sigma Aldrich), hydrogen peroxide (H_2O_2, 50%, Prime Chemicals Group), *tert*-butyl hydroperoxide (*t*-BuOOH, 70%,ABCR), and 1-butyl-3-methylimidazolium tri(pentafluoroethyl) trifluorophospate (99%, Merck). ^1H NMR spectra were recorded with a Varian=XR-400 spectrometer with working frequency of 400 MHz. We used 2% solutions of samples in deuterated water or deuterated dimethyl sulfoxide. The chemical shifts are given in ppm on a scale relative to hexamethyldisiloxane as internal standard.

The structure of the compounds obtained was confirmed by ^1H NMR spectroscopy, ESI-MS mass spectrometry, and also by the method of elemental analysis.

ESI-MS spectra were recorded with a Dionex Ultimate 3000 liquid chromatograph with an AB Sciex Qtrap tandem quadrupole mass-spectrometric detector and sample ionized via electrospraying (ESI) in the mode with positive ions recorded. As a mobile phase served a mixture of 0.1% formic acid in water and acetonitrile. A sample was introduced with an autosampler via a zero-volume connector directly into the mass spectrometer. The flow rate of the mobile phase was 0.3 mL min^{-1}. The mass-spectrometric detection was performed in the scanning mode within the m/z range 50–143 Da. The samples were prepared in deionized water, with the mass fraction of the substance being 2%.

The elemental composition was examined by X-ray fluorescence microanalysis (XFMA) with an ARL Perform'X X-ray fluorescence wave spectrometer (Thermo Fisher Scientific, New Wave).

Samples were prepared by the following procedure: powdered samples were compacted into pellets on a boric acid substrates and covered with a Lavsan film, which was pressed with an annular casing against a cuvette. Liquid samples placed in the cuvette and covered with a Lavsan film, which was pressed with a casing.

The composition of the reaction products was determined and the purity of the starting substances was controlled by gas chromatography on a Kristall-2000M chromatograph with flame-ionization detector, Zebron column (L = 30 m, d = 0.32 mm), ZB-1 liquid phase, temperature programmed within the range from 100 to 250°C. The chromatograms were recorded and analyzed with a computer and Khromatek Analitik 1.5 software. The reaction mixture was analyzed before and after the oxidation under the following conditions:

– nitrogen as carrier-gas (p = 200 kPa), with the volumetric flow rate of 30 mL min^{-1};

– initial column temperature 100°C:

– injector temperature 150°C;

– detector temperature 250°C;

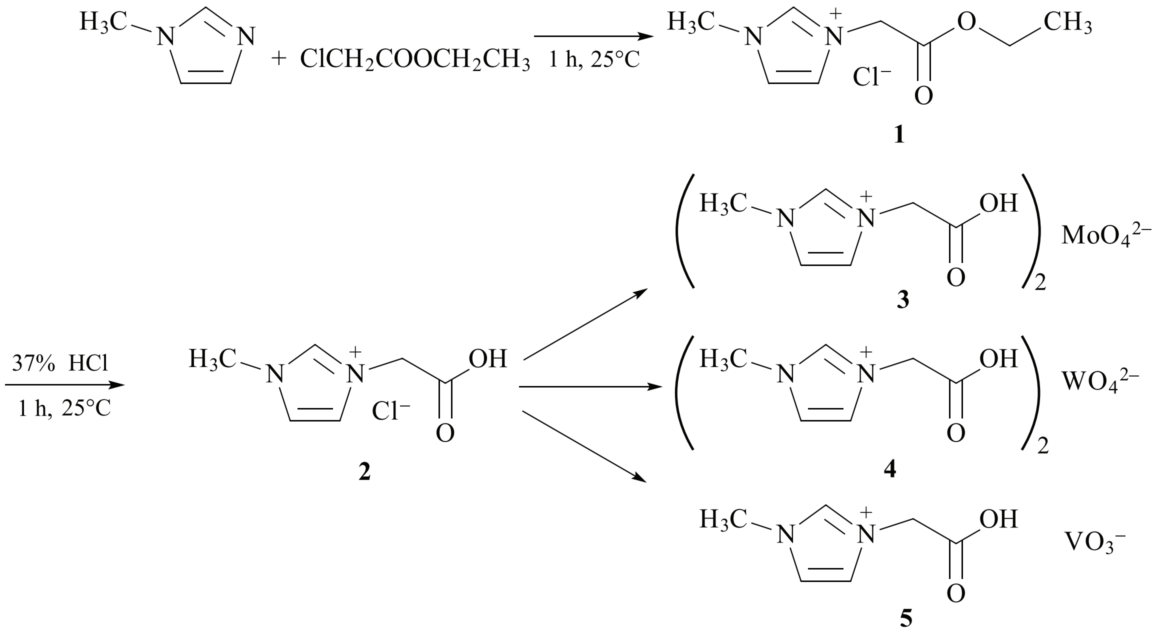
– column heating rate 20 deg min^{-1}.

Synthesis of ionic liquids. The ionic liquids (**3**)–(**5**) used in the study as catalysts for oxidation of sulfurous compounds were synthesized in accordance with Scheme 1.

Synthesis of 3-(2-ethoxy-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium chloride (IL-1). The quaternization rection was performed by the procedure described [22]. The product was analyzed by the NMR and ESI-MS methods. ^1H NMR spectrum (DMSO, 400 MHz): δ = 1.20–1.23 m (3H), 3.85–3.92 s (3H), 4.15–4.20 m (2H), 5.38 s (2H), 7.82–7.84 m (2H), 9.41 s (1H), ESI-MS: m/z = 169.

Synthesis of 3-carboxymethyl)-1-methyl-1*H*-imidazol-3-ium chloride (IL-2). The product of the quaternization reaction was subjected to hydrolysis in the presence of an excess amount of a 37% aqueous solution of hydrochloric acid [22]. The product was analyzed by the NMR and ESI-MS methods. ^1H NMR spectrum (DMSO, 400 MHz): δ = 3.90 s (3H), 5.16 s (2H), 7.74–7.76 d (2H), 9.26 s (1H). ESI-MS: m/z = 141.

Scheme 1. Synthesis of ionic liquids containing Brønsted acid centers in the cation and a transition metal atom in the cation.



Exchange reactions of 3-carboxymethyl)-1-methyl-1*H*-imidazol-3-ium chloride (IL-2) with transition metal salts to give IL-3–IL-5. IL-2 (0.5 g) was dissolved in 5 mL of distilled water, the resulting solution was added dropwise to 10 mL of an aqueous solution of sodium molybdate (the amount of sodium molybdate was calculated to obtain IL-2 : sodium molybdate molar ratio of 2 : 1). The resulting white precipitate was separated, washed with water until sodium chloride was fully removed, which was verified by a qualitative reaction for chloride ions with the use of silver nitrate, and dried at room temperature for 24 h. The anion exchange with sodium tungstate and vanadate was performed in a similar way (in the case of sodium vanadate, the IL-2 : sodium vanadate molar ratio was 1 : 1). The thus synthesized compounds were analyzed by the XFMA (see the table) and ESI-MS methods. According to ESI-MS, *m/z* = 141.

Preparation of a catalytic oxidizing mixture. To 0.2–0.8 mL of a 50% solution and hydrogen peroxide or *tert*-butyl hydroperoxide was added under permanent agitation 0.015–0.035 G of an ionic liquid (IL-2–IL-5). The agitation was continued for 5 min till the ionic liquid was fully dissolved.

Oxidation of model mixtures of organosulfur compounds. The reaction of oxidation of model mixtures (Scheme 2) was performed as follows: to 5 mL of a solution of an organosulfur compounds, which contains 2000 ppm of total sulfur, was added 0.02–0.08 mL of a catalytic oxidizing mixture containing hydrogen peroxide or *tert*-butyl hydroperoxide and ionic liquid (IL-2–IL-5) at a metal : hydrogen peroxide molar ratio of 1 : 600 to 1 : 48. The reaction was performed under permanent agitation at 20–80°C in the course of 0.5–6 h. The composition of the reaction mixture was analyzed, after the reaction was complete, by gas chromatography. In each case, the corresponding sulfones are oxidation products.

RESULTS AND DISCUSSION

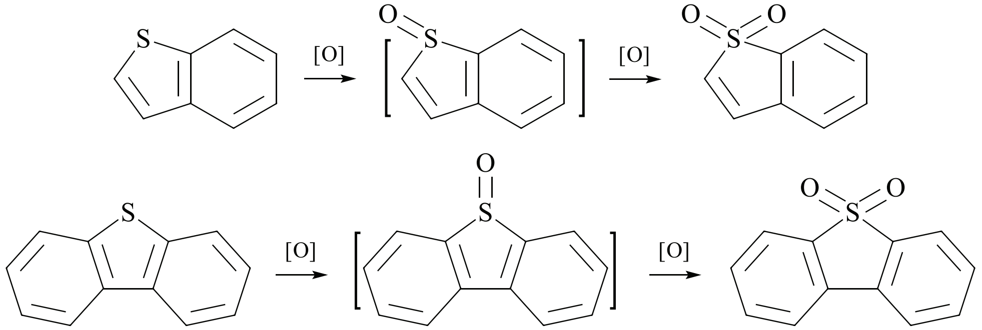
To compare under identical conditions the efficiencies of the catalysts obtained, we performed reactions in the presence of a catalytic system containing sodium molybdate and a model ionic liquid, tri(pentafluoroethyl)

Content of metals in the ionic liquids synthesized in the study according to elemental analysis data

Ionic liquid	Metal	Amount of a metal	
		calculated	actual
IL-3	Molybdenum	21.4	20.5
IL-4	Tungsten	34.1	34.7
IL-5	Vanadium	13.0	12.6

Scheme 2. Reactions of oxidation of sulfur-containing compounds.

$$\mathrm{MeSPh} \xrightarrow{[O]} [\mathrm{MeSOPh}] \xrightarrow{[O]} \mathrm{MeSO_2Ph}$$



trifluorophosphate of 1-butyl-3-methylimidazolium (IL) and ionic liquids obtained in the study with various anions (IL-2–IL-5, Scheme 1). A mixture of sodium molybdate and a model ionic liquid was used to evaluate the effect of Brønsted acid centers contained in the catalysts synthesized in the study (IL-2–IL-5) on the conversion of methyl phenyl sulfide (MeSPh).

It can be seen in Fig. 1 that the most efficient catalyst is the ionic liquid synthesized in the present study with a molybdenum atom in its anion (IL3). Ionic liquids with molybdenum and tungsten exhibit a high activity because these metals for active peroxo complexes in the presence of hydrogen peroxide or alkyl peroxides. The data obtained suggest that the catalysts synthesized in the study are more efficient as compared with pure sodium molybdate or a mixture of sodium molybdate with an ionic liquid (IL). This indicates that the cationic part containing a carboxy group is involved in the oxidation process.

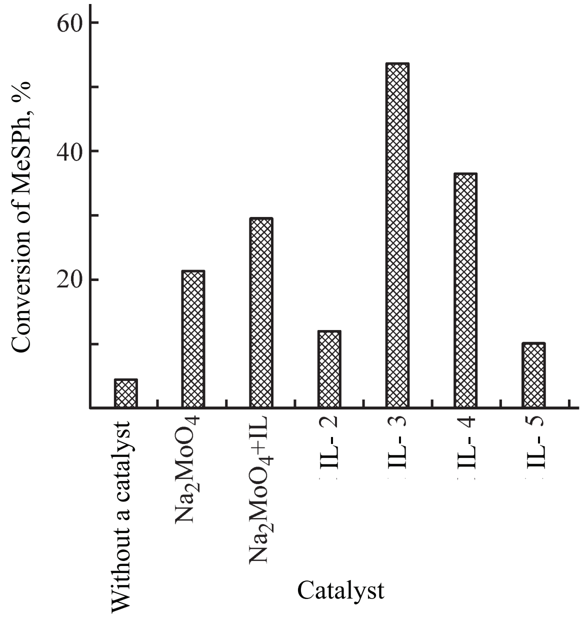


Fig. 1. Effect of the catalyst on the conversion of methyl phenyl sulfide [H_2O_2 : S = 6 : 1 (mol/mol), S : metal = 24 : 1 (mol/mol), 2 h, 40°C]. IL = 1-butyl-3-methylimidazolium tri(pentafluoroethyl)trifluorophosphate.

Thus, the results obtained are indicative of the efficiency of using polyfunctional ionic liquids containing both an acidic center and a transition metal ion. This approach makes it possible to improve the results as compared with using ionic liquids containing no Brønsted acid centers. It is important to note here that an IL containing an acid functional group, but having no metal, exhibits a catalytic activity due to the formation of a peroxy acid under oxidation conditions, which is characteristic of a peroxide oxidation of sulfur-containing compounds in the presence [1].

The effect of the oxidation temperature on the conversion of methyl phenyl sulfide was examined in the presence of IL-3 containing a molybdenum atom in the anion (Fig. 2). As oxidizing agents were chosen hydrogen peroxide and tert-butyl hydroperoxide with a molar ratio between oxidant and total sulfur of 6 : 1. It can be seen in Fig. 2 that hydrogen peroxide is a more effective oxidizing agent, compared with *tert*-butyl hydroperoxide. The optimal oxidation temperature is 60°C for hydrogen peroxide and 80°C for *tert*-butyl hydroperoxide.

The influence exerted by the oxidation duration on the conversion of methyl phenyl sulfide was examined in the presence of hydrogen peroxide and IL-3 ionic liquid (Fig. 3) at 40°C. Under these conditions, full oxidation is reached in 8 h.

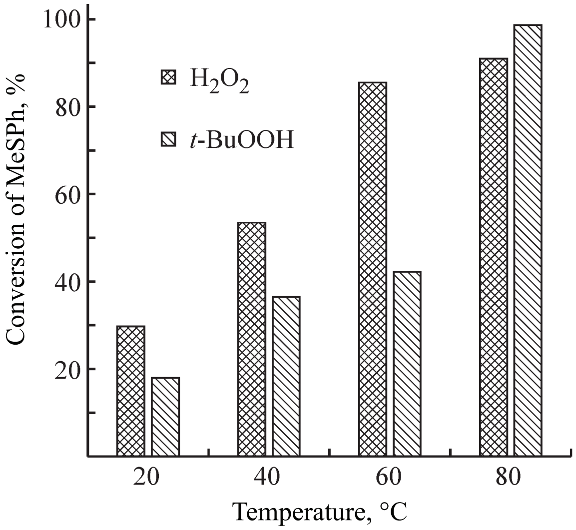


Fig. 2. Effect of temperature on the conversion of methyl phenyl sulfide [oxidant : total sulfur = 6 : 1 (mol/mol), IL-3 as catalyst, S : Mo = 24 : 1 (mol/mol), 2 h, 40°C].

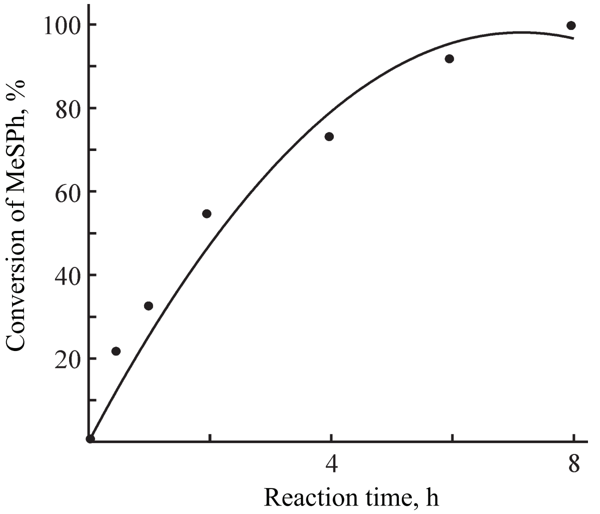


Fig. 3. Effect of the oxidation duration on the conversion of methyl phenyl sulfide [H_2O_2 : S = 6 : 1 (mol/mol), IL-3 as catalyst, S : Mo = 24 : 1 (mol/mol), 40°C].

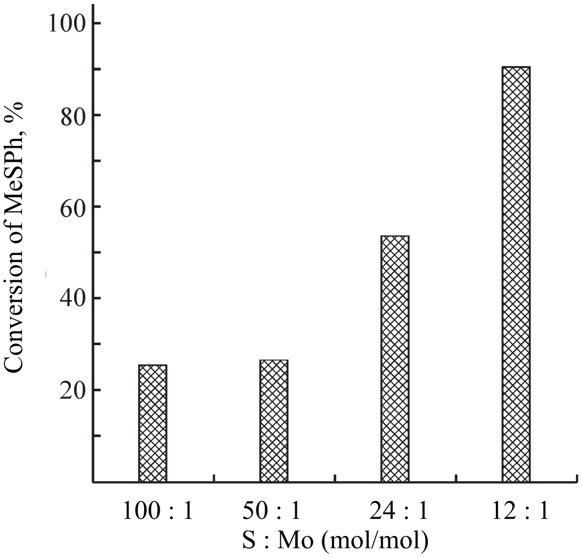


Fig. 4. Effect of the amount of catalyst on the conversion of methyl phenyl sulfide [H_2O_2 : S = 6 : 1 (mol/mol), IL-3 as catalyst, 2 h, 40°C].

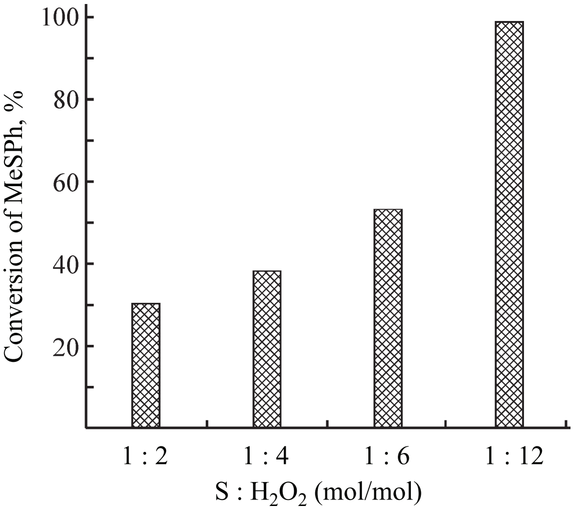


Fig. 5. Effect of the amount of hydrogen peroxide on the conversion of methyl phenyl sulfide [IL-3 as catalyst, S : Mo = 24 : 1 (mol/mol), 2 h, 40°C].

Varying the sulfur : molybdenum ratio (and, as a consequence, the sulfur : catalyst ratio) demonstrated (Fig. 4) that raising the amount of added catalyst leads to a higher conversion of methyl phenyl sulfide. A sulfur : molybdenum molar ratio smaller than 12 : 1 cannot be reached because of the limited solubility of the catalyst in a hydrogen peroxide solution.

A study of the influence exerted by the amount of hydrogen peroxide on the conversion of methyl phenyl sulfide at a molar excess of hydrogen peroxide with respect to the sulfide in the range from 2 to 12 (Fig. 5) demonstrated that a 12-fold excess of hydrogen peroxide makes it possible to fully oxidize methyl phenyl sulfide to the corresponding sulfone.

We carried out a comparative study of the oxidation of sulfur-containing compounds in the presence of IL-3 (Fig. 6). It follows from these data that methyl phenyl sulfide and dibenzyl sulfide are nearly fully oxidized, dibenzothiophene is 30% oxidized, and benzothiophene is worst of all in oxidation, which correlates with published

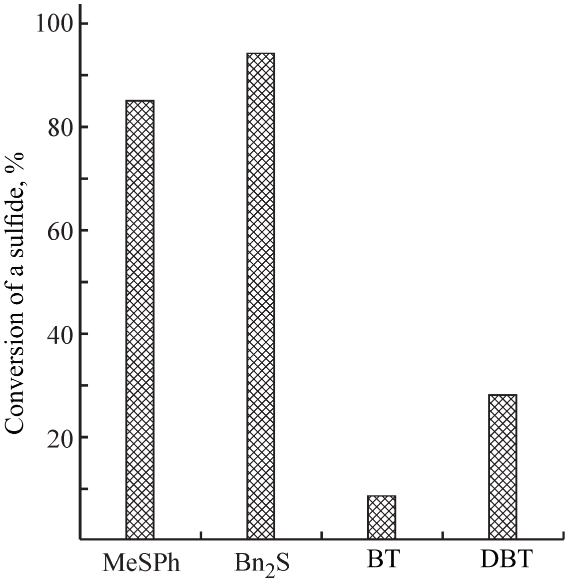


Fig. 6. Oxidation of various organosulfur compounds [H_2O_2 : S = 6 : 1 (mol/mol), IZ-3 as catalyst,S : Mo = 24 : 1 (mol/mol), H_2O_2 : S = 6 : 1 (mol/mol), IL-3 as catalyst, S : Mo = 24 : 1 (mol/mol), 2 h, 60°C].

data on how the activity of sulfurous compounds decreases in the order sulfide > dibenzothiophene > thiophene [23].

CONCLUSIONS

Ionic liquids having acid centers in the imidazolium cation and molybdenum, tungsten, and vanadium atoms in the anion were synthesized and their catalytic activity in the oxidation of organosulfur compounds was examined. It was shown that the highest catalytic activity is exhibited by the ionic liquid containing a molybdenum atom. The influence exerted by the reaction duration and by the amount of the ionic liquid and oxidizing agent on the conversion of methyl phenyl sulfide. Conditions were found in which the 100% conversion of methyl phenyl sulfide can be reached under mild conditions in the presence of the ionic liquids obtained in the study [ionic liquid 3-(carboxymethyl)-1-methyl-1H-imidazol-3-ium molybdate, hydrogen peroxide : sulfur molar ratio 12 : 1, sulfur : molybdenum molar ratio 24 : 1, 2 h, 40°C]. It was shown that the efficiency of using polyfunctional catalysts based on ionic liquids containing a Brønsted acid center in the cation for oxidation of organosulfur compounds as compared with application of a simple mixture of an ionic liquid and a transition metal salt.

FUNDING

The study was supported by the Russian Science Foundation (project no. 18-79-00116).

CONFLICT OF INTERESTS

The authors maintain that there is no conflict of interests to be disclosed in the present study.

REFERENCES

1. Akopyan, A.V., Fedorov, R.A., Andreev, B.V., Tarakanova, A.V., Anisimov, A.V., and Karakhanov, E.A., *Russ. J. Appl. Chem.*, 2018, vol. 91, no. 4, pp. 529–542.
2. Ma, X., Sun, L., and Song, C., *Catal. Today*, 2002, vol. 77, nos. 1–2, pp. 107–116.
3. Bhutto, A.W., Abro, R., Gao, S.R., Abbas, T., Chen, X.C., and Yu, G.R., *J. Taiwan Inst. Chem. Eng.*, 2016, vol. 62, pp. 84–97.
4. Ismagilov, Z., Yashnik, S., Kerzhentsev, M., Parmon, V., and Bourane, A., *Catal. Rev.: Sci. Eng.*, 2011, vol. 53, no. 3, pp. 199–255.
5. Akopyan, A.V., Grigoriev, D.A., Polikarpova, P.D., Eseva, E.A., Litvinova, V.V., Rakhmanov, E.V., and Anisimov, A.V., *Petrol. Chem.*, 2017, vol. 57, no. 10, pp. 904–907.
6. Babich, I.V. and Moulijn, J.A., *Fuel*, 2003, vol. 82, pp. 607–631.
7. Rafiee, E. and Rezaei, S., *J. Taiwan Inst. Chem. Eng.*, 2016, vol. 61, pp. 174–180.
8. Conte, V. and Bortolini, O., *J. Inorg. Biochem.*, 2005, vol. 99, pp. 1549–1557.
9. Kadijani, J.A. and Narimani, E., *Pet. Coal*, 2014, vol. 56, no. 1, pp. 116–123.
10. Li, H.M., He, L.N., Lu, J.D., Zhu, W.S., Jiang, X., Wang, Y., Yan, Y.S., *Energy Fuels*, 2009, vol. 23, pp. 1354–1357.
11. Lü, H., Deng, C., Ren, W., and Yang, X., *Fuel Process. Technol.,* 2014, vol. 119, pp. 87–91.
12. Xun, S., Zhu, W., Zheng, D., Li, H., Jiang, W., Zhang, M., Qin, Y., Zhao, Z., and Li, H., *RSC Adv.,* 2015, vol. 5, pp. 43528–43536.
13. Akopyan, A.V., Ivanov, E.V., Polikarpova, P.D., Tarakanova, A.V., Rakhmanov, E.V., Polyakova, O.V., Anisimov, A.V., Vinokurov, V.A., and Karakhanov, E.A., *Petrol. Chem.*, 2015, vol. 55, no. 7, pp. 571–574.
14. Shang, H. and Zhang, H., *J. Ind. Eng. Chem.*, 2013, vol. 19, no. 5, pp. 1426–1432.
15. Muhammad, Y., Shoukat, A., Rahman, A.U., Rashid, H.U.,

and Ahmad, W., *Chin. J. Chem. Eng.,* 2018, vol. 26, no. 3, pp. 593–600.

16. Gui, J., Liu, D., Sun, Z., Liu, D., Min, D., Song, B., and Peng, X., *J. Mol. Catal. A: Chem*., 2010, vol. 331, pp. 64–70.
17. Liu, D., Gui, J., Song, L., Zhang, X., and Sun, Z., *Petrol. Sci. Technol*., 2008, vol. 26, pp. 973–982.
18. Zhao, D., Sun, Z., Li, F., and Shan, H., *Fuel Chem. Technol*., 2009, vol. 37, no. 2, pp. 194–198.
19. Kulkarni, P. and Afonso, C., *Green Chem*., 2010, vol. 12, pp. 1139–1149.
20. Zhu, W., Li, H., Jiang, X., Yan, Y., Lu, J., He, L., and Xia, J., *Green Chem.,* 2008, vol. 10, pp. 641–646.
21. Zhang, J., Wanga, A., Li, X., and Ma, X., *J. Catal.,* 2011, vol. 279, no. 2, pp. 269–275.
22. Fei, Z., Zhao, D., Geldbach, T., Scopelliti, R., and Dyson, P., *Chem. Eur. J.,* 2004, vol. 10, no. 19, pp. 4886–4893.
23. Polikarpova, P., Akopyan, A., Shigapova, A., Glotov, A., Anisimov, A., and Karakhanov, E., *Energy Fuels*, 2018, vol. 32, pp. 10898–10903.