# Oxidation of diethyl disulfide with atmospheric oxygen in the presence of 1,3-dimethylimidazolium dimethyl phosphate\*

E. G. Krivoborodov, \* A. A. Zanin, E. P. Novikova, and Ya. O. Mezhuev

D. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya pl., 125047 Moscow, Russian Federation. Fax: +7 (499) 978 8660. E-mail: vv1992@vandex.ru

Oxidation of diethyl disulfide with atmospheric oxygen at 363 K in the presence of 1,3-dimethylimidazolium dimethyl phosphate is described. On the basis of the <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR data, it is shown that oxidation of diethyl disulfide results in ethyl sulfonates. Formation of ethyl alcohol, which is a product of a side reaction of ethyl sulfonate hydrolysis, probably, catalyzed by the 1,3-dimethylimidazolium cation, was detected using HPLC and <sup>1</sup>H and <sup>13</sup>C NMR.

Key words: ionic liquids, 1,3-dimethylimidazolium dimethyl phosphate, sulfonate, disulfide.

Ionic liquids traditionally attract attention as extractants and solvents often exhibiting a catalytic activity and providing a significant change in reactivity of solvated reactants.<sup>1,2</sup> Due to the minimal environmental impact, ionic liquids are considered as "green" solvents, which are promising for the implementation of various technological processes.<sup>3–5</sup> One of the significant applications of ionic liquids is the removal of sulfur-containing compounds from hydrocarbons in the extraction process,<sup>6–8</sup> which is often combined with oxidation of organosulfur compounds (usually, with hydrogen peroxide).<sup>9,10</sup>

The presence of ionic liquids affects the reactivity of sulfur-containing compounds in a number of reactions. In particular, oxidation of thiols to disulfides occurs with an acceptable rate at room temperature already, <sup>11</sup> whereas elemental sulfur is capable to interact with ionic liquids containing anion of dimethyl phosphate under very soft conditions. <sup>12</sup> Though the reasons for the changes in the reactivity of organic compounds, including organosulfur compounds, in the presence of ionic liquids are often not entirely clear, the need for further study of specificity of chemical processes in these media is not in doubt. In this regard, the reported here transformation of diethyl disulfide into ethyl sulfonates in the presence of 1,3-dimethylimid-azolium dimethyl phosphate [1,3-MeIm]Me<sub>2</sub>PO<sub>4</sub> under moderate heating in air appears to be of particular interest.

### **Experimental**

Ethanethiol (Reachem, RF) in an amount of 3.88 g  $(6.25 \cdot 10^{-2} \text{ mol})$  was oxidized under stirring for 2 h to diethyl

\* Based on the materials of the XXI Mendeleev Congress on General and Applied Chemistry (September 9–13, 2019, St. Petersburg). disulfide with 50% aqueous hydrogen peroxide taken in an amount of 0.7 mL ( $\rho = 1.2 \text{ g mL}^{-1}$ ) containing 0.42 g (1.24 · 10<sup>-2</sup> mol) of hydrogen peroxide. The reaction was carried out in an excess of ethanethiol, which made it possible to prevent the secondary oxidation of diethyl disulfide in the course of its synthesis:

 $2 \text{ Et}-\text{SH} + \text{H}_2\text{O}_2 = \text{Et}-\text{S}-\text{S}-\text{Et} + 2 \text{H}_2\text{O}.$ 

1,3-Dimethylimidazolium dimethyl phosphate (Sigma-Aldrich), an ionic liquid, in an amount of  $0.9 \text{ g} (4.05 \cdot 10^{-3} \text{ mol})$  was added under stirring to the reaction mixture. Then, the reaction mixture was heated to 363 K for 2 h under vigorous stirring in a bulb equipped with a direct condenser and a receiver for the condensate. After the completion of the reaction, the composition of the obtained condensate was determined by HPLC using a L-3000 chromatograph equipped with a L-3500 UV-vis detector (180–250 nm, Rigol, China) and a Luna 5u C 18(2) 100A column. The HPLC analysis was carried out for mixtures containing 1  $\mu$ L of isopropyl alcohol as an internal standard and 1  $\mu$ L of the condensate.

The <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra of starting 1,3-dimethylimidazolium dimethyl phosphate were recorded in methanol. The <sup>13</sup>C NMR spectrum of the reaction mixture was recorded after the completion of the reaction at 298 K. When the reaction system was cooled to 283 K, formation of a precipitate was observed, the melting point of which was 298 K. After separation of the precipitate, the <sup>1</sup>H and <sup>31</sup>P NMR spectra of the residual mother liquor were recorded. Spectra of all mixtures obtained after completion of the reaction were recorded in CD<sub>3</sub>OD with the use of the equipment of the Center of Collective Usage of the D. Mendeleev University of Chemical Technology of Russia.

# **Results and Discussion**

There are four signals in the <sup>13</sup>C NMR spectrum of 1,3-dimethylimidazolium dimethyl phosphate with  $\delta_{\rm C}$  139.93, 125.89, 53.85, and 37.57, they correspond to

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 5, pp. 0986-0989, May, 2020.

1066-5285/20/6905-0986 © 2020 Springer Science+Business Media LLC

the carbon atoms of the imidazole ring in position 2 and in equivalent positions 4 and 5 and to carbon atoms of methyl groups of the 1,3-dimethylimidazolium cation and dimethyl phosphate anion, respectively (Fig. 1, a). In the <sup>13</sup>C NMR spectrum recorded after the completion of the reaction (Fig. 1, b) these signals were shifted to high field. The multiplet with  $\delta_{\rm C}$  47–50 that was observed in the <sup>13</sup>C NMR spectrum of the starting ionic liquid in methanol and in the spectrum of the reaction mixture in CD<sub>3</sub>OD belongs to the methanol carbon atom. The signals with  $\delta_{\rm C}$  9.26 and 46.08 belong to the methyl and methylene groups of the ethyl sulfonate anion, respectively. The observation of the signals with  $\delta_{C}$  17.84 and 57.77 is consistent with the formation of ethanol, which is a product of a side reaction of the ethyl sulfonate anion hydrolysis, which can be catalyzed by the 1,3-dimethylimidazolium cation.

Formation of ethanol is corroborated by its detection in the condensate using HPLC (Fig. 2). A chromatographic peak with a retention time of 1.28 min corresponds to propan-2-ol (internal standard), and peaks with retention times of 3.96 and 1.66 min correspond to ethyl mercaptan and ethanol, respectively, which are present in the condensate in a ratio equal to 1.67 according to the ratio of their peak areas.

As can be seen from Fig. 1, there are no signals characteristic of the initial diethyl disulfide in the <sup>13</sup>C NMR



**Fig. 1.** <sup>13</sup>C NMR spectra of 1,3-dimethylimidazolium dimethyl phosphate (in MeOH) (*a*) and the reaction system after the completion of the reaction (in  $CD_3OD$ ) (*b*).



**Fig. 2.** Chromatogram obtained by HPLC for the condensate formed in the course of removal of the volatile products from the reaction system at 363 K for 2 h.

spectrum of the reaction system, which indicates its almost complete oxidation by atmospheric oxygen. The <sup>1</sup>H NMR detection of starting diethyl disulfide was possible only after separation of 1,3-dimethylimidazolium ethyl sulfonate by cooling.

Four signals with  $\delta_H$  9.29, 7.83, 3.63, and 3.56 are observed in the <sup>1</sup>H NMR spectrum of 1,3-dimethylimidazolium dimethyl phosphate, they belong to protons at the carbon atoms of the imidazole ring in position 2 and in equivalent positions 4 and 5 and at the carbon atoms of the methyl groups of the 1,3-dimethylimidazolium cation and dimethyl phosphate anion, respectively. The signals with  $\delta_{\rm H}\,5.19$  and 4.09 correspond to the methanol protons (Fig. 3, *a*). In the <sup>1</sup>H NMR spectrum of the reaction mixture obtained after precipitation of 1,3-dimethylimidazolium ethyl sulfonate by cooling (Fig. 3, b), all signals of protons of initial ionic liquid are shifted to high field by 0.5–0.7 ppm. Signals in the region of  $\delta_{\rm H}$  0.8–1.2 correspond to superposition of signals of methyl groups of several different compounds present in the reaction system. A multiplet with a chemical shift of about 2.5 ppm, which corresponds to a methylene group of diethyl disulfide, is clearly distinguished. Quadruplet with  $\delta_H$  3.30 is due to the methylene group of ethanol. An intensive signal with  $\delta_{\rm H}$  5.38 corresponds to protons of hydroxyl groups of hydroxyl-containing compounds present in the mixture, including water, and indicates that there is a fast proton exchange in the system. As can be seen, the amount of unreacted diethyl disulfide is rather small, which indicates its almost complete oxidation.

Finally, in the <sup>31</sup>P NMR spectrum, a slight shift of the phosphorus atom signal from 3.32 to 0.6 ppm is observed (Fig. 4). This is, apparently, related to the change in the nature of interaction of the dimethyl phosphate anion with counterions.

The obtained spectroscopic data along with the observation of precipitation from the reaction mixture at 283 K



**Fig. 3.** <sup>1</sup>H NMR spectra of 1,3-dimethylimidazolium dimethyl phosphate (in MeOH) (*a*) and the reaction system after the completion of the reaction (in  $CD_3OD$ ) (*b*).

after the completion of the reaction indicate that the process occurring in the reaction mixture follows the sequence of reactions shown in Scheme 1.

## Scheme 1



**Reagents and conditions:** *i*.  $O_2/H_2O$ , 363 K, [1,3-Me<sub>2</sub>Im]Me<sub>2</sub>PO<sub>4</sub>. *ii*. [1,3-Me<sub>2</sub>Im]Me<sub>2</sub>PO<sub>4</sub>, 283 K. *iii*.  $H_2O + [1,3-Me_2Im]^+$ , 363 K.

Probably, the capability of disulfides to interact with atmospheric oxygen under the used mild conditions is determined by solvation of radical-cations formed in oneelectron oxidation of disulfides or by solvation of thioethyl radicals by the ionic liquids if one assumes in the latter case that homolysis of the S—S bond precedes the oxidation. It should be expected that the energy of solvation of radical-cations<sup>13</sup> by ionic liquids is higher than that of free



Krivoborodov et al.



**Fig. 4.** <sup>31</sup>P NMR spectra of 1,3-dimethylimidazolium dimethyl phosphate (in MeOH) (*a*) and the reaction system after the completion of the reaction (in  $CD_3OD$ ) (*b*).

radicals, which is in favor of the former assumption. Nevertheless, the intermediate formation of free radicals cannot be ruled out, especially, if one takes into account the recently revealed possibility of their solvation by ionic liquids.<sup>14</sup>

The formation of a precipitate in the course of cooling the reaction mixture below room temperature is consistent with the known melting point of 1-ethyl-3-methylimidazolium methyl sulfonate, an isomer of 1,3-dimethylimidazolium ethyl sulfonate, equal to 308 K. The formation of 1,3-dimethylimidazolium ethyl sulfonate is a result of an ion-exchange reaction consisting in the replacement of the dimethyl phosphate anion of 1,3-dimethylimidazolium dimethyl phosphate by the ethyl sulfonate anion, which is formed in the course of oxidation of diethyl disulfide with atmospheric oxygen.

Apparently, the reported reaction can be of certain technological interest for the purification of hydrocarbon fuels from sulfur-containing compounds.

In conclusion, it is established that diethyl disulfide can be oxidized with atmospheric oxygen in the presence of 1,3-dimethylimidazolium dimethyl phosphate at 363 K for 2 h with formation of ethyl sulfonates. It is shown that decreasing the temperature of the reaction mixture to 283 K results in precipitation of 1,3-dimethylimidazolium ethyl sulfonate, which is a product of an ion exchange involving the replacement of the dimethyl phosphate anion by the ethyl sulfonate anion. The structures of the obtained compounds are confirmed by <sup>13</sup>C, <sup>1</sup>H, and <sup>31</sup>P NMR spectroscopy. Occurrence of a side reaction of hydrolysis of ethyl sulfonate anion to ethyl alcohol, which can be catalyzed by the 1,3-dimethylimidazolium cation, was demonstrated.

This work was financially supported by D. Mendeleev University of Chemical Technology of Russia (Project No. 036-2018).

#### References

- 1. V. I. Pârvulescu, C. Hardacre, Chem. Rev., 2007, 107, 2615.
- 2. K. J. Fraser, D. R. MacFarlane, Austral. J. Chem., 2009, 62, 309.
- E. A. Chernikova, L. M. Glukhov, V. G. Krasovskiy, L. M. Kustov, M. G. Vorobyeva, A. A. Koroteev, *Russ. Chem. Rev.*, 2015, 84, 875.

- 4. A. E. Rosamilia, C. R. Strauss, J. L. Scott, Pure Appl. Chem., 2007, 79, 1869.
- V. G. Krasovskiy, E. A. Chernikova, L. M. Glukhov, G. I. Kapustin, A. A. Koroteev, L. M. Kustov, *Russ. Chem. Bull.*, 2018, 67, 1621.
- J.-L. Wang, D.-S. Zhao, E.-P. Zhou, Z. Dong, J. Fuel Chem. Technol., 2007, 35, 293.
- Y. Wang, H. Li, W. Zhu, X. Jiang, L. He, J. Lu, Y. Yan, *Petrol. Sci. Technol.*, 2010, 28, 1203.
- A. R. Ferreira, M. G. Freire, J. C. Ribeiro, F. M. Lopes, J. G. Crespo, J. A. P. Coutinho, *Fuel*, 2014, **128**, 314.
- 9. P. S. Kulkarni, C. A. M. Afonso, *Green Chem.*, 2010, 12, 1139.
- 10. H. Zhao, G. A. Baker, Front. Chem. Sci. Eng., 2015, 9, 262.
- R. Hosseinzadeh, H. Golchoubian, M. Nouzarian, *Res. Chem. Intermed.*, 2014, 41, 4713.
- N. P. Tarasova, A. A. Zanin, P. S. Sobolev, E. G. Krivoborodov, Dokl. Chem., 2017, 473, 78.
- H. Fu, Z. Xing, X. Cao, G. Wu, Chin. Sci. Bull., 2012, 57, 2752.
- Y. Akdogan, J. Heller, H. Zimmermann, D. Hinderberger, Phys. Chem. Chem. Phys., 2010, 12, 7874.

Received October 1, 2019; in revised form January 17, 2020; accepted February 18, 2020