

Conference paper

Natalia Tarasova*, Efrem Krivoborodov, Anna Egorova, Alexey Zanin, Lev Glukhov, Ilya Toropygin and Yaroslav Mezhuev

Reaction of 1,3-dimethylimidazolium dimethylphosphate with elemental sulfur

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Abstract: By the methods of MALDI and mass spectroscopy with the detection of positively and negatively charged ions, it was found that the reaction of elemental sulfur and 1,3-dimethylimidazolium dimethylphosphate is accompanied by the opening of the S₈ ring. ¹H, ¹³C, ¹⁵N and ³¹P NMR spectroscopy showed that the interaction of S₈ and 1,3-dimethylimidazolium dimethylphosphate proceeds exclusively on the oxygen atom of the dimethylphosphate anion carrying a negative charge. Kohn-Sham calculations at B3LYP/STO-3G, B3LYP/6-31G* and B3LYP/6-311G** levels of theory confirmed that the reaction of S₈ with dimethylphosphate anion is possible.

Keywords: 1,3-dimethylimidazolium dimethylphosphate; ionic liquids; Mendeleev-21; quantum chemistry methods; sulfur.

Introduction

The combination of high mechanical strength, elasticity, and low cost ensured the growth of interest in the synthesis of sulfur-based polymers and copolymers [1, 2]. The polymer form of elemental sulfur is formed reversibly by a radical mechanism as a result of homolysis of S-S-bonds [3], and at room temperature the equilibrium is shifted towards depolymerization to form S₈ [3–6]. The equilibrium shift towards polymerization is possible only when the temperature increases to 432 K, thus limiting the possibility of using elemental sulfur polymer [2, 7]. Thermal opening of the S₈ ring made it possible to carry out radical copolymerization of sulfur with unsaturated compounds, and the resulting copolymers are thermodynamically stable at room temperature and do not depolymerize [8–11]. The processes of synthesis of homopolymer and copolymers of elemental sulfur correspond to the principles of green chemistry, and apparently have significant prospects for upscaling [12].

S₈ ring opening can occur not only by thermal dissociation or as the result of radical reactions, but also via nucleophilic attack. For example, the copolymerization of S₈ and thiiranes in the presence of typical initiators

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***Corresponding author: Natalia Tarasova**, D. Mendeleev University of Chemical Technology of Russia, Moscow, 125047, Russia; and Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow, 119017, Russia, e-mail: tarasnp@muctr.ru

Efrem Krivoborodov, Anna Egorova, Alexey Zanin and Yaroslav Mezhuev: D. Mendeleev University of Chemical Technology of Russia, Moscow, 125047, Russia

Lev Glukhov: N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991, Russia

Ilya Toropygin: V.N. Orekhovich Research Institute of Biomedical Chemistry, Russian Academy of Sciences, Moscow, 119121, Russia

of anionic polymerization is described [13, 14]. It is known that N-methylimidazole opens the S_8 ring to form polysulfide anions [15, 16], and sodium sulfide reacts with elemental sulfur in an aqueous medium [17–19]. Vulcanization of rubbers associated with S_8 ring opening is also accelerated in the presence of a number of nucleophiles [16]. These facts leave no doubt that the cyclo-octasulfur is able to undergo the ring opening via the anionic mechanism with the formation of a negatively charged sulfur atom at the end of the chain.

Ionic liquids, which are promising green solvents [20, 21] and in some cases have a catalytic effect [22], also showed efficiency in accelerating the vulcanization of rubbers [23–25]. However, elemental sulfur is insoluble in ionic liquids. In this regard, the recently discovered reaction of S_8 with tri-*n*-butylmethylphosphonium dimethylphosphate ionic liquid, proceeding with ring opening and accompanied by the formation of a mixture of sulfur oligomers [26], is of great interest. Whether this example of low-temperature initiation of sulfur oligomerization is a common property of ionic liquids with dimethylphosphate anion, remains to be determined. In this paper, it is reported that the interaction of S_8 with 1,3-dimethylimidazolium dimethylphosphate is also accompanied by the opening of the S_8 ring with the formation of short chains containing a terminal dimethylphosphate group.

Experimental part

Materials and methods

Elemental sulfur (S_8) and benzene were purchased from Sigma-Aldrich. 1,3-Dimethylimidazolium dimethylphosphate was purchased from Merck. 1H , ^{13}C , ^{31}P and ^{15}N NMR spectra of the reagents and products were recorded at Shared Resource Center of Dmitry Mendeleev University of Chemical Technology of Russia, Shared Resource Center of A. N. Nesmeyanov Institute of Organoelement compounds of the Russian Academy of Sciences. Mass spectra of the reaction products of S_8 and 1,3-dimethylimidazolium dimethylphosphate were recorded after dispersion of the sample in a nebulizer at a temperature of 473 K (Shared Use Center of N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences). MALDI spectra were recorded on a mass spectrometer with nitrogen laser with a wavelength of 337 nm (Shared Resource Center of V. N. Orekhovich Institute of Biomedical Chemistry of the Russian Academy of Sciences).

Interaction of 1,3-dimethylimidazolium dimethylphosphate with elemental sulfur

Elemental sulfur powder (S_8 , 1.46 g) was dispersed in 50 ml of benzene while stirring on a magnetic stirrer, and 1 ml of 1,3-dimethylimidazolium dimethylphosphate was added. The reaction system was kept at the temperature of 298 K for 60 min. Within 15 min after mixing, a deepening of the brown color of the reaction system was observed. After complete dissolution of sulfur, the mixing was stopped; the reaction system was maintained for 45 min at the same temperature, while phase separation was observed. The dark red reaction product accumulated in the lower layer was isolated using a separatory funnel.

Quantum chemical simulation of dimethylphosphate anion interaction with S_8

The possibility of the S_8 ring opening as a result of nucleophilic attack by dimethylphosphate anion was modeled by the Kohn-Sham method with exchange-correlation functional B3LYP with STO-3G, 6-31G* and 6-311G* basis sets using the Firefly program (Alex A. Granovsky, Firefly version 8, <http://classic.chem.msu.su/gran/firefly/>). A complete quantitative analysis of the reactivity requires the construction of the potential energy surface of the system for interacting dimethylphosphate anion and S_8 , followed by the identification of the reaction path, the transition state and the calculation of the activation energy. This approach presents a considerable difficulty. Therefore, this paper presents the estimations based on the consideration of the

structure and energy of a supermolecule formed when the interacting particles approach at a distance of 1.717 Å, equal to the sum of the covalent radii of sulfur and oxygen. Also, the method of quantum-topological analysis of electron density (QTAIMC theory) [27] was used for supermolecules optimized by B3LYP/6-31G* and B3LYP/6-311G* methods using Multiwfn software (Multiwfn.Codeplex. – URL: <https://multiwfn.codeplex.com/>).

Results and discussion

In the ^1H NMR spectrum of the initial 1,3-dimethylimidazolium dimethylphosphate ionic liquid, the singlets with the chemical shifts of 9.30 ppm, 7.83 and 4.10 ppm are observed. They correspond to the protons of the 1,3-dimethylimidazolium cation at position 2, equivalent positions 4 and 5, as well as methyl groups at nitrogen atoms. A doublet with a chemical shift of 3.61 ppm corresponds to the protons of the methyl groups of the dimethylphosphate anion in spin-spin interaction with the phosphorus atom. A similar interpretation of signals in the ^1H NMR spectrum of 1,3-dimethylimidazolium dimethylphosphate is given in [28]. ^{13}C NMR spectrum of the initial 1,3-dimethylimidazolium dimethylphosphate contains signals with chemical shifts of 139.93 ppm, 125.89 and 37.57 ppm, which correspond to carbon atoms at position two, equivalent positions four and five of the imidazolium ring, and to the carbon atoms of methyl groups at nitrogen atoms. A signal with a chemical shift of 53.90 ppm corresponds to the carbon atoms of the methyl groups of the dimethylphosphate anion. After the reaction of 1,3-dimethylimidazolium dimethylphosphate with elemental sulfur in the benzene medium, the chemical shifts of all hydrogen and carbon atoms in the ^1H and ^{13}C NMR spectra of the reaction product practically do not change, and their multiplicities are also preserved. However, in the ^1H and ^{13}C NMR spectra, new singlets appear at 7.44 and 130.71 ppm, respectively. These signals may probably correspond to a product of some reaction involving 1,3-dimethylimidazolium cation, or may simply refer to benzene used as a solvent. Registration of ^1H – ^{15}N two-dimensional NMR spectrum (Fig. 1) of the reaction product whose signals were detected by the inverse method (by protons) showed the absence of spin-spin interaction of the proton responsible for the appearance of the new signal with nitrogen atoms of the 1,3-dimethylimidazolium cation, which allows us to confidently attribute it to benzene protons. The presence of benzene in the reaction product is associated with the difficulties of its removal, since benzene removal by distillation may lead to the equilibrium shift towards increasing the chain length of the formed sulfur oligomers, and freezing, on the contrary, will contribute to reducing their length [2]. Because benzene is a toxic

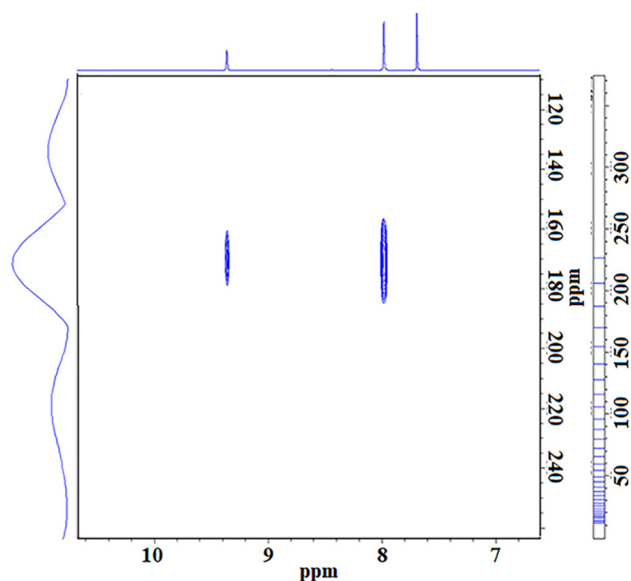


Fig. 1: Two-dimensional ^1H – ^{15}N NMR spectrum measured by the inverse method (by protons) of the product of interaction of 1,3-dimethylimidazolium dimethylphosphate with S_8 .

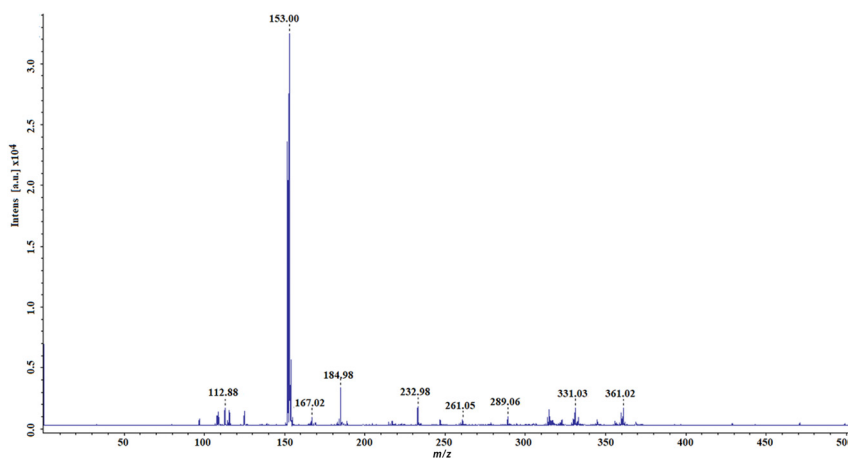


Fig. 2: MALDI spectrum (negative ion mode) of the products of 1,3-dimethylimidazolium dimethylphosphate interaction with S_8 .

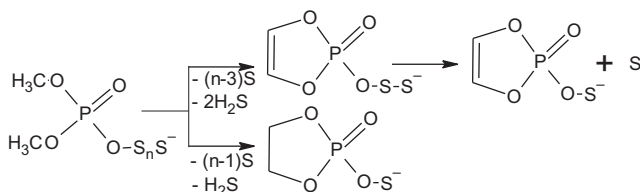
compound, it can be further replaced by the natural terpene *p*-Cymene as a solvent. In the present work we used benzene as a solvent to simplify the analysis of the obtained spectral data.

Thus, 1,3-dimethylimidazolium cation is inactive in this reaction, and the reaction is associated only with the presence of a dimethylphosphate anion. This conclusion is fully consistent with the fact that S_8 does not interact with ionic liquids not containing dimethylphosphate anion, such as 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate, 1,3-dimethylimidazolium hexafluorophosphate. It is also noteworthy that in the ^{31}P NMR spectra of the reaction product and of the initial 1,3-dimethylimidazolium dimethylphosphate, only one signal with a chemical shift of 1.17 and 1.83 ppm, respectively, is observed. Thus, the only potential site for the interaction of 1,3-dimethylimidazolium dimethylphosphate with S_8 is the negatively charged oxygen atom of the dimethylphosphate anion, since in case of the reaction on other atoms, the changes in chemical shifts in ^1H , ^{13}C , ^{31}P NMR spectra would be significant. Registration of ^{17}O NMR spectra confirms this assumption, since two signals of two nonequivalent oxygen atoms are observed for the initial ionic liquid and after its interaction with S_8 , the signals of three nonequivalent oxygen atoms were observed [26].

In the MALDI spectrum of the interaction product of 1,3-dimethylimidazolium dimethylphosphate with sulfur, the most intense signal in the negative ion mode is observed at $m/z = 153.00$, suggesting the formation of $\text{C}_2\text{H}_2\text{PO}_4\text{S}^-$ anion (Fig. 2, Scheme 1).

The presence of a signal at $m/z = 153.00$ and the absence of a signal with $m/z \approx 125$ corresponding to the dimethylphosphate anion, is consistent with the reaction between 1,3-dimethylimidazolium dimethylphosphate and S_8 . The signals with $m/z = 184.98$ and 167.02 correspond to the $\text{C}_2\text{H}_2\text{PO}_4\text{S}_2$ anion and its dehydration product, respectively. The signal at $m/z = 232.98$ appears to correspond to the particle $\text{C}_6\text{H}_6 \times \text{C}_2\text{H}_4\text{PO}_4\text{S}^-$ (Fig. 2, Scheme 1).

Although the registration of MALDI spectra assumes mild ionization conditions, the cyclodehydrogenation processes in accordance with scheme 1, which explains the appearance of signals at $m/z = 153.00$, 184.98 and 232.98 , is possible. Such cyclodehydrogenation processes have long been described for the interaction of hydrocarbons with sulfur [29].



Scheme 1: Reactions expected to proceed during laser desorption of the products of 1,3-dimethylimidazolium dimethylphosphate interaction with S_8 .

In the positive ion mode, a series of signals with a molecular mass difference of 32 is observed in the MALDI spectrum (Fig. 3). A similar pattern of fragmentation is characteristic of elemental sulfur [30]. Since in the MALDI spectrum of the product of interaction of equimolar quantities of 1,3-dimethylimidazolium dimethylphosphate and S_8 , the signal with $m/z \sim 125$ was not observed in the negative ion mode, we can assume that dimethylphosphate anion nearly quantitatively reacted with S_8 . Therefore, the appearance of signals characteristic of elemental sulfur in the MALDI spectrum in the positive ion mode is associated with its release during the decomposition of $C_2H_6PO_4S_n^-$ (Scheme 1). In addition to signals $(S_n)^+$ with different n , there is also a signal of 1,3-dimethylimidazolium cation ($m/z = 96.99$), which is consistent with its stability in the reaction of 1,3-dimethylimidazolium dimethylphosphate with S_8 (Fig. 3).

In the ESI mass spectrum obtained in the positive ion mode, the fragmentation pattern characteristic of sulfur was not observed. This can be explained by the thermal decomposition of $C_2H_6PO_4S_n^-$ when the sample is dispersed in a nebulizer at a temperature of 473 K for 30 s before the sample is fed to the ionization chamber. The signals with $m/z = 97.0761$ and $m/z = 319.1533$ correspond to the 1,3-dimethylimidazolium cation and to the positively charged ionic associate $[(1,3-Me_2Im)_2Me_2PO_4]^+$ (Fig. 4). The low-intensity signal at $m/z = 252.9727$ probably corresponds to the loss of hydrogen by the addition of one sulfur atom to 1,3-dimethylimidazolium dimethylphosphate. The low intensity of this signal is also indirectly consistent with the thermal decomposition of $C_2H_6PO_4S_n^-$ before entering the ionization chamber.

In the ESI mass spectrum obtained in the negative ion mode, the most intense signal with $m/z = 125.0000$ corresponds to dimethylphosphate anion. Since no signals typical for the initial ionic liquid were observed in MALDI spectra, the detection of the $C_2H_6PO_4^-$ anion is probably associated with the decomposition of $C_2H_6PO_4S_n^-$ when the sample is dispersed in a nebulizer before entering the ionization chamber. Also, the signals at $m/z = 255.2321$ and 414.9618 with significant intensities were observed in the mass spectrum (Fig. 5). These signals probably correspond to the products of hydride ion addition, as well as one sulfur atom and six sulfur atoms addition to the initial ionic liquid, respectively. Hydride ion transfer processes are described in the literature [31–33]. Since only monomolecular reactions are possible under the conditions of mass spectra registration, it is possible that hydride ion transfer can be realized in ionic associates, the formation of which

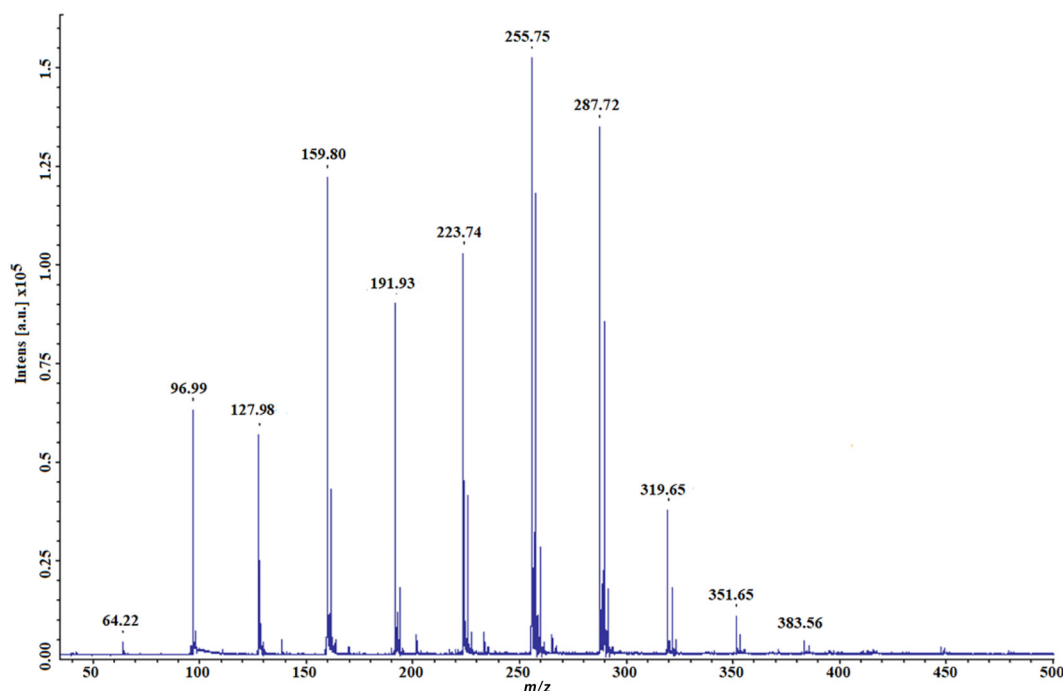


Fig. 3: MALDI spectrum (positive ion mode) of the product of 1,3-dimethylimidazolium dimethylphosphate interaction with S_8 .

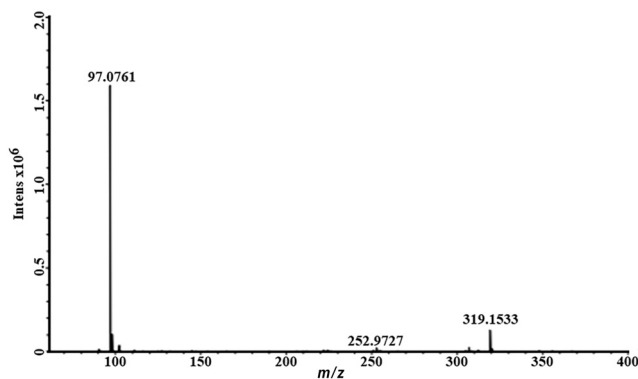


Fig. 4: ESI mass spectrum (positive ion mode) of the product of interaction of 1,3-dimethylimidazolium dimethylphosphate with S_8 .

was noted above. In this case, the signal at $m/z \approx 223$, the presence of which would be expected for the unreacted 1,3-dimethylimidazolium dimethylphosphate, was not observed.

Summarizing the data obtained by ^1H , ^{13}C , ^{15}N , ^{31}P , ^{17}O NMR spectroscopy, MALDI and ESI mass spectra, we can conclude that the studied reaction can be described as the addition of sulfur to a negatively charged oxygen atom of dimethylphosphate anion of the initial ionic liquid (Scheme 2). Since in the MALDI spectra there are no signals corresponding to high molecular weight compounds, we suppose that only the products with short sulfur chains for in the studied reaction. It should be noted that 1,3-dimethylimidazolium dimethylphosphate ionic liquid was used in equimolar amounts with respect to S_8 . This contributes to the formation of low molecular weight products, especially if the initiation stage is rapid. In the reaction of S_8 with tri-*n*-butylmethylphosphonium dimethylphosphate, the products of higher molecular weight were formed [26], indicating a lower activity of this ionic liquid in reaction with S_8 compared to 1,3-dimethylimidazolium dimethylphosphate.

Higher reactivity of 1,3-dimethylimidazolium dimethylphosphate in the reaction with S_8 can be described on the basis of the Pearson hard and soft acids and bases (HSAB) theory. The oligomeric anion is a soft Lewis base, while the hardness of the tri-*n*-butylmethylphosphonium cation is higher than that of 1,3-dimethylimidazolium cation in which the positive charge is delocalized. Then, in accordance with the

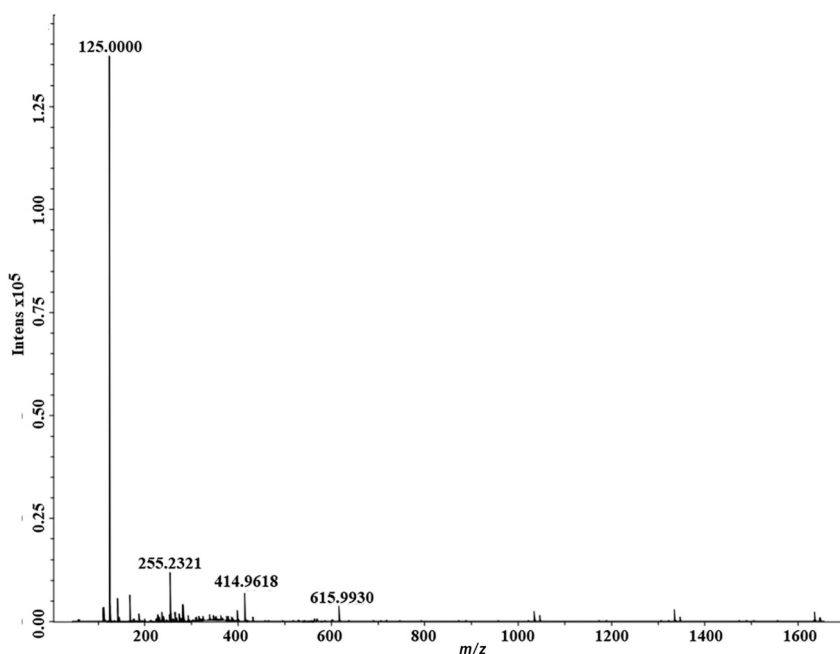
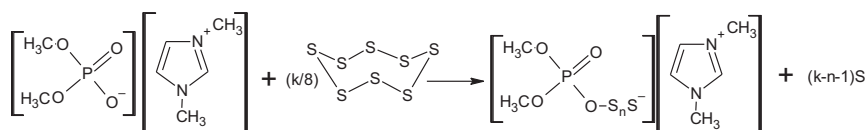


Fig. 5: ESI mass spectrum (negative ion mode) of the product of interaction of 1,3-dimethylimidazolium dimethylphosphate with S_8 .



Scheme 2: Reaction of 1,3-dimethylimidazolium dimethylphosphate with elemental sulfur.

HSAB theory [34, 35], one should expect a higher decrease in the energy of the system resulting from the interaction of oligomeric anion with 1,3-dimethylimidazolium cation than with tri-*n*-butylmethylphosphonium.

In the theoretical study of the possibility of S_8 ring opening in the interaction with dimethylphosphate anion, the Kohn-Sham method at the B3LYP/STO-3G level of theory predicts spontaneous S_8 ring opening upon approaching the dimethylphosphate anion at a distance of 1.717 Å. It is accompanied by a decrease in the total energy of the system by $242 \text{ kJ} \times \text{mol}^{-1}$ compared to infinitely distant reagents. Modeling at B3LYP/6-31G* and B3LYP/6-311G* levels of theory also shows a decrease in the total energy of the system upon formation of a supermolecule by $399 \text{ kJ} \times \text{mol}^{-1}$ and $55 \text{ kJ} \times \text{mol}^{-1}$, respectively. After geometry optimization by B3LYP/6-31G* and B3LYP/6-311G* methods, the calculated distances in the supermolecule between the oxygen atom of the dimethylphosphate anion carrying a negative charge and the sulfur atom entering the S_8 ring are 2.400 Å and 2.421 Å, respectively, and an imaginary frequency is present in the vibrational spectrum.

Thus, the convergence of the S_8 ring and the dimethylphosphate anion at a distance of 1.717 Å in the B3LYP/STO-3G approximation leads to the opening of the S_8 ring, and the energy minimum was achieved upon formation of the reaction product shown in Scheme 2. Calculations at the B3LYP/6-31G* and B3LYP/6-311G* levels of theory predict the formation of supermolecules with distances between reagents greater than the originally specified (1.717 Å). These structures are transient states realized when the system moves along the reaction coordinate from the initial compounds to the reaction products, as evidenced by the presence of imaginary frequencies. The QTAIMC theory for B3LYP/6-31G* and B3LYP/6-311G* optimized supermolecules indicates a bound state between the oxygen atom of the dimethylphosphate anion and the sulfur atom of the S_8 ring: there is a critical bond point (3, -1) between these atoms. The electron density (ρ_b) values at the critical coupling point are 0.0425 (B3LYP/6-31G*) and 0.0399 a.u. (B3LYP/6-311G*). The electron density Laplacian ($\nabla^2 \rho_b$) values are 0.1122 (B3LYP/6-31G*) and 0.1138 (B3LYP/6-311G*) a.u.

Conclusions

It is shown that the interaction of 1,3-dimethylimidazolium dimethylphosphate with elemental sulfur is accompanied by the S_8 ring opening. The reaction proceeds only with the participation of dimethylphosphate anion due to the addition of sulfur to the oxygen atom carrying negative charge. The 1,3-dimethylimidazolium cation does not participate in the reaction. The possibility of the S_8 ring opening as a result of nucleophilic attack by dimethylphosphate anion is confirmed by modeling the interaction of these particles by the Kohn-Sham method at the B3LYP/STO-3G level of theory.

References

- [1] S. Diez, A. Hoeffling, P. Theato, W. Pauer. *Polymers* **9**, 59 (2017).
- [2] A. V. Tobolsky. *J. Polym. Sci. Part C: Polym. Symp.* **12**, 71 (2007).
- [3] F. Fairbrother, G. Gee, G. T. Merrall. *J. Polym. Sci.* **16**, 459 (1955).
- [4] A. V. Tobolsky, A. Eisenberg. *J. Am. Chem. Soc.* **81**, 780 (1959).
- [5] K. S. Andrikopoulos, A. G. Kalampounias, S. N. Yannopoulos. *J. Chem. Phys.* **124**, 146101 (2006).
- [6] V. F. Kozhevnikov, W. B. Payne, J. K. Olson, C. L. McDonald, C. E. Inglefield. *J. Chem. Phys.* **121**, 7379 (2004).
- [7] J. J. Griebel, R. S. Glass, K. Char, J. Pyun. *Prog. Polym. Sci.* **58**, 90 (2016).
- [8] A. L. Klebanskiĭ, N. J. Zukerman, L. P. Fomina. *Rubber Chem. Technol.* **32**, 588 (1959).

- [9] D. J. Parker, H. A. Jones, S. Petcher, L. Cervini, J. M. Griffin, R. Akhtar, T. Hasell. *J. Mater. Chem. A*, **5**, 11682 (2017).
- [10] V. Gupta, S. Ghosh, V. Phapale. *Phosphorus, Sulfur, Silicon Relat. Elem.* **193**, 752 (2018).
- [11] S. Oishi, K. Oi, J. Kuwabara, R. Omoda, Y. Aihara, T. Fukuda, T. Takahashi, J.-C. Choi, M. Watanabe, T. Kanbara. *ACS Appl. Polym. Mater.* **1**, 1195 (2019).
- [12] M. J. H. Worthington, R. L. Kucera, J. M. Chalker. *Green Chem.* **19**, 2748 (2017).
- [13] S. Penczek, R. Ślazak, A. Duda. *Nature* **273**, 738 (1978).
- [14] S. Penczek, A. Duda. *Phosphorus, Sulfur, Silicon Relat. Elem.* **59**, 47 (1991).
- [15] Y. Zhang, R. S. Glass, K. Char, J. Pyun. *Polym. Chem.* **10**, 4078 (2019).
- [16] Y. Zhang, N. G. Pavlopoulos, T. S. Kleine, M. Karayilan, R. S. Glass, K. Char, J. Pyun. *J. Polym. Sci. Part A: Polym. Chem.* **57**, 7 (2019).
- [17] N. Hartler, J. Libert, A. Teder. *Ind. Eng. Chem. Proc. Des. Dev.* **6**, 398 (1967).
- [18] W. E. Kleinjan, A. de Keizer, A. J. H. Janssen. *Coll. Surf. B: Biointerface* **43**, 228 (2005).
- [19] H. Shin, J. Kim, D. Kim, V. H. Nguyen, S. Lee, S. Han, J. Lim, K. Char. *J. Mater. Chem. A*, **6**, 23542 (2018).
- [20] A. E. Rosamilia, C. R. Strauss, J. L. Scott. *Pure Appl. Chem.* **79**, 1869 (2007).
- [21] K. J. Fraser, D. R. MacFarlane. *Austral. J. Chem.* **62**, 309 (2009).
- [22] V. I. Pârvulescu, C. Hardacre. *Chem. Rev.* **107**, 2615 (2007).
- [23] J. Pernak, F. Walkiewicz, M. Maciejewska, M. Zaborski. *Ind. Eng. Chem. Res.* **49**, 5012 (2010).
- [24] M. Maciejewska, F. Walkiewicz, M. Zaborski. *Ind. Eng. Chem. Res.* **52**, 8410 (2013).
- [25] M. Maciejewska, M. Zaborski. *Polym. Bull.* **75**, 4499 (2018).
- [26] N. Tarasova, E. Krivoborodov, A. Zanin, Y. Mezhuev. *Doklady Chem.* **484**, 8 (2019).
- [27] R.F.W. Bader. *Atoms in Molecules: A Quantum Theory*, Oxford University Press, New York (1990).
- [28] H.F. Sangian, J. Kristian, S. Rahma, S. Y. Agnesty, S. Gunawan, A. Widjaja. *J. Eng. Technol. Sci.* **47**, 137 (2015).
- [29] H. Berger. *J. Prakt. Chem.* **133**, 331 (1932).
- [30] A. Kruegel, A. B. Attygalle. *J. Am. Soc. Mass Spectr.* **21**, 112 (2010).
- [31] F. H. Field, F. W. Lampe. *J. Am. Chem. Soc.* **80**, 5587 (1958).
- [32] V. M. Matyuk, V. K. Potapov. *High Energy Chem.* **34**, 122 (2000).
- [33] D. M. Brouwer, C. F. Roobeek, J. A. van Doorn, A. A. Kiffen. *Recl. Trav. Chim. Pays-Bas* **92**, 563 (2010).
- [34] R. G. Pearson. *J. Am. Chem. Soc.* **85**, 3533 (1963).
- [35] P. K. Chattaraj, H. Lee, R. G. Parr. *J. Am. Chem. Soc.* **113**, 1855 (1991).