Multibubble sonolysis and sonoluminescence in molten elementary sulfur and sulfur—styrene mixture

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The effect of saturation with argon, as well as styrene and iodine additives on the temperature dependence of multibubble sonoluminescence intensity in molten sulfur at 120—230 °C was studied. The shape of the temperature dependence with a maximum at 170—200 °C is determined by the viscosity variations related to the changes in the molecular structure of molten elemental sulfur. At high temperatures, cyclooctasulfane (S_8) molecules break to radical products, which then undergo polymerization that can be slowed down by the additives. Sulfurization of styrene during sonolysis of a sulfur—styrene mixture resulting in products of the thiophene series was detected. Unlike thermal sulfurization that affords 2,5-diphenylthiophene as a major product, sonochemical sulfurization results mainly in 2,4-diphenylthiophene. The mechanism of 2,4-diphenylthiophene formation initiated by the reaction of styrene molecules with S^+ ions produced upon fragmentation of S_8 within cavitation bubbles is proposed. The glow of electronically excited S^{+*} ions is responsible for the band with a maximum at 560 nm in the sonoluminescence spectrum of molten sulfur, which is suppressed by the styrene additive.

Key words: sonolysis, sonochemical reactions, multibubble sonoluminescence, sulfurization, elemental sulfur, styrene, synthesis of thiophenes.

Recently,[1] we have reported the observation of luminescence during sonolysis of molten elemental sulfur. Interest in studies of this phenomenon is due to two reasons. First, investigations of sonochemical reactions of elemental sulfur, abundant raw material for chemical industry,[2] are important in connection with the need for sulfurization of unsaturated hydrocarbons resulting in useful organosulfur products, which is a topical problem. Second, information on the regularities of luminescence during sonolysis of liquid substances in the form of high-temperature viscous melts is essential for understanding the mechanisms of multibubble sonoluminescence (MBSL) in liquids, which are still to be clarified in spite of long-term research.[3,4] Examples of sonoluminescence in melts are scarce. The glow observed during sonolysis of a number of molten metals and polymers[3] can differ from the MBSL of water and aqueous solutions that have been well studied. For water and aqueous solutions, the luminescence intensity is maximum near the melting point and monotonically decreases as the temperature increases.[3] This type of temperature behavior is also characteristic of molten tin.[5] However, the intensity of MBSL in a very viscous polyethylene melt increases with temperature.[6] Abnormal temperature dependence of molten elemental sulfur was also observed.[1]

In the present work, in a continuation of our studies[1] on sonochemical reactions of elemental sulfur we investigated the effect of various additives and temperature on MBSL in molten elemental sulfur and the possibility of sulfurization during sonolysis of a mixture of molten sulfur and unsaturated hydrocarbon, styrene.

Experimental

Molten elemental sulfur for sonolysis was prepared by heating a weigh of crystalline orthorhombic allotrope of yellow sulfur ("chemically pure" grade) with the chemical formula S_8 (see Ref. 2) in a muffle furnace to 120 °C. Then, the melt (10—20 mL) was heated from 120 to 230 °C at an average rate of about 0.3 deg s^{-1} by sonication in glass reactors equipped with a thermostatting jacket. As the melt was heated to a specified temperature, one could maintain this temperature by thermo-

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statting and by repeated sonication. In the case of sonolysis of a styrene—sulfur mixture with high styrene content the liquid mixture with a specified high temperature was obtained by heating a suspension of sulfur in styrene by sonication directly from room temperature. Sonolysis was carried out using conventional instruments for sonication of solutions including UZDN-A, UZDN-2T, IL 10-0.6, and ACE GLASS equipped with immersion horns (operating frequency range 20—22 kHz, total acoustic power 5—60 W). The MBSL intensity and spectra were recorded using equipment described elsewhere.[1,7] EPR spectra of the thermolysis and sonolysis products of molten sulfur were recorded on a Bruker EMX spectrometer. The products of thermolysis and sonolysis of the styrene—sulfur mixture were separated and identified following known procedures.[8—10] The product ratios in the reaction mixtures were determined by chromato-mass spectrometry (Finnigan-4021, glass capillary column 50000×0.25 mm, HP-5 as a stationary phase, helium as the carrier gas, temperature programming from 50 to 300 °C at a rate of 5 deg min^{-1}, vaporizer temperature 280 °C, ion source temperature 250 °C, ionizing voltage 70 eV). The MBSL was recorded using freshly prepared styrene; sonolysis of styrene—sulfur mixtures with isolation of sonolysis products was carried out with styrene containing a stabilizer (4-*tert*-butylpyrocatechol, about 1%), which is an efficient inhibitor of radical polymerization.

Results and Discussion

The intensity of MBSL in molten sulfur at 120 °C, which is near the melting point of rhombohedral sulfur (112.8 °C),[2] is 10^9 photon s^{-1} at an acoustic power of 11 W cm^{-2} (determined by comparison with a standard radioluminescent source of light). This is comparable with intensity of room-temperature MBSL in water* (Fig. 1).

MBSL in liquids is emitted from the gas medium (cavitation bubbles).[3] When analyzing the MBSL spectra of colored liquids, one should take into account the absorption of MBSL within the bulk of the liquid. At 130 °C, a 1-cm layer of molten sulfur is opaque to the glow with $\lambda < 470$ nm (Fig. 2, curve *2*). In the course of sonolysis the brown color of the melt becomes more intense because the process is accompanied by heating. As a consequence, a possible (and characteristic of most liquids) luminescence in the UV and (partially) visible spectral region (400—500 nm) is self-absorbed by the melt and its registration is difficult. Nevertheless, we believe that the only band (λ_{max} = 560 nm, half-width about 90 nm) in the MBSL spectrum of the melt recorded at 130—150 °C in the course of sonolysis over a period of 2 min prior to intense coloration is individual in character rather than is a result of the absorption of the short-wavelength region of a continuum whose width exceeds that of the band 560 nm (see Fig. 2, curve *1*). Most probably, taking into account a rather low spectral resolution ($\Delta\lambda$ = 10 nm) and broadening of spectral lines in cavitation bubbles, this band appears as a result of the overlap of the spectral lines of sulfur. It seems that the main emitter of the band at 560 nm is the S^{+}* ion. It is this spectral region that corresponds to a group of the most intense lines of singly ionized sulfur[11] atom in the luminescence spectrum obtained upon spark discharge (see Fig. 2). The spark luminescence spectrum shows that not only S^{+}*, but also the other minor emitter, S*, can contribute to the band in the MBSL spectrum.

Production of excited sulfur ions during sonolysis of the melt can be explained in the simplest manner from the standpoint of the theory of local electrization of cavitation bubbles. According to this theory, MBSL is a result of electric discharge, which leads to preferred formation of ionic products in the ground and excited states upon primary electronic excitations.[4]

Saturation of melt with argon or oxygen has little effect on the bandshape of the observed MBSL in sulfur;

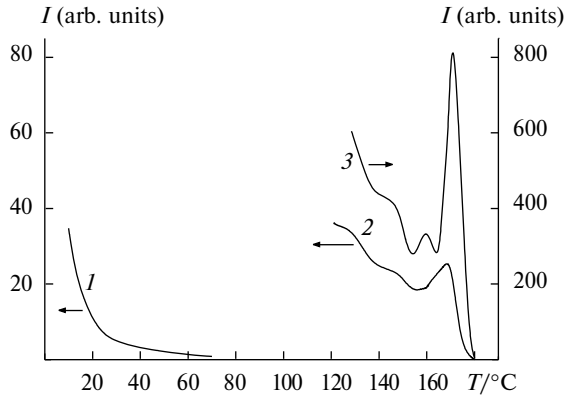


Fig. 1. Temperature dependence of MBSL intensity in water (*1*) and in molten sulfur saturated with air (*2*) and argon (*3*).

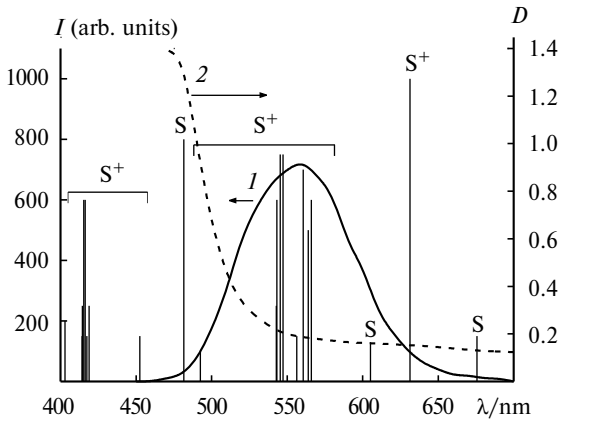


Fig. 2. MBSL spectra (*1*) and absorption spectra (*2*) of molten sulfur at 130—140 °C. Lines denote the emission of sulfur atoms and ions generated upon spark discharge.

* Water exhibits a rather intense luminescence in the course of sonolysis and is a liquid whose sonoluminescence has been best studied.[3] Therefore, it is water that should be used as a reference when comparing the intensities of sonoluminescence in different liquids.

however, the intensity of the glow increases by a factor of 1.5 in the presence of O_2 and by more than an order of magnitude in the presence of argon. This behavior of MBSL is typical of many liquids including water. A slight increase in MBSL intensity in the presence of oxygen can be explained by a simple increase in the number of cavitation bubbles. In addition to this effect, the stronger action of argon is also associated within the framework of the thermal theory of MBSL (see Ref. 12) with the decrease in the heat conductivity of bubbles filled with the monatomic gas and with an increase in the limiting pressure achieved in the compression phase. This causes the temperature and the number of inelastic exciting collisions of "hot" particles with potential emitters to increase. Another explanation consists in that atoms of argon and heavier noble gases are efficient sensitizers, *i.e.*, they transfer energy from primary excited species with high-lying energy levels (most probably, these are the noble gas atoms themselves[3]) to the secondary emitters observed in the MBSL spectrum. With no sensitization, the primary species mainly undergo nonradiative deactivation or, if these species are the noble gas atoms themselves, are simply formed in a lower content. This action mechanism of the noble gas is in good agreement with the electrical theory of MBSL.

Thus, assuming that electrical discharges in cavitation bubbles produce electrons accelerated by the electric field (ê) and taking into account the fact that the weight-average temperature in the pulsating bubbles in the compression phase can be as high as a few thousands of degrees,[3] thus ensuring fragmentation of low-volatile bubbles of S_8 molecules which vaporize into the bulk of the bubbles with no discharge,[2] the mechanism of MBSL in molten sulfur can be represented by the following scheme:

$$(S_8)_{liq} \xrightarrow{i} (S_8)_{gas} \xrightarrow{i} S,\ S^+,\ \hat{e},$$

$$\hat{e} + S,\ S^+ \longrightarrow S^*,\ S^{+*} + e,$$

$$S^*,\ S^{+*} \longrightarrow S,\ S^+ + h\nu,$$

augmented with additional reactions as the melt is saturated with argon:

$$Ar + \hat{e} \longrightarrow Ar^* + e,$$

$$Ar + \hat{e} \longrightarrow Ar^+ + 2e,$$

$$Ar^+ + e \longrightarrow Ar^*,$$

$$Ar^* + S,\ S^+ \longrightarrow Ar + S^*,\ S^{+*}$$

i. Sonolysis.

This explanation for the action of argon on MBSL of molten sulfur also seems to be more realistic because it better correlates with similarity between the temperature dependences of the MBSL intensity obtained for the sonolysis of untreated and argon-saturated molten sulfur (see Fig. 1).

The monotonic decrease in the intensity of MBSL in water and other liquids with an increase in temperature (see Fig. 1, curve *1*) is usually explained by an increase in the saturated vapor pressure and a decrease in saturated vapor condensation on the walls of a cavitation bubble; which leads to an increase in the weight of gas within the bubble and precludes its fast compression.

In addition, a very important factor affecting cavitation is the viscosity of the liquid. We believe that it is the changes in the viscosity that determine the anomalous shape of the temperature dependences of the MBSL intensity of molten polyethylene[6] and sulfur (see Fig. 1). As in the case of water, the intensity of MBSL in molten sulfur in the interval from 120 to 155 °C decreases, but at 160 °C begins to increase, reaches a maximum value near 170 °C, and then abruptly decreases to zero near 180 °C. The dependence for the argon-saturated melt is similar in shape; only the point corresponding to the increase in MBSL and the maximum of MBSL intensity is slightly shifted.

The dependences obtained correlate with the known temperature variations of the viscosity of liquid sulfur.[2] In the range 120—160 °C, molten sulfur is composed of S_8 molecules and has a low viscosity ($1.1 \cdot 10^{-2}$ Pa s at 120 °C), which can be explained by the ease of motion of cyclooctasulfane molecules relative to one another. As the temperature increases, the viscosity slowly decreases to a value of $6.5 \cdot 10^{-3}$ Pa s at 155 °C, which is typical of conventional liquids. In the temperature range from 159 to 187 °C, the melt viscosity abruptly increases to a maximum value of 93.3 Pa s due to the fact that in this temperature interval the eight-membered sulfur rings rapidly break down to linear biradicals $^{\bullet}S—S_6—S^{\bullet}$; subsequent radical attack on the unbroken rings may lead to polymerization. The longest polymer chains may include about 10^6 sulfur atoms.[2]

The formation of radical products upon sonolysis of molten sulfur was detected by EPR spectroscopy. The EPR spectrum of such radicals matches that of the radicals produced by simply heating the melt. A singlet with a g-factor of 2.0046 ± 0.0002 observed in the room-temperature EPR spectrum of the sonicated melt matches the signal observed after thermolysis of identically prepared samples. However, in the case of sonothermal action the signal intensity was much higher. The concentration of paramagnetic radical centers accumulated upon sonolysis under identical conditions (160 °C, duration 20 min, sonication power 10 W per milliliter of melt) was 18 ± 2 times higher than in the case of thermolysis. This is not surpris-

ing because cavitation bubbles are a powerful source of radical centers in addition to thermal generation.

Apparently, disappearance of MBSL at 180 °C is due to cessation of cavitation in the very viscous melt, which was also observed visually. However, in the initial stage an increase in viscosity undoubtedly favors an increase in the intensity of MBSL. Thus, there exists an optimum interval of viscosity values corresponding to the maximum intensity of MBSL.

The assumptions of the effect of viscosity on the intensity of MBSL and on the determining role of the molecular structure of the melt are confirmed by the observation of MBSL in the melt containing molecular iodine as an additive which terminates polymer chains following the reaction[2]:

$$\bullet S_n \bullet + I_2 \longrightarrow I{-}S_n{-}I.$$

This reduces the melt viscosity and allows MBSL to be observed at temperatures above 180 °C (Fig. 3, curve *1*). Owing to more intense color of the iodine-containing melt, the total MBSL intensity decreases by about an order of magnitude; the curve is similar in shape to the temperature dependence obtained in the absence of iodine and shows a slight decrease in the MBSL in the initial stage and a maximum at ~200 °C. It should be noted that in these experiments the melt viscosity after passage of the maximum did not reduce to the critical value corresponding to cessation of cavitation and a weak MBSL accompanied by an irregular increase in luminescence and individual flashes of glow up to 280—300 °C was observed.

The addition of unsaturated hydrocarbon, *viz.*, styrene, has a similar effect on the MBSL of molten sulfur. Biradicals ($\bullet S_n \bullet$) produced in molten sulfur under thermolysis conditions readily attack electron-deficient carbon atoms with the formation of various insertion products of sulfur atoms into the hydrocarbon.[2] For instance, the primary reaction of biradicals at the C_α atom of the styrene double bond results in 2,5-diphenylthiophene as a major product. Being an inhibitor of the formation of $\bullet S_n \bullet$ biradicals, styrene should affect the MBSL of molten sulfur, thus controlling the melt viscosity. Indeed, the addition of styrene causes the maximum of luminescence in the temperature dependence to be shifted toward high temperatures (see Fig. 3) but the MBSL spectrum remains unchanged. As the styrene concentration increases, the MBSL intensity substantially decreases despite the fact that styrene, unlike iodine, causes no additional coloration of the melt and the glow in the styrene—sulfur (1 : 1) mixture is almost completely quenched. Apparently, styrene efficiently reacts in such mixtures not only with biradicals in the bulk of the solution, but also with products of sulfur fragmentation within cavitation bubbles, in particular, with electronically excited S^{+}* and S*, thus leading to quenching of MBSL.

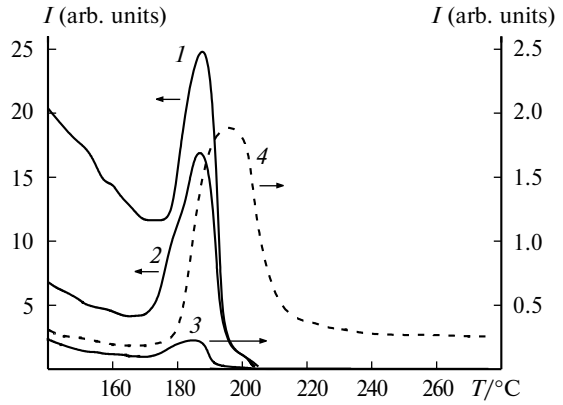
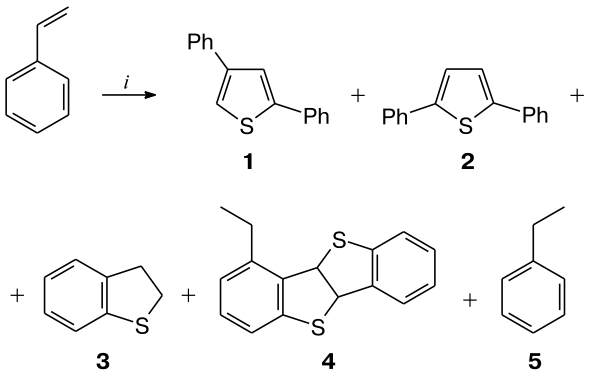


Fig. 3. Temperature dependence of sonoluminescence in molten sulfur in the presence of styrene additives at a sulfur : styrene mole ratio of 1000 : 1 (*1*), 100 : 1 (*2*), and 20 : 1 (*3*) and iodine additive at a sulfur : iodine mole ratio of 100 : 1 (*4*).

Indeed, the products of this reaction were detected after sonolysis.[10] For instance, sonolysis of a styrene—sulfur (1 : 3) mixture at 150—160 °C for 1 h results in 2,4-diphenylthiophene (**1**), 2,5-diphenylthiophene (**2**), benzothiophane (**3**), 4-ethylbenzothiophano[3,2-*b*]benzothiophane (**4**), and ethylbenzene (**5**) in 57, 15, 15, 11, and 2% yields, respectively, at an overall styrene conversion of 70% (Scheme 1).

The major sonolysis product of molten sulfur, 2,4-diphenylthiophene (**1**), is formed in a low yield (about 2%) under thermolysis conditions.[13] The yield of **1** under thermolysis conditions can be increased up to 15% only in the presence of a palladium catalyst.[14] At the same time, thermolysis results in 2,5-diphenylthiophene (**2**) as major product whose yield strongly depends on the reaction conditions, being at most 30% (see Refs 13—15).

Scheme 1

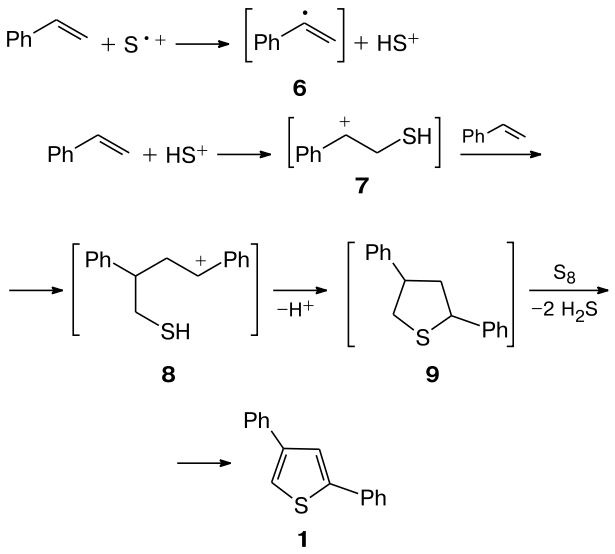


i. S_8, sonolysis 160 °C , 1 h

These facts can be related to cavitation-initiated sulfurization proceeding by the ion mechanism owing to the interaction of styrene with S^{+}. Indeed, elemental sulfur is similar in properties to $\bullet S_n \bullet$ biradicals. It can not

cause the formation of products different from those of thermolysis which proceeds by the radical mechanism (*e.g.*, 2,5-diphenylthiophene). At the same time, the S^+ ion, which is in essence an $S^{\bullet+}$ radical ion, can abstract a hydrogen atom from the C_α atom of the styrene double bond in the initial stage, thus producing radical **6** and the thiyl cation HS^+. Radical **6** under the conditions of this reaction is more stable than the $PhCH{=}CH^\bullet$ radical produced in the reaction of styrene with an S atom or $^\bullet S_n{}^\bullet$ biradicals; this route leads to 2,5-diphenylthiophene (**2**). The HS^+ cation attacks the C_β atom of the styrene double bond and thus initiates the formation of **1** as a result of successive reactions including the addition of thiol **7** to styrene, cyclization of intermediate **8**, and dehydrogenation of 2,4-diphenylthiophane (**9**) (Scheme 2).

Scheme 2



Summing up, ultrasonic irradiation of styrene—sulfur mixtures at high temperatures leads to formation of unstable sonolysis product, S^+ ion, in cavitation bubbles and to its sonothermal reactions identified from the MBSL in molten sulfur and the synthesis of 2,4-diphenylthiophene. This allows one to recommend ultrasonic activation as a method for sulfurization of unsaturated hydrocarbons. The temperature dependence of the MBSL intensity is determined by viscosity variations due to the changes in the molecular structure of molten sulfur owing to breakdown of S_8 molecules at high temperatures and production of biradicals followed by polymerization.

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References

1. A. M. Abdrakhmanov, G. L. Sharipov, I. V. Rusakov, V. R. Akhmetova, R. G. Bulgakov, *Pis´ma v Zh. Eksperim. Teor. Fiz.*, 2007, **85**, 495 [*JETP Letters* (*Engl. Transl.*), 2007, **85**, 410].
2. M. G. Voronkov, N. S. Vyazankin, E. N. Deryagina, A. S. Nakhmanovich, V. A. Usov, *Reaktsii sery s organicheskimi soedineniyami* [*Reactions between Sulfur and Organic Compounds*] Nauka, Moscow, 1979, 368 pp. (in Russian).
3. M. A. Margulis, *Uspekhi Fiz. Nauk*, 2000, **170**, 263 [*Physics-Uspekhi* (*Engl. Transl.*), 2000, **43**, 259].
4. M. A. Margulis, I. M. Margulis, *Zh. Fiz. Khim.*, 2007, **81**, 136 [*Russ. J. Phys. Chem. A* (*Engl. Transl.*), 2007, **81**, 129].
5. M. A. Margulis, L. M. Grundel´, G. I. Eskin, P. N. Shvetsov, *Dokl. Akad. Nauk SSSR*, 1987, **295**, 1170 [*Dokl. Chem.* (*Engl. Transl.*), 1987, **295**].
6. M. A. Margulis, L. M. Grundel´, A. V. Kapshtyk, *Dokl. Akad. Nauk SSSR*, 1988, **300**, 1399 [*Dokl. Chem.* (*Engl. Transl.*), 1988, **300**].
7. G. L. Sharipov, R. Kh. Gainetdinov, A. M. Abdrakhmanov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 1341 [*Russ. Chem. Bull., Int. Ed.,* 2005, **54**, 1383].
8. M. G. Voronkov, E. N. Deryagina, M. A. Kuznetsova, *Zh. Organ. Khim.*, 1982, **18**, 1743 [*J. Org. Chem. USSR* (*Engl. Transl.*), 1982, **18**].
9. U. M. Dzhemilev, N. Z. Baibulatova, T. E. Tkachenko, R. V. Kunakova, L. M. Khalilov, A. A. Berg, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1989, 655 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1989, **38**, 581].
10. Russian Federation Patent 2321587, *Byul. Izobret.*, 2008, 10 [*Chem. Abstr.*, 2008, **148**, 403069].
11. A. N. Zaidel´, V. K. Prokof´ev, S. M. Raiskii, *Tablitsy spektral´nykh linii* [*Tables of Spectral Lines*], GITTL, Moscow—Leningrad, 1952, 560 pp. (in Russian).
12. B. E. Noltingk, E. A. Neppiras, *Proc. Phys. Soc. B*, 1950, **63**, 674.
13. S. V. Yas´ko, N. A. Korchevin, N. K. Gusarova, T. I. Kazantseva, N. A. Chernysheva, L. V. Klyba, B. A. Trofimov, *Khim. Geterotsikl. Soedinenii*, 2006, 1728 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 2006, **42**, 1486].
14. R. V. Kunakova, DSc (Chem.) Thesis, Institute of Organic Chemistry, Bashkirskiy Filial of the USSR Academy of Sciences, Ufa, 1989, 434 pp. (in Russian).
15. M. G. Voronkov, V. E. Udre, in *Khimiya seraorganicheskikh soedinenii, soderzhashchikhsya v neftyakh i nefteproduktakh* [*Chemistry of Organosulfur Compounds Containing in Petroleum and Petrochemicals*], Vysshaya Shkola, Moscow, 1972, **9**, 233 pp. (in Russian).

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