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Radiation-Chemical Transformation of Elemental Sulfur in the Presence of Ionic Liquids

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There is currently a worldwide overproduction of elemental sulfur, a large-scale by-product of oil and gas refining [1]. Therefore, the challenge is to develop modern ways of its transformation into various compounds, e.g., into the polymeric form having a number of valuable properties (high resistance to aggressive media, high impact strength, absence of thermal shrinkage strains in composites, insolubilities in rubbers, etc.), which could drive up the demand for elemental sulfur and its modifications.

An interesting possibility of synthesizing sulfur-containing polymers could be the use of ionic liquids. Ionic liquids have recently received much attention because they can be used as "green" solvents, a potential alternative to volatile organic solvents [5]. Ionic liquids are incombustible and thermally stable [6] and have low vapor pressure [5]; their physicochemical properties can be controlled by varying the structure of the cation or anion [4]. Such liquids can be used not only as a solvent, but also as a catalyst [7] and a stabilizing medium [5].

In this work, we for the first time studied the behavior of elemental sulfur under the action of high-energy radiation in a benzene solution in the presence of ionic liquids. It was found that, under these conditions, elemental sulfur transforms into sulfur-containing compounds, including sulfur-containing oligomers, without the formation of polymeric forms. Such behavior significantly distinguishes sulfur from another inorganic monomer, elemental (white) phosphorus, which under similar conditions mainly changes to a polymeric form, red phosphorus [8–11]. The reaction orders and the effective reaction rate constants were determined. It was established that the presence of ionic liquids accelerates the transformation of elemental sulfur. By varying the structure of the ionic liquid present in a reaction system, the characteristics of the system and the process can be controlled.

EXPERIMENTAL

In this work, we studied a number of systems, which were solutions of elemental sulfur in benzene and in benzene–ionic liquid mixtures at various initial elemental sulfur concentrations (table). In the experiments, we used sulfur S_8 (special-purity grade, Specifications TU 6-09-2546-77, Reakhim), benzene C_6H_6 (chemically pure, State Standard GOST 5955-75, Khimmed), and dimethyl sulfoxide (DMSO) $(CH_3)_2SO$ (chemically pure, Specifications TU 6-09-3818-77, Laverna). Benzene was chosen as a solvent owing to its high radiation resistance and relatively high elemental sulfur solvency.

The components of complex reaction systems were ionic liquids based on the cations imidazolium (1-butyl-3-methylimidazolium trifluoromethanesulfonate [*n*-BuMeIm]CF_3SO_2, 1-butyl-3-methylimidazolium tetrafluoroborate [*n*-BuMeIm]BF_4, and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [*n*-BuMe$_2$Im]BF_4: chemically pure, 99.9%, Merck, Germany) and phosphonium (3-ethyloctylphosphonium bis(trifluoromethylsulfonyl)imide [Et$_3$OcP]N$(SO_2CF_3)_2$, 3-ethyldodecylphosphonium bis(trifluoromethylsulfonyl)imide [Et$_3$DdP]N$(SO_2CF_3)_2$, 3-*n*-butylmethylphosphonium bis(trifluoromethylsulfonyl)imide [*n*-Bu$_3$MeP]N$(SO_2CF_3)_2$, 3-*n*-butyloctylphosphonium bis(trifluoromethylsulfonyl)imide [*n*-Bu$_3$OcP]N$(SO_2CF_3)_2$, 3-*n*-butyldodecylphosphonium bis(trifluoromethylsulfonyl)imide [*n*-Bu$_3$DdP]N$(SO_2CF_3)_2$, 3-*n*-butyloctylphosphonium tetrafluoroborate [*n*-Bu$_3$OcP]BF_4, and 3-*n*-butyldodecylphosphonium tetrafluoroborate [*n*-Bu$_3$DdP]BF_4: chemically pure, 98%, Nippon Chemical Industrial Co. Ltd., Japan).

The obtained systems were exposed to γ-radiation of the radionuclide ^{60}Co on setups MRKh-MPX-γ-

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Characteristics of the radiation-chemical transformation of elemental sulfur at various initial elemental sulfur concentrations

No. of system	System	$[S_8]_0$, mM	α_{max}	D, kGy	Reaction order	k_{eff}, s^{-1} (I), L/mol s (II)	R
I	$S_8–C_6H_6$	96	0.88	3.4	I	$1.1 \cdot 10^{-4}$	0.99
II	$S_8–C_6H_6–[n\text{-}BuMe_2Im]BF_4$	107	0.68	0.9	II	$1.2 \cdot 10^{-3}$	0.85
III	$S_8–C_6H_6–[n\text{-}BuMeIm]BF_4$	196	0.89	0.9	II	$5.5 \cdot 10^{-4}$	0.99
IV	$S_8–C_6H_6–[n\text{-}BuMeIm]CF_3SO_3$	203	0.83	1.8	II	$3.3 \cdot 10^{-4}$	0.98
V	$S_8–C_6H_6–[n\text{-}Bu_3MeP]N(SO_2CF_3)_2$	99	0.73	3.6	II	$7.3 \cdot 10^{-4}$	0.99
VI	$S_8–C_6H_6–[n\text{-}Bu_3DdP]N(SO_2CF_3)_2$	136	0.78	3.6	II	$5.2 \cdot 10^{-4}$	0.96
VII	$S_8–C_6H_6–[Et_3OcP]N(SO_2CF_3)_2$	160	0.81	3.6	II	$5.4 \cdot 10^{-4}$	0.99
VIII	$S_8–C_6H_6–[Et_3DdP]N(SO_2CF_3)_2$	215	0.80	1.8	II	$5.4 \cdot 10^{-4}$	0.95
IX	$S_8–C_6H_6–[n\text{-}Bu_3OcP]BF_4$	62	0.68	1.7	II	$2.6 \cdot 10^{-3}$	0.94
X	$S_8–C_6H_6–[n\text{-}Bu_3DdP]BF_4$	115	0.73	3.4	II	$1.0 \cdot 10^{-3}$	0.99
XI	$S_8–C_6H_6–DMSO–[n\text{-}Bu_3OcP]BF_4$	150	0.97	3.4	I	$2.2 \cdot 10^{-4}$	0.98

k_{eff}, effective rate constant for elemental sulfur transformation; α_{max}, maximal elemental sulfur conversion; D, absorbed dose at which α_{max} is reached; and R, correlation coefficient; 298 K, $D^\bullet = 0.126$ Gy/s, $[\text{Ionic liquid}]_0 = 0.025$ M.

100 and RKhM-PXM-γ-20 at absorbed dose rates of $D^\bullet = 0.237$ and 0.126 Gy/s, respectively.

In the kinetic experiments, the elemental sulfur concentrations in the solutions were determined by titrimetric methods. Blank experiments showed that the presence of an ionic liquid in a system introduces no error to the determination of the elemental sulfur content.

RESULTS AND DISCUSSION

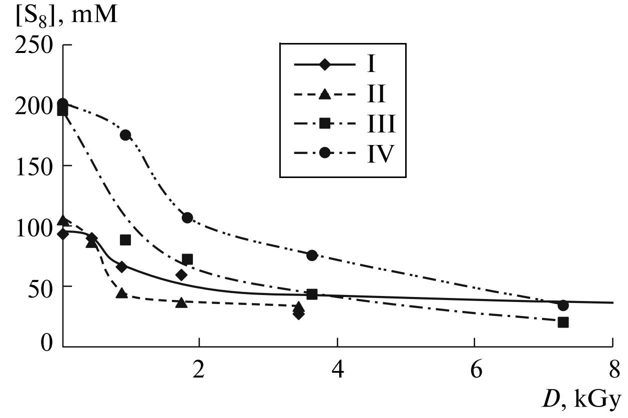
In all the studied systems, initially, the elemental sulfur content of the solution quite sharply drops, after which the curves for the elemental sulfur concentration and conversion reach plateaus: in most systems, at an absorbed dose of 2–4 kGy; in systems II–IV and VIII, at about 1 kGy, with the elemental sulfur conversion in most systems being 0.7–0.9 (table; figure).

The consideration of the elemental sulfur transformation kinetics in systems II–IV, which contain structurally similar ionic liquids $[n\text{-}BuMe_2Im]BF_4$, $[n\text{-}BuMeIm]BF_4$, and $[n\text{-}BuMeIm]CF_3SO_3$ showed that an increase in the number of alkyl radicals in the cation of an ionic liquid decreases the solvency of the system. At the same time, the fact that there is an induction period and that the maximal conversion α_{max} in system IV containing an imidazolium ionic liquid with the trifluoromethanesulfonate anion is twice as high as that in systems II and III containing imidazolium ionic liquids with the tetrafluoroborate anions demonstrated that that the effect of the anionic part of an ionic liquid on the kinetic parameters of the elemental sulfur transformation exceeds that on the physicochemical characteristics of the system.

The analysis of the behavior of systems V–X containing ionic liquids based on the phosphonium cation showed that an increase in the length of an alkyl radical increases the elemental sulfur solvency of the system. In systems IX and X containing ionic liquids with the tetrafluoroborate anions in comparison with systems V–VIII containing ionic liquids with the bis(trifluoromethylsulfonyl)imide anions, the elemental sulfur conversions are lower and the absorbed dose at which α_{max} is reached is 2–4 times lower. A distinguishing feature of systems V and VI containing 3-*n*-butylalkylphosphonium ionic liquids is induction period.

The effect of varying the cationic part of an ionic liquid on the solvency of the system exceeds the effect of varying the anion. This can be due to the emergence of S_8-rich fluctuations stabilized by an ionic liquid through the formation of micelle-like structures based on the cation of the ionic liquid and the S_8 molecule, which is a nucleophile because of lone pairs of electrons.

The systems with phosphonium ionic liquids generally have lower elemental sulfur conversions than the systems with imidazolium ionic liquids (0.68–0.81 and 0.83–0.89, respectively). This can be related to the difference in rate constant for the reaction with the solvated electron between the phosphonium and imidazolium cations (1.6×10^{10} and 3.8×10^9, respectively) [12]. This difference leads to more efficient removal of primary active particles from the reaction in the systems with phosphonium ionic liquids. A qualitative analysis of the reaction products detected thiophenols (intense black coloration in the lead sul-



Plots of elemental sulfur concentration [S_8] versus absorbed dose D in (I) benzene and the solutions (II) benzene–[n-BuMe$_2$Im]BF$_4$, (III) benzene–[n-BuMeIm]BF$_4$, and (IV) benzene–[n-BuMeIm]CF$_3$SO$_3$ at 298 K and D = (I, II) 0.237 and (III, IV) 0.126 Gy/s.

fide test; in system XI containing DMSO, the coloration was much weaker, which was indicative of lower concentrations of the forming thiophenols), residual elemental sulfur, and also resinous brownish deposit (after evaporation of the solution), which is likely to be oligomeric sulfur-containing products. This is consistent with the results of studying the elemental sulfur radiolysis in benzene under the action of ionizing radiation [13].

Based on the experimental results and the data on the chemical stages of benzene radiolysis [14], the following scheme can be proposed for the radiation-chemical transformation of elemental sulfur in a nonaqueous solvent:

$$C_6H_6 \rightsquigarrow C_6H_6^{+\cdot} + \bar{e},$$

$$\bar{e} \to \bar{e}_{\text{solv}} \text{ (solvated electron)},$$

$$C_6H_6^{+\cdot} + \bar{e}_{\text{solv}} \to C_6H_6^*,$$

$$C_6H_6^* \to C_6H_5^{\cdot} + H^{\cdot},$$

$$C_6H_5^{\cdot} + S_8 \to C_6H_5 - S_8^{\cdot} \to C_6H_5S_x^{\cdot} + S_y,$$

$$H^{\cdot} + S_8 \to HS_8^{\cdot} \to HS_x^{\cdot} + S_y.$$

A fragment (a ring of $y < 8$ atoms or a linear diradical) of the sulfur molecule S_y is unstable and continue to break up into smaller radical fragments, which, as S_8, can enter into various processes, in particular, add the thiophenyl radical:

$$C_6H_5S^{\bullet} + S_y \to C_6H_5(S_{y+1})^{\bullet},$$

$$C_6H_5S^{\bullet} + S_8 \to C_6H_5S{-}S_8^{\cdot},$$

$$C_6H_5S^{\bullet} + H^{\bullet} \to C_6H_5SH,$$

$$2C_6H_5S^{\bullet} \to C_6H_5S{-}SC_6H_5,$$

$$SH^{\bullet} + H^{\bullet} \to H_2S,$$

$$\left.\begin{array}{l} C_6H_5S_x^{\cdot} + S_y \\ 2C_6H_5S_x^{\cdot} \\ 2S_y: \end{array}\right\} \to \text{products (including oligomers).}$$

Not only the presence of organic fragments in the structure of the sulfur-containing products can stabilize the compound, this also can favor the solubility of the polymer, which leads to its further participation in radiation-chemical processes.

Thus, in benzene solutions in the presence of ionic liquids, the radiation-chemical transformation of elemental sulfur is primarily accompanied by the formation of thiophenols, and the process rate is much higher than that in the absence of ionic liquids.

We previously showed that the polarity of a medium influences the elemental phosphorus conversion to phosphorus-containing polymers under the action of ionizing radiation in the presence of ionic liquids [15]. In this study, we found that an increase in the polarity of a reaction medium (by adding 5 mol % DMSO, system XI) leads to the absence of thiophenols in the mixture of final products and to an increase in the sulfur conversion (to 0.97 as compared with 0.68 for similar system IX containing no DMSO). This can be caused by the ability of DMSO to oxidize thiols to disulfides. The primary products (short-lived DMSO radical cation $(CH_3)_2S^+{=}O$ and $\bar{e}$) of DMSO radiolysis can also be initiating agents in reactions in the studied systems.

The residual sulfur concentration versus irradiation time plots are linearized in the coordinates (ln[S_8])–t for systems I and XI and in the coordinates (1/[S_8])–t for systems II–X, which corresponds to the first and second orders of reaction, respectively, with respect to elemental sulfur (table). The process rate in the systems containing tetrafluoroborate ionic liquids is higher, which can be due to the compactness of the tetrafluoroborate anion in comparison with the trifluoromethanesulfonate and bis(trifluoromethylsulfonyl)imide anions. The importance of the steric factor is also indicated by the decrease in the effective reaction rate constant with increasing chain length of the allyl radical in the structure of the cation for phosphonium ionic liquids.

Thus, for the first time, we have studied the behavior of elemental sulfur under the action of high-energy radiation in a benzene solution in the presence of ionic liquids. It has been shown that, on exposure to such radiations, elemental sulfur in a benzene solution transforms into sulfur-containing compounds, including sulfur-containing oligomers. We have detected no formation of polymeric forms of elemental sulfur at high degrees of polymerization in the studied systems. The presence of ionic liquids accelerates the transformation of elemental sulfur. The conversion 70–90% is reached at an adsorbed dose of 2–4 kGy. By varying the structure of the ionic liquid present in a reaction system, the characteristics of the system and the process can be controlled. Varying the cationic part of an ionic liquid has a stronger effect on the physicochemical characteristics (in particular, solvency) of the system, whereas varying the anionic has a stronger influence on the kinetic parameters of the elemental sulfur transformation. The effective reaction rate constants are higher for the systems containing tetrafluoroborate ionic liquids. For the systems S_8–C_6H_6 and S_8–C_6H_6–DMSO–[n-Bu_3OcP]BF_4, the process was of the first order with respect to elemental sulfur, and for the systems S_8–C_6H_6–ionic liquid, it was of the second order with respect to elemental sulfur.

REFERENCES

1. Medvedeva, G.A., Porfir'eva, R.T., and Gerasimov, V.V., *Materialy dokl. VIII aspirantsko-magisterskogo nauchn. seminara KGEU* (Proceedings of VIII Scientific Seminar of PhD and Magister Students of KGEU), Kazan: Kazan. Gos. Energ. Univ., 2005.
2. Vygodskii, Ya.S., Lozinskaya, E.I., and Shaplov, A.S., *Ross. Khim. Zh.*, 2006, vol. 47, no. 6, pp. 40–50.
3. Liu, S., Zhou, L., Yu, S., Xie, C., Liu, F., and Song, Z., *Biomass Bioenerg.*, 2013, vol. 57, pp. 238–242.
4. Garvey, S.L. and Dietz, M.L., *Sep. Purif. Technol.,* 2014, vol. 123, pp. 145–152.
5. Zhang, Q., Zhang, S., and Deng, Y., *Green Chem.*, 2011, vol. 13, no. 10, pp. 2619–2637.
6. Sakaebe, H., Matsumoto, H., and Tatsumi, K., *Electrochim. Acta,* 2007, vol. 53, no. 3, pp. 1048–1054.
7. Heidarizadeh, F., Rezaee, Nezhada, E., and Sajjadifar, S., *Sci. Iran*, 2013, vol. 20, no. 3, pp. 561–565.
8. Tarasova, N.P., Smetannikov, Y.V., Vilesov, A.S., and Zanin, A.A., *Pure Appl. Chem.*, 2009, vol. 81, no. 11, pp. 2115–2122.
9. Tarasova, N.P., Smetannikov, Yu.V., and Zanin, A.A., *Usp. Khim.*, 2010, vol. 79, no. 6, pp. 516–531.
10. Tarasova, N.P., Smetannikov, Y.V., Vilesov, A.S., and Zanin, A.A., *C. R. Chim.*, 2010, no. 13, pp. 1028–1034.
11. Tarasova, N.P., Smetannikov, Yu.V., and Zanin, A.A., *Dokl. Chem.*, 2013, vol. 449, part 2, pp. 111–113.
12. Pikaev, A.K. and Kabakchi, S.A., *Reaktsionnaya sposobnost' pervichnykh produktov radioliza vody. Spravochnik* (Reactivity of Primary Radiolysis Products: A Reference Book), Moscow: Energoizdat, 1982.
13. Ando, W., Sugimoto, K., and Oae, S., *Bull. Chem. Soc. Jpn.*, vol. 36, no. 8, pp. 893–897.
14. Pikaev, A.K., *Sovremennaya radiatsionnaya khimiya. Tverdoe telo i polimery. Prikladnye aspekty* (Modern Radiation Chemistry. Solids and Polymers. Applied Aspects), Moscow: Nauka, 1987.
15. Lavrov, I.A., *Cand. Sci. (Chem.) Dissertation*, Moscow, 2005.

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