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Electrochemical Oxidation of Disulfides Derived from Isocyanuric Acid

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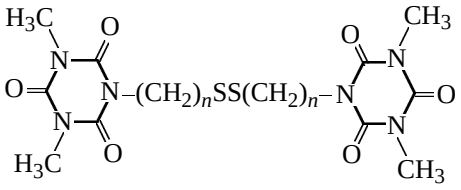
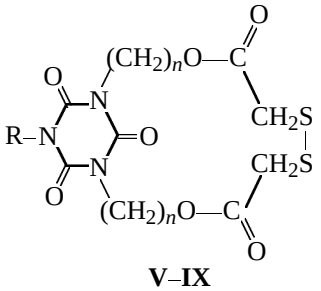
Abstract — Anodic oxidation of linear and bicyclic disulfides derived from isocyanuric acid was studied by cyclic voltammetry and numerical simulation. The PM3 molecular modeling revealed three types of the highest occupied molecular orbitals determining the electrochemical reactivity of these compounds: *n* electrons of the sulfur atoms of the disulfide bridge in linear and N–Me- and N–Ph-substituted bicyclic disulfides, π electrons of the aromatic fragment in the disulfide with the *N*-2-(2-methoxyphenoxy)ethyl isocyanurate substituent, and *n* electrons of the sulfide sulfur atoms in the compound with the –SS– and –S– fragments in the aliphatic chain. Oxidation of the disulfides with the SS-localized highest occupied molecular orbital follows the scheme with reversible electron transfer, followed by a fast potential-determining second-order reaction and a slow current-determining first-order reaction (ECC mechanism). The isocyanurate heterocycle does not participate directly in redox transformations but stabilizes the electrochemically generated radical cations by the mechanism of transannular interaction.

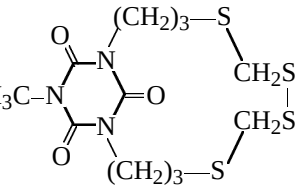
Linear and cyclic disulfides are being actively studied in view of their important role in the metabolism of living bodies (sulfur-containing enzymes [1], intra- and intercellular ion transfer [2–5], stabilization of proteins [2, 4], etc.), and also because of their specific properties used in redox-reversible systems [6, 7], for selective complexation, determination, and extraction, and in fields based on molecular recognition [6, 8, 9]. New prospects are opened by a combination of a disulfide bridge with O- and N-containing fragments and with groups bearing known or potential bioactive centers. The electrochemical methods is one of the most convenient tools for studying redox transformations of these compounds. Despite the fact that organic disulfides were among the first objects in organic electrochemistry, the majority of studies on their electrochemistry concerned the behavior of the thiol–disulfide couple; the anodic processes involving disulfides are less studied [10–12]. Depending on the experimental conditions, oxidation of diorganyl disulfides can yield oxygen-containing compounds [13] or S-centered electrophilic intermediates reacting with unsaturated compounds [14]. Oxidation of diaryl [15–17] and dialkyl [18–21] disulfides in aprotic and weakly nucleophilic media is also well studied. Much less data are available on oxidation of biologically active disulfides [22]. To reveal the character of the electron transfer and elucidate the primary steps of electrochemical transformations in oxidation of biologically active disulfides containing isocyanurate fragment, we considered in this work the oxidation of **I**–**X**.



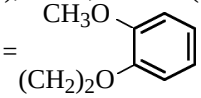
I–**IV**



V–**IX**



X

I–**IV**, *n* = 2 (**I**), 3 (**II**), 4 (**III**), 6 (**IV**); **V**–**IX**, *n* = 2, R = CH_3 (**V**); *n* = 3, R = CH_3 (**VI**); *n* = 2, R = Ph (**VII**); *n* = 3, R = Ph (**VIII**); *n* = 2, R =  (**IX**).

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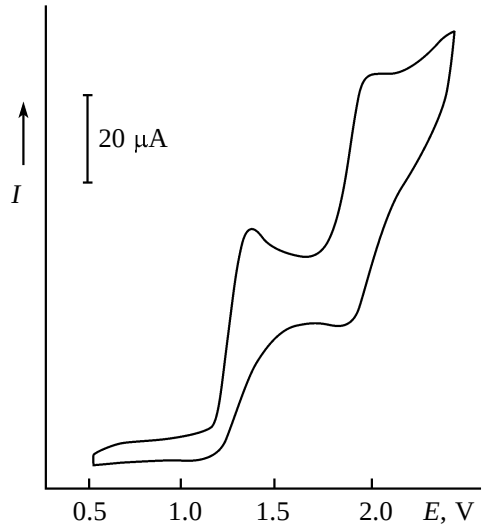


Fig. 1. Voltammogram of the oxidation of disulfide **I** on a glassy carbon electrode vs. saturated calomel electrode, c 10^{-3} M (MeCN/0.1 M Bu_4NBF_4, 20°C, v 0.05 V s^{-1}).

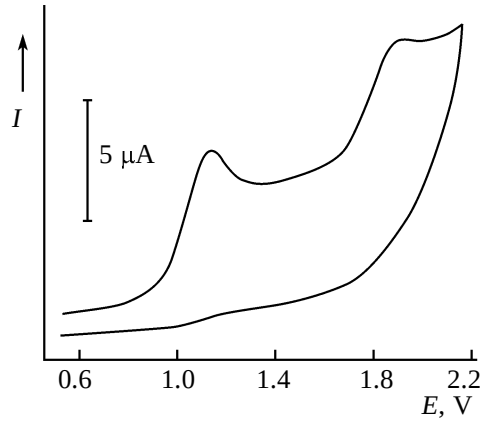


Fig. 2. Voltammogram of the oxidation of disulfide **III** on a glassy carbon electrode vs. saturated calomel electrode, c 10^{-3} M (MeCN/0.1 M Bu_4NBF_4, 20°C, v 0.2 V s^{-1}).

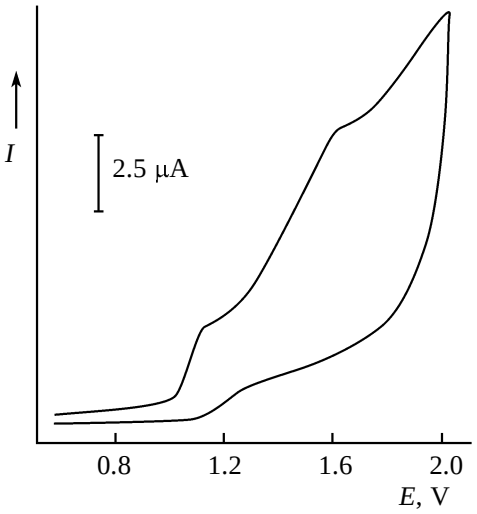


Fig. 3. Voltammogram of the oxidation of disulfide **X** on a glassy carbon electrode vs. saturated calomel electrode, c 10^{-3} M (MeCN/0.1 M Bu_4NBF_4, 20°C, v 0.2 V s^{-1}).

Disulfides **I**–**X** show a strong tendency to electrode passivation; therefore, to obtain reproducible voltammograms, the electrode surface should be thoroughly cleaned and polished before recording each curve. On the properly pretreated electrode, compounds **I**–**X** are usually oxidized in two steps with $E_p^1 - E_p^2 \cong$ 500 mV (Figs. 1–3). The number of electrons transferred in the first oxidation step was determined by comparison with the current of one-electron oxidation of ferrocene at each sweep rate v (see table). The peak current of these compounds I_p is a nonlinear function of $v^{1/2}$, and the current function $I_p/v^{1/2}$ decreases with an increase in the sweep rate v in the range 0.02–0.5 V s^{-1} (Fig. 4), suggesting the kinetic nature of the limiting current. At the sweep rate increasing further ($v \geq$ 1–2 V s^{-1}), the shape of the curves gets worse, making their quantitative treatment impossible. It is interesting that, even at relatively low sweep rates ($v \sim$0.5 V s^{-1}), the kinetic constituent of the limiting current can be substantially restricted. The peak width $E_p - E_{p/2}$ varies from 50 to 110 mV (see table). The smallest width (50–60 mV) suggests that the electron transfer is electrochemically reversible and the absence of the reduction peak of the radical cations at back sweeping is due to their subsequent fast chemical transformation.

The oxidation potentials E_p of disulfides **I**–**X** show a clear dependence on the sweep rate: As v is increased by a factor of 10, the oxidation potentials of **I**–**VIII** shift by 30 mV toward more positive values ($\Delta E_p/\Delta \log v$ = 30 mV, Fig. 5), which corresponds to electrochemically reversible electron transfer followed by a potential-determining reaction of the first order with respect to the radical cation. For **IX** and **X**, $\Delta E_p/\Delta \log v$ is 20 mV, which distinguishes these compounds from the other disulfides of the reaction series. The linear analysis of the voltammograms of **I**–**VIII** in the range I/I_p = 0.5–0.7 [23] gave $dE/d(I/I_p)$ = 67 ± 5 mV, which is also consistent with the electrochemically reversible electron transfer followed by a first-order reaction.

For the majority of disulfides of this reaction series, the number of electrons approaches unity even at $v \geq$

Characteristics of electrochemical oxidation of disulfides **I**–**X** in MeCN/0.1 M Bu_4NBF_4

Comp. no.	E_p^1, mV[a]	$\Delta(E_p^1 - E_{p/2})$, mV	$\Delta E_p/\Delta\log v$, mV	PI_1 ($-\varepsilon_{HOMO}$), eV[b]	n[c]	k_{cd}, s^{-1}	E_p^2, V
I	1355	110	28 ± 5	9.71	1.5	1.41	1.91
II	1235	70	29 ± 4	9.62	–	0.60	1.91
III	1171	60	35 ± 1	9.31	1.8	7.97	1.80
IV	776	100	35 ± 6	9.09	1.2	0.48	1.46
V	1443	57	26 ± 1	9.66	1.9	27.2	1.93
VI	1396	62	36 ± 2	9.45	1.9	32.7	2.05
VII	1450	95	29 ± 6	9.76	1.3	0.32	1.96
VIII	1419	106	37 ± 4	9.47	1.4	0.36	1.96
IX	1188	50	21 ± 3	9.32	1.7	–	–
X	1142	57	18 ± 3	8.99	1.2	–	1.59

[a] Vs. saturated calomel electrode at v 0.05 V s^{-1}, 20°C. [b] Ionization potential calculated by the PM3 method as the orbital energy with the opposite sign. [c] Number of electrons transferred in the process.

0.2 V s^{-1}, but no reverse peak (reduction of radical cations) appears in the voltammograms. Furthermore, in oxidation of simple dialkyl disulfides (Me_2S_2, Et_2S_2) at rates of up to 14 kV s^{-1} in perfluoro-2-propanol [24], the reverse peak was not observed either. Hence, the limiting current I_p of oxidation of **I**–**VIII** is not controlled by the rate of cleavage of radical cations proper; in other words, the relatively slow current-determining step with the rate constant k_{cd} (its limitation at v ~0.5 V s^{-1} for **I, II, IV, VII**, and **VIII** corresponds to $k \le 2$–4 s^{-1}) is separated from the electron transfer step by a fast potential-determining step with the rate constant k_{pd}, $k_{cd} \ll k_{pd}$.

For the potential-determining reaction with $\Delta E_p/\Delta\log v$ ~30 mV, two mechanisms are possible: monomolecular disproportionation (DISP1) and reversible electron transfer followed by chemical reaction (EC)[1] [25]. For these mechanisms, the parameter $\Delta E_p/\Delta\log c$ characterizing the dependence of E_p on the concentration c is 0 and 30 mV, respectively. Therefore, we considered the dependence of E_p on $\log c$ for the disulfides in hand. The experiments show that E_p tends to increase with increasing c, but the voltammograms taken at different concentrations are insufficiently reproducible to determine $\Delta E_p/\Delta\log c$. Proceed-

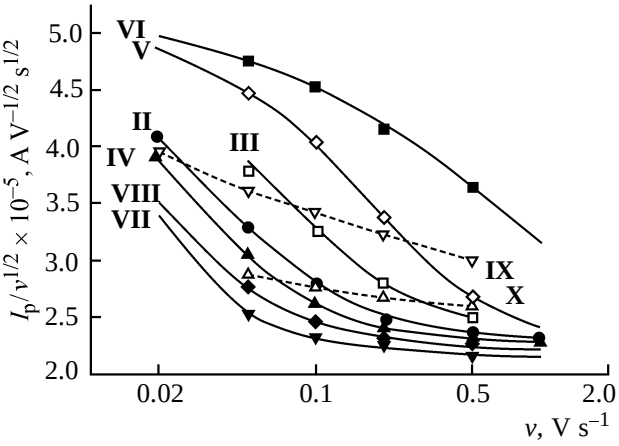


Fig. 4. Reduced limiting current $I_p/v^{1/2}$ as a function of the potential sweep rate for disulfides **II**–**X**. Solid lines correspond to the current functions calculated for the ECC mechanism (c 10^{-3} M, MeCN/0.1 M NBu_4BF_4, 22°C), and dashed lines, to the current functions of **IX** and **X** for the DISP1 mechanism (see text).

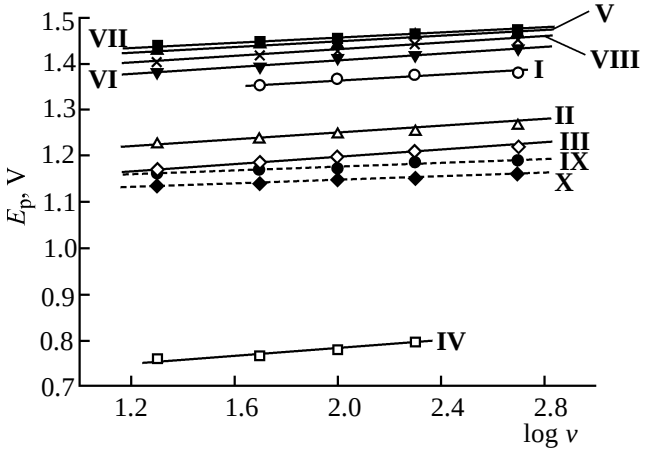


Fig. 5. E_p–log$v$ plots for disulfides **I**–**X** (c 10^{-3} M, MeCN/0.1 M Bu_4NBF_4, 22°C). The potentials are given vs. saturated calomel electrode.

[1] Here and hereinafter, we follow the IUPAC recommendations for designation of mechanisms of electrochemical reactions: (E) electrochemical step and (C) chemical step; subscripts denote the reaction type: (C_{dim}) dimerization and (C_{disp}) disproportionation.

ing from different shapes of the current functions ($I_p/v^{1/2}$)–v for the DISP1 and EC mechanisms, we simulated the voltammetric behavior for both schemes (Fig. 4) using the DIGISIM 2.1 program package. The ECCE scheme with a fast potential-determining reaction of radical cations with the starting molecule (k_{pd} ~5×10^6 l mol^{-1} s^{-1}) and slow current-determining cleavage of the resulting intermediate (k_{cd} 0.3–30 s^{-1}), occurring between two electrochemical steps, adequately describes the electrochemical behavior of **I**–**VIII** (Fig. 4); on the contrary, the dependences for the DISP1 mechanism appreciably deviate from the experimental data, especially at high k_{cd} (Fig. 4, curves for **III** and **VI**). As seen, the current functions $I_p/v^{1/2}$ for **IX** and **X** again lie out of the general pattern, suggesting that the mechanism of oxidation of these substances is different.

Thus, the mechanism of oxidation of **I**–**VIII** is similar, with the only difference that in linear disulfides **I**–**IV** the current-determining step yields independent cationic and radical species, whereas in cyclic compounds **V**–**VIII** the spacially separated radical and cationic centers formed on cleavage of the S–S bond still belong to the same species. Thus, oxidation of **I**–**IV** can be described by the following scheme:

$$\mathrm{RSSR} \underset{E_p^1}{\overset{-\bar{e}}{\rightleftarrows}} \mathrm{R\overset{+}{S}\dot{S}R},$$

$$\mathrm{R\overset{+}{S}\dot{S}R} + \mathrm{RSSR} \xrightarrow[k_1]{} \mathrm{D^{+\cdot}},$$

$$\mathrm{D^{+\cdot}} \xrightarrow[k_2]{} \mathrm{RS^{\cdot}} + \mathrm{RS^{+}} + \mathrm{RSSR},$$

$$\mathrm{RS^{\cdot}} \xrightarrow[E < E_p^1]{-\bar{e}} \mathrm{RS^{+}},$$

$$\mathrm{D^{+\cdot}} \xrightarrow[E_p^2]{-\bar{e}} \mathrm{D^{++}},$$

where $D^{+\cdot}$, D^+, and D^{++} are, respectively, the radical cation, cation, and dication of the intermediate dimer; E_p^1 and E_p^2 are the potentials of the first and second oxidation peak of the starting disulfide; and E is the oxidation potential of the intermediate radical.

For disulfides **V**–**VIII**, this scheme is somewhat different:

$$\subset\!\mathrm{X–SS}\!\supset \underset{E_p^1}{\overset{-\bar{e}}{\rightleftarrows}} \subset\!\mathrm{X–\overset{+\cdot}{S}S}\!\supset,$$

$$\subset\!\mathrm{X–\overset{+\cdot}{S}S}\!\supset + \subset\!\mathrm{X–SS}\!\supset \xrightarrow[k_1]{} \mathrm{D^{+\cdot}},$$

$$\mathrm{D^{+\cdot}} \xrightarrow[k_2]{} {}^{+}\mathrm{S–X–S^{\cdot}} + \subset\!\mathrm{X–SS}\!\supset,$$

$${}^{+\cdot}\mathrm{S–X–S^{\cdot}} \xrightarrow[E < E_p^1]{-\bar{e}} {}^{+}\mathrm{S–X–S^{+}},$$

where ${}^{+}S–X–S^{\cdot}$ is the product of the cleavage of the S–S bond in the intermediate dimer.

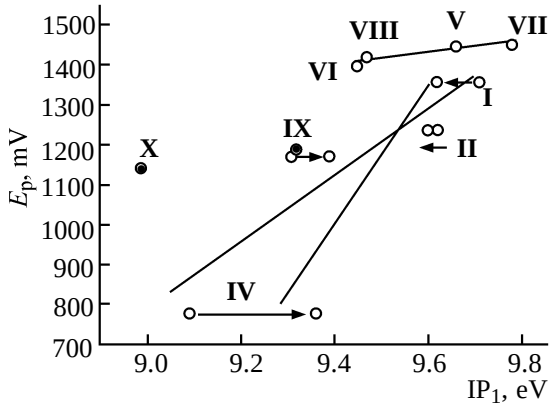


Fig. 6. Correlation of the oxidation potentials E_p with the first oxidation potentials PI_1 of disulfides (hollow circles) **I**–**VIII** and (filled circles) **IX** and **X**. Arrows denote transitions from (a) vertical to (b) "adiabatic" ionization potentials for **I**–**IV**, see text (the point numbering corresponds to that given in the table; the potentials are given vs. saturated calomel electrode).

The oxidation potentials of AlkS$^{\cdot}$ radicals (Alk ≠ *t*-Bu) are usually lower than the potentials of their formation from the corresponding disulfides [11, 26] ($E_1 > E_2$ in the E_1CCE_2 scheme); therefore, the second peaks in the voltammograms of **I**–**III** and **V**–**VIII** apparently belong to oxidation of the intermediate dimer ($D^{+\cdot}$) or radical cation. Such a scheme is also well consistent with the $EC_{dim}CE$ mechanism of oxidation of diaryl disulfides, studied by the method of rotating disc electrode and by spectroscopy of charge-transfer complexes [15, 27].

The 20 mV slope of the dependence $\Delta E_p/\Delta \log v$ for **IX** can correspond to several mechanisms in which the potential-determining reaction is of the second order with respect to $\mathbf{IX}^{+\cdot}$; among these mechanisms, we can reject only ECC (disproportionation), for which $E_p \neq f(\log c)$. However, without knowing $\Delta E_p/\Delta \log c$ (20 or 30 mV), it is impossible to clearly distinguish the EC_{dim} and ECC_h mechanisms (C_{dim} denotes dimerization of two radical cations; C, coupling of the radical cation with the initial molecule; and C_h, homogeneous electron transfer). Nevertheless, numerical simulation of the I_p–$v^{1/2}$ dependence for these two schemes allows us to choose the second mechanism, though this choice is tentative because of a small set of experimental data (Fig. 4). This mechanism corresponds to the oxidation schemes suggested for di- [28] and trialkoxybenzenes [29].

To elucidate the nature of the frontier molecular orbitals and electronic interactions determining the electrochemical reactivity of disulfides **I**–**X**, we performed semiempirical simulation of these compounds.

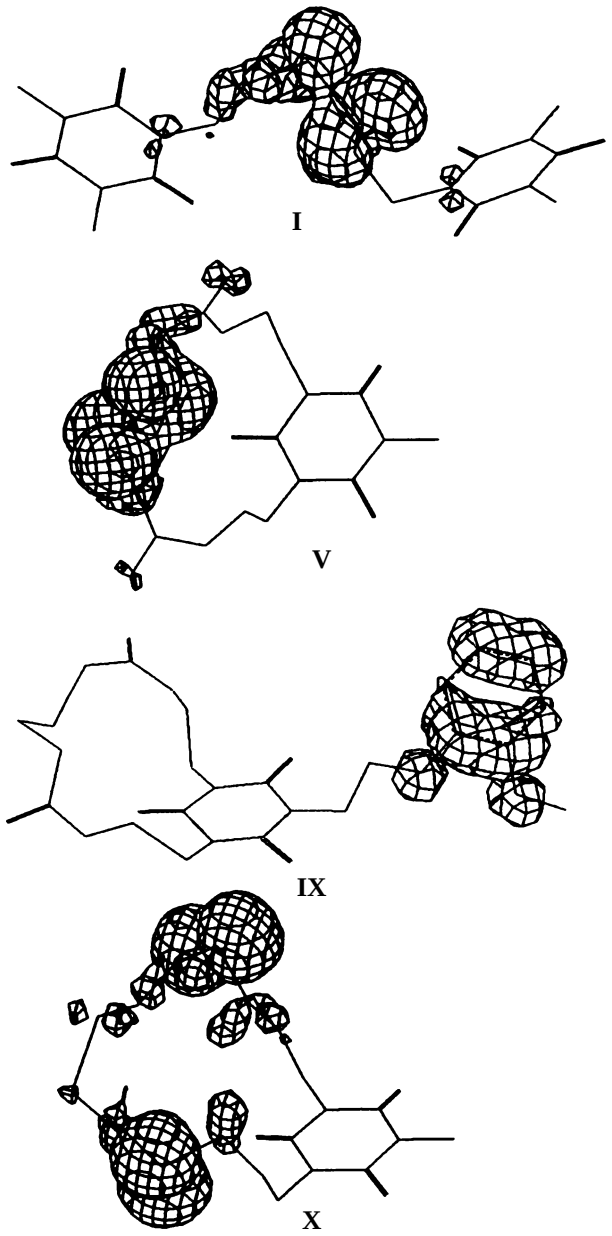


Fig. 7. Different types of HOMO (wave function squared) in the reaction series of disulfides **I, V, IX**, and **X**, according to the results of PM3 simulation. In **X**, both virtually degenerate orbitals (*n* electrons of S) are shown; each of them can play the role of HOMO.

Disulfides **I**–**X** contain only the atoms well parametrized by semiempirical methods; therefore, MNDO derivatives of the model (MNDO/d, AM1, PM3) should reproduce well the geometry and structure of the frontier orbitals of such molecules. The results of AM1 and PM3 calculations are virtually identical, but the AM1 method appeared to be somewhat less accurate for the levels of aromatic systems; therefore, subsequently we always used the PM3 method.

The first ionization potentials PI_1 of **I**–**X**, calculated by the PM3 method (see table), are plotted in Fig. 6 against the oxidation potentials E_p. Although the potentials E_p differ from the standard potential E_0 by the quantity ΔE_k caused by the potential-determining reaction, the kinetic shift of the potential ΔE_k should be linear or virtually constant for structurally related compounds with the same potential-determining reaction of the radical cation. Even the difference in the rates of this reaction by two orders of magnitude causes the change in E_p by only $\Delta E_p = 0.03 \times \log 100 = 0.06$ V; thus, compounds characterized by the same oxidation mechanism should form groups in the E_p–PI_1 correlations. As seen, linear (**I**–**IV**) and cyclic (**V**–**VIII**) disulfides, indeed, form certain correlations, whereas data for **IX** and **X** lie apart from other data for the corresponding reaction series (Fig. 6). This pattern becomes understandable when considering the structure of the highest occupied molecular orbital (HOMO) responsible for the redox properties of **I**–**X** (Fig. 7). The restricted PM3 method gives for disulfides **I**–**IV** the delocalized orbital on the –SS– bridge with the coefficients of p_z orbitals of 0.62 on the S^1 atom and 0.42 on the S^2 atom. Thus, HOMO in disulfides **I**–**IV** involves *n* electrons of the lone electron pairs of the S atoms with asymmetric contributions. Therefore, in oxidation, the positive charge in the forming radical cation preferentially localizes on one of the two sulfur atoms. The HOMO of **V**–**VIII** is similar in nature with the only difference that the disulfide bridge is a part of a cyclic structure. In **IX**, HOMO is formed by a combination of ψ_a functions of the aromatic substituent and two p_z orbitals of the *o*-O atoms (Fig. 7); the energy of this delocalized orbital ($-\varepsilon_{HOMO}$, see table) is 0.53 eV higher than the energy of the *n* electrons of the S atoms of the disulfide bridge; therefore, the redox properties in oxidation of **IX** are determined by the $MeOC_6H_4OCH_2$ fragment. The fact that the oxidation potential E_p of **IX** is 250 mV lower than E_p of **V**–**VIII** and is within the range characteristic of dialkoxybenzenes (E_p ~1.05–1.12 V [28, 30]) also supports this conclusion. The HOMO of **X** is again localized on the S atom, but on that of the sulfide, and not disulfide, fragment (Fig. 7).

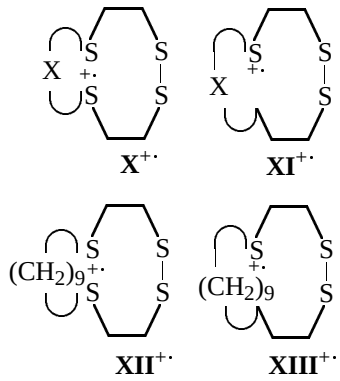
The lowest unoccupied molecular orbital (LUMO) in all the compounds **I**–**X** is the σ*(SS) orbital of the disulfide bridge, and only the next, higher-lying unoccupied orbital belongs to the nitrogen-containing heterocycle. The isocyanurate ring in disulfides **I**–**X** is the most rigid fragment of these molecules; its energy gap [31] is larger than that of the fragments bearing the frontier orbitals (HOMO, LUMO). Therefore, the heteroring is directly involved neither in oxidation nor in reduction. Nevertheless, in oxidation

of **I**–**VII** and **X**, when the sulfur atom (whose lone electron pair forms HOMO) acquires a positive charge and HOMO transforms into singly occupied molecular orbital, the occupied p_z-type orbitals of the heteroring become the highest doubly occupied orbitals of the corresponding radical cations. These donor centers can be involved in intramolecular interaction with the positive charge localized on the S atom and thus can stabilize the radical cation by the mechanism of transannular interaction.

The PM3 analysis of the electronic interactions in disulfides **I**–**IV** and **X** revealed the role of stereoelectronic effects in the reactivity of these compounds. In contrast to compounds **V**–**VIII** in which the flexibility of the ring containing the –SS– fragment is strongly restricted by the atoms of the planar isocyanurate ring, in the molecules of **I**–**IV** there is free rotation around many bonds, providing more possibilities for the mutual approach of the heterocycle and disulfide bridge. This fact explains why the potentials E_p of linear disulfides **I**–**IV** are considerably more sensitive to the length of the chain between the isocyanurate ring and –SS– bridge (see table) than the oxidation potentials of the cyclic compounds, despite the similar HOMO structure. The structures of radical cations **I**–**IV** optimized by the PM3/UHF method show that, as the alkyl chain increases from $(CH_2)_2$ to $(CH_2)_6$, the radical cations assume the "scorpion" conformation with the "tail," disulfide bridge, more and more approaching the heteroring. Such a configuration is particularly advantageous in **IV**, where the S···O transannular interaction increases the HOMO level, appreciably decreasing the oxidation potential E_p of this compound. The part of the sulfur p_z orbital oriented outwards interacts with the second heteroring by a similar mechanism, shielding the singly occupied molecular orbital of the radical cation from two sides.

To take into account the transannular effect in oxidation of disulfides **I**–**IV**, we calculated by the PM3 method the ionization potentials of these compounds for the geometries of the corresponding radical cations $\mathbf{I}^{+\cdot}$–$\mathbf{IV}^{+\cdot}$. The resuting potentials, being more likely "adiabatic" (PI_1^a), also fairly well correlate with E_p of **I**–**IV** (Fig. 6). The slope of the E_p–PI_1^a correlation is larger than that of the correlation with the vertical ionization potentials PI_1, which is quite reasonable: The potentials PI_1^a take into account additional stabilization of the radical cations and hence correspond to the potentials E_p with a smaller kinetic shift ΔE_k.

The transannular effect is also noticeable in oxidation of disulfide **X** whose HOMO is similar in nature to those of aliphatic thioethers, but E_p is ~150 mV lower than the values typical for these compounds [10–12]. To check this assumption, we simulated the structures of compound **X**, its analog with the CH_2 group instead of one of the two sulfide sulfur atoms (**XI**), and two model compounds: 1,2,5,15-tetrathiacycloheptadecane **XII** and 1,2,5-trithiacycloheptadecane **XIII**, and also the structures of the corresponding radical cations. The PM3 calculations gave approximately equal values of ~0.2 eV for the ionization potential differences PI_1(**XI**) – PI_1(**XI**) and PI_1(**XIII**) – PI_1(**XII**), characterizing the transannular effect. In the electron detachment from the HOMO of **X** and **XII**, this effect results in stabilization of the intermediates by an intramolecular two-center three-electron bond, whereas in $\mathbf{XI}^{+\cdot}$ and $\mathbf{XIII}^{+\cdot}$ there is no such possibility.



$\mathbf{X}^{+\cdot}$ $\mathbf{XI}^{+\cdot}$ $\mathbf{XII}^{+\cdot}$ $\mathbf{XIII}^{+\cdot}$

Thus, the disulfides studied obey the rule which is apparently fairly general for the anodic electrochemistry of thioethers and disulfides [12, 27]: Radical cations electrochemically generated from compounds with the S-centered HOMO are characterized by second-order reactions (dimerization, disproportionation, reactions with the starting molecules) followed by the redistribution of the spin and electron density in the resulting radical cations; the latter process is current-determining and formally corresponds to the first kinetic order.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a WM-250 spectrometer (250 MHz, internal reference TMS).

Voltammetric measurements were performed with a PAR-362 potentiostat in the three-electrode mode. The reference electrode (silver wire in 0.1 M solution of Bu_4NBF_4 in MeCN) was separated from the test solution by an electrolytic key filled with a 0.1 M solution of Bu_4NBF_4 in MeCN; the auxiliary electrode was a glassy carbon rod 50 mm long and 2 mm in diameter. For more accurate correlation of the potentials obtained in different runs, we used ferrocene whose oxidation potential $E^0_{(Fc^+/Fc)}$ is 0.158 V relative to saturated calomel electrode. As working

electrode we used a glassy carbon or platinum disc electrode 1 and 0.5 mm in diameter, respectively. Before recording each curve, the working electrode was thoroughly polished and washed successively with acetonitrile, acetone, and diethyl ether.

Analytically pure grade acetonitrile (Aldrich) was additionally passed through a column packed with activated Al_2O_3 and was stored over 4 Å molecular sieves. Bu_4NBF_4 (Aldrich) was stored in a desiccator over P_2O_5 and was used without additional purification.

Bis[2-(3,5-dimethyl-1,3,5-triazine-2,4,6-trion-1-yl)ethyl] sulfide I. A solution of 1.6 g of dimethyl 2-mercaptoethyl isocyanurate [32] in 5 ml of DMSO was heated at 90–95°C for 6 h. The cooled solution was diluted with water, and the precipitate was separated, washed with water and diethyl ether, and recrystallized from benzene with addition of diethyl ether. Yield 1.2 g.

Compounds **II**–**IV** were prepared similarly.

Given below are the yield, %; mp, °C; and ^{1}H NMR spectrum ($CDCl_3$, δ, ppm). **I**: 75; 195–197; 2.94 t (4H, CH_2S), 3.28 s (3H, CH_3), 4.20 t (4H, NCH_2). **II**: 50; 174; 1.85–2.10 m (4H, CH_2), 2.72 t (4H, CH_2S), 3.25 s (3H, CH_3), 3.93 t (4H, NCH_2). **III**: 33; 110; 1.65–1.93 m (8H, CH_2), 2.68 t (4H, CH_2S), 3.29 s (3H, CH_3), 3.87 t (4H, NCH_2). **VI**: 30; 84–86; 1.40–1.70 m (16H, CH_2), 2.70 t (4H, CH_2S), 3.32 s (3H, CH_3), 3.86 t (4H, NCH_2).

The synthesis and physicochemical properties of **V**–**X** were described previously [33, 34].

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REFERENCES

1. Lehn, J.-M. and Sirlin, C., *Chem. Commun.*, 1978, no. 21, p. 949.
2. Mathews, C.K. and Van Holde, K.E., *Biochemistry*, Menlo Park: Benjamin Cummings, 1996.
3. Kirch, M. and Lehn, J.-M., *Angew. Chem.*, 1975, vol. 87, no. 15, p. 555.
4. *The Chemistry of the Thiol Group*, Patai, S. and Rappoport, Z., Eds., 1974, part 2, ch. 13, p. 589.
5. Lester, P., *Drug Metab. Rev.*, 1998, vol. 30, p. 245.
6. Shinkai, S., Inuzuka, K., Miyazaki, O., and Manabe, O., *J. Org. Chem.*, 1984, vol. 49, no. 18, p. 3440.
7. Shinkai, S., Inuzuka, K., and Manabe, O., *Chem. Lett.*, 1983, vol. 49, no. 5, p. 747.
8. Weber, E., *Angew. Chem.*, 1979, vol. 91, no. 3, p. 219.
9. Boulas, P.L., Gomez-Kaifer, M., and Echegoyen, L., *Angew. Chem., Int. Ed.*, 1998, vol. 37, no. 3, p. 216.
10. *Elektrokhimiya elementoorganicheskikh soedinenii elementov IV gruppy* (Electrochemistry of Organometallic Compounds of Group IV Elements), Teodoradze, G.A., Ed., Moscow: Nauka, 1986.
11. *Organic Electrochemistry*, Lund, H. and Hammerich, O., Eds., New York: Marcel Dekker, 2000, p. 621.
12. *Encyclopedia of Electrochemistry*, Bard, A., Ed., New York: Wiley, 2003, vol. 8, p. 1.
13. Bontempelli, G., Magno, F., and Mazzocchin, G.-A., *J. Electroanal. Chem.*, 1973, vol. 42, no. 1, p. 57.
14. Bewick, A., Coe, D.E., Mellor, J.M., and Owton, W.M., *J. Chem. Soc., Perkin Trans. 1*, 1985, no. 5, p. 1033.
15. Latypova, V.Z., Chichirov, A.A., Zhuikov, V.V., Yakovleva, O.G., Vinokurova, R.I., Ustyugova, I.A., and Kargin, Yu.M., *Zh. Obshch. Khim.*, 1989, vol. 59, no. 6, p. 1344.
16. Latypova, V.Z., Zhuikov, V.V., and Kargin, Yu.M., *Zh. Obshch. Khim.*, 1990, vol. 60, no. 12, p. 2759.
17. Boryczka, S., Elothmani, D., Do, Q.T., Simonet, J., and Le Guillanton, G., *J. Electrochem. Soc.*, 1996, vol. 143, no. 1, p. 4027.
18. Machion, P.D., Pardini, V.L., and Viertler, H., *Synth. Commun.*, 1990, vol. 20, no. 3, p. 365.
19. Bewick, A., Coe, D., Mellor, J., and Walton, D.J., *Chem. Commun.*, 1980, vol. 23, p. 51.
20. Elothmani, D., Do, Q.T., Simonet, J., and Le Guillanton, G., *Chem. Commun.*, 1993, no. 8, p. 715.
21. Le Guillanton, G., Do, Q.T., and Elothmani, D., *J. Electrochem. Soc.*, 1996, vol. 143, no. 10, p. L223.
22. Linders, C.R., Patriarche, G.J., Kaufmann, J.M., and Guibault, G.G., *Anal. Lett.*, 1986, vol. 19, nos. 1–2, p. 193.
23. Aalstad, B. and Parker, V.D., *J. Electroanal. Chem.*, 1980, vol. 112, no. 1, p. 163.
24. Glass, R. and Jouikov, V., *Tetrahedron Lett.*, 1999, vol. 40, no. 35, p. 6357.
25. *Investigations of Rates and Mechanisms of Reactions*, Bernasconi, C., Ed., New York: Wiley, 1986, vol. 6, 4/E, part 2, p. 305.
26. Simonet, J., *The Chemistry of Sulfur-Containing Functional Groups*, Patai, S. and Rappoport, Z., Eds., New York: Wiley, 1993, p. 475.
27. Jouikov, V., *Curr. Top. Electrochem.*, 1997, vol. 4, no. 1, p. 1.

28. Aalstad, B., Ronlan, A., and Parker, V.D., *Acta Chem. Scand.*, 1982, vol. 36, no. 3, p. 171.
29. Said, A.H., Mhalla, F.M., Amatore, C., Thouin, L., Pebay, C., and Verpeaux, J.-N., *J. Electroanal. Chem.*, 2002, vol. 537, nos. 1–2, p. 39.
30. Chapuzet, J.M. and Simonet, J., *Tetrahedron*, 1991, vol. 47, nos. 4–5, p. 791.
31. Butin, K.P., Reutov, O.A., and Beletskaya, I.P., *CH-Kisloty* (CH Acids), Moscow: Nauka, 1980.
32. Shulaeva, M.M., Fattakhov, S.G., and Reznik, V.S., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 11, p. 1909.
33. Fattakhov, S.G., Shulaeva, M.M., Gubaidullin, A.T., Litvinov, I.A., Nafikova, A.A., Latypov, Sh.K., and Reznik, V.S., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 8, p. 1371.
34. Fattakhov, S.G., Shulaeva, M.M., Saifina, L.F., Efremov, Yu.Ya., Rizvanov, I.Kh., Solov'eva, S.E., Nafikova, A.A., Azancheev, N.M., Gubaidullin, A.T., Litvinov, I.A., and Reznik, V.S., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 8, p. 1368.