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Reactions of thiols and organic disulfides with iron and its oxides

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The influence of O_2 and H_2O on the formation of iron dithiolates (IDTs) by the reactions of thiols and organic disulfides with the iron powder was studied under the static (without mechanical activation of the reaction) and dynamic (with mechanical activation of the reaction) conditions. Under the static conditions in the absence of O_2 or H_2O, only BnSH and PhSH give IDTs, whereas DdSH (Dd is dodecyl) produces IDTs in the presence of O_2 or H_2O. For the mechanical activation of the reactions of organic disulfides with the iron powder, the formation of IDTs is possible if the reaction mixture contains H_2O. On the interaction with iron oxides excess thiols are oxidized to organic disulfides and also afford IDTs.

Key words: butanediol, dodecanethiol, phenylmethanethiol, benzenethiol, dipropyl disulfide, didodecyl disulfide, dibenzyl disulfide, diphenyl disulfide, iron dithiolates, iron, iron oxides, mechanochemical reactions, X-ray photoelectron spectroscopy.

Organic disulfides are widely used as additives decreasing friction and frictional wear of steel surfaces. In this case, disulfides partially decompose to thiols under boundary friction conditions.[1] Mechanochemical reactions occurring *via* the reactions of organic disulfides and thiols with iron favor continuous service of steel mechanisms. However, chemical methods for analysis of products of mechanochemical reactions have not been developed up to recently. We have previously[2] proposed the method for studying mechanochemical reactions with the help of a mechanochemical vibrational mill. It has been shown[2] that, contrary to the popular opinion,[3,4] IDTs appear from thiols rather than from organic disulfides.

The purpose of the present work is to study the influence of O_2 and H_2O on the formation of IDTs by the reactions of thiols and organic disulfides with the iron powder under the static and dynamic conditions.

Results and Discussion

The following reactions were studied:

$$\underset{\mathbf{1a-e}}{2\ \mathrm{RSH}} + \mathrm{Fe} \longrightarrow \underset{\mathbf{2a-e}}{\mathrm{Fe(SR)_2}} + \mathrm{H_2},$$

$$\underset{\mathbf{3a-e}}{\mathrm{R_2S_2}} + \mathrm{Fe} \longrightarrow \underset{\mathbf{2a-e}}{\mathrm{Fe(SR)_2}},$$

where R = Pr (**a**), Bu (**b**), Dd (dodecyl, **c**), Bn (**d**), and Ph (**e**).

The influence of O_2 in the reaction medium was studied in the processes involving thiols **1b—e**, and the effect of an H_2O admixture was examined in the reactions of thiol **1c** and disulfide **3a**. The results are presented in Table 1.

Static conditions. Some IDTs are formed without mechanochemical activation of the reactions of thiols with the iron powder. For instance, the formation of IDTs **2b,d,e** was visually observed by the appearance of the color several minutes or hours after mixing the reactants. When IDTs **2d**,**e** were formed, hydrogen bubbles evolved for several weeks. In the first case, in several months a black product with metallic luster formed instead of brown IDT **2d**, whereas red-brown IDT **2e** did not change its color. If the reaction mixture is sealed in an air atmosphere, thiols **1b—e** initially turned to green. The brown color characteristic of IDTs appears in several days.

In the absence of O_2, thiol **1c** with the iron powder forms no IDT **2c**. No changes on the iron surface were visually observed even after many-year contact of the reactants in an evacuated ampule. However, if the ampule containing thiol **1c** and the iron powder was sealed off under atmospheric pressure without degassing, then the brown color characteristic of IDTs appears already in 30—60 min, and a brown precipitate is formed in 1 month. An H_2O admixture acts similarly in a degassed reaction medium. Probably, the reaction proceeds as follows:

$$\underset{\mathbf{1c}}{4\ \mathrm{DdSH}} + \mathrm{O_2} \longrightarrow \underset{\mathbf{3c}}{2\ \mathrm{Dd_2S_2}} + 2\ \mathrm{H_2O},$$

$$\mathrm{Fe} + 2\ \mathrm{H_2O} \longrightarrow \mathrm{Fe(OH)_2} + \mathrm{H_2},$$

$$\mathrm{Fe(OH)_2} + \underset{\mathbf{1c}}{2\ \mathrm{DdSH}} \longrightarrow \underset{\mathbf{2c}}{\mathrm{Fe(SDd)_2}} + 2\ \mathrm{H_2O}.$$

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Table 1. Results of qualitative analysis[a] of IDTs formed upon the reactions of organosulfur compounds (OSC) with the Fe powder and the results of XPS analysis of the surface of the Fe powders modified by OSC

OSC + admixture	Atmosphere	In quartz ampules, static conditions, qualitative analysis	In steel reactor, dynamic conditions	
			Qualitative analysis	E_{S2p}/eV (XPS)
BuSH (**1b**)	Vacuum	+	—	—
	Argon	—	+	168.6
1b + O_2	Air	+	—	—
DdSH (**1c**)	Vacuum	–	—	—
	Argon	—	+	168.7
1c + O_2	Air	+	—	—
1c + H_2O	Vacuum	+	—	—
BnSH (**1d**)	Vacuum	+	—	—
	Argon	—	+	163.5; 168.8
1d + O_2	Air	+	—	—
PhSH (**1e**)	Vacuum	+	—	—
	Argon	—	+	168.6
1e + O_2	Air	+	—	—
Pr_2S_2 (**3a**)	Vacuum	–	—	—
	Argon	—	–	168.8
3a + H_2O	Vacuum	–	+[b]	—
Dd_2S_2 (**3c**)	Argon	—	–	—[c]
Bn_2S_2 (**3d**)	Argon	—	–	169.3
Ph_2S_2 (**3e**)	Argon	—	–	168.9

[a] Signs "+" and "–" indicate the qualitative reaction to IDTs (positive and negative, respectively), "—" means that no experiment was carried out.

[b] In quartz ampule.

[c] No signal was detected by XPS.

The formation of dithiolate **2b** is possibly related to a higher reactivity of thiol **1b** compared to that of thiol **1c** or to a higher concentration of O_2 in the reaction medium (it is more difficult to remove O_2 from low-boiling thiol **1b**).

On contacting the reactants for several years disulfide **3a** forms no IDT **2a** with the iron powder. No IDT **2a** is either formed under static conditions when the iron powder, disulfide **3a**, and two—three droplets of H_2O are introduced successively into the ampule.

Dynamic conditions. The reactions of thiols **1b—e** and disulfide **3a** with the iron powder were carried out in quartz ampules sealed *in vacuo*. All thiols **1b—e** react with Fe to form the corresponding IDTs **2b—e**. So-called "self-assembled monolayers" (SAM) of Fe thiolates have been prepared earlier[5] by ultrasonication of solutions of thiols and amorphous iron. However, SAM of Fe thiolates differ from IDTs, in our opinion, by the fact that in the SAM the Fe atom is linked only with one thiolate group, whereas IDTs are individual compounds.

Disulfide **3a** forms no IDTs **2a** with the iron powder. For the reaction of disulfide **3a** with the iron powder in the presence of two—three drops of H_2O, the formation of IDT **2a** is observed several days after mechanical activation of the reaction. Probably, the process proceeds as follows:

$$\mathrm{Fe^* + 2\,H_2O \longrightarrow Fe(OH)_2 + H_2,}$$

$$\underset{\mathbf{3a}}{\mathrm{Pr_2S_2}} + \mathrm{H_2} \xrightarrow{\mathrm{Fe^*}} 2\,\underset{\mathbf{1a}}{\mathrm{PrSH}},$$

$$\mathrm{Fe(OH)_2 + 2\,PrSH \longrightarrow Fe(SPr)_2 + 2\,H_2O,}$$

where Fe* is mechanically activated iron.

The overall process can be written as

$$\mathrm{Fe^*} + \underset{\mathbf{3a}}{\mathrm{Pr_2S_2}} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{2a}}{\mathrm{Fe(SPr)_2}}.$$

When *n*-alkylthiols interact with the iron powder, the presence of chemisorbed O_2 on the iron surface does not prevent IDT formation, because oxygen forms water in excess thiols in the reaction mixture.

Let us consider the results of XPS studies of the surface of the iron powders obtained by the mechanochemical reactions of thiols **1b—e** and disulfides **3a,c—e** with the iron powder in a steel reactor in an argon atmosphere (see Table 1).

According to published data,[6] the bond energies of the S(2p) level (*E*) indicated by XPS for Fe modified by thiols and organic disulfides, are associated with the compounds presented below.

Compound	E/eV
Alk—S—Fe	161.5—162.4
Alk—S—H/Alk—S—S—Alk	162.8—163.9
Alk—SO_2^-	166.1—167.1
Alk—SO_3^-	168.6—169.2

An analysis of these and our results shows that the signal of the S(2p) level of the thiolate bond is characteristic only of the iron powder modified by thiol **1d**. Indeed, after this spectrum was decomposed to the components, two maxima with energies of 162.7 and 164.2 eV are observed (Fig. 1, *a*). As can be seen from the data in Fig. 1, the X-ray photoelectronic spectrum of the iron powder modified by thiol **1d** is similar to the spectrum of O-containing thiolate **4d** in which the presence of thiolate bonds was confirmed by the formation of FeS upon thermal decomposition *in vacuo*.

The IDT samples in the individual state are very sensitive to the presence of O_2. Some of them are ignited in air. However, the partial oxidation of IDT **2d** forms O-containing thiolate **4d**, which is stable for unrestrictedly long time, whereas the other products of the incomplete oxidation of IDTs **2b,c,e** under similar conditions are oxidized very rapidly. Evidently, the thiolate bond is not detected by X-ray photoelectron spectroscopy when the iron powder is modified by thiols **1b,c,e**.

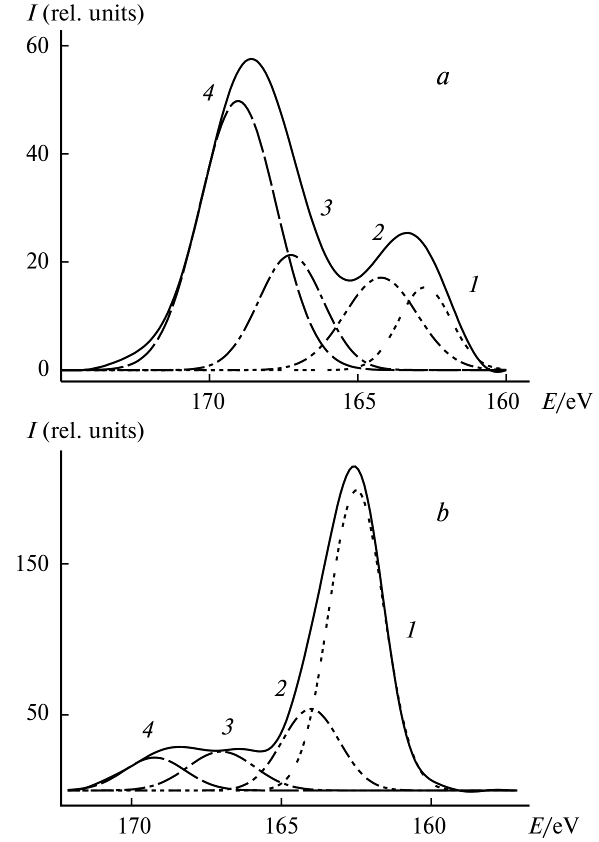

Fig. 1. X-ray photoelectronic spectra of the S(2p) level of the iron powder obtained by the mechanical modification of iron with thiol **1d** in the steel reactor (*a*) and compound **4d** (*b*): *1*, Bn—S—Fe (162.6 eV); *2*, Bn—S—S—Bn (164.1 eV); *3*, Bn—SO_2^- (167.1 eV); *4*, Bn —SO_3^- (169.1 eV).

Organic disulfides form no IDTs upon the interaction with the iron powder as indicated by negative qualitative reactions to IDTs and the absence of a maximum with an energy of 161.5—162.4 eV in the X-ray photoelectronic spectra. The signals of the S(2p) level with the energy 168.6—169.3 eV indicate that the oxidation products of organic disulfides rather than of IDTs are present on the iron powder surface.

Reactivity of iron oxides toward thiols. Since O_2 is highly reactive, the interacting steel surfaces are always covered, to this or another extent, by iron oxides, which actively reduce friction and wear at a certain concentration.

According to published data[7], Fe_2O_3 oxidizes thiols to disulfides. In the present work, it is shown for the first time that iron oxides oxidize thiols and, moreover, form IDTs. When thiol **1b** reacts with FeO in the absence of O_2, IDT **2b** is formed in 8 days; the reaction with Fe_2O_3 affords **2b** in 10 days; in the presence of an H_2O admixture IDT **2b** is formed already in 1 h. Thiol **1c** reacts with iron oxides much more slowly than thiol **1b**. Self-assembled monolayers of iron dithiolates have been prepared previously[5] by ultrasonication of solutions of thiols and amorphous Fe_2O_3. In authors´ opinion, in these SAM the AlkS radical is bonded to Fe^{III}.

Thus, it is shown in the work that under the static conditions IDTs **2d,e** appear already at room temperature as a result of the reactions of thiols **1d,e** with the iron powder. The presence of O_2 and H_2O in catalytic amounts favors the formation of IDTs **2b,c** under the static conditions. It is confirmed by X-ray photoelectron spectroscopy that no ITD is formed by the mechanical activation of the reaction of organic disulfides with iron. The reaction of disulfide **3a** with the iron powder under the dynamic conditions in the presence of H_2O was established to afford IDT **2a**. When reacting with excess thiols, iron oxides oxidize them to organic disulfides and also give IDTs.

Experimental

Experiments under the dynamic conditions were carried out in an M35L vibrational mill (vibration amplitude ~4 mm, vibrational frequency 48 Hz, electric engine power 1.7 kW). A steel cylindrical reactor (height 35 mm, diameter 46 mm) was held in a vertical position and accomplished virtually circular motion without rotation around its axis in the horizontal plane.

Iron powder samples obtained after the mechanical modification of iron in the steel reactor by thiols and organic disulfides were studied by X-ray photoelectron spectroscopy in an XSAM-800 two-chamber instrument (Kratos Analytical Ltd). The characteristic line Mg-Kα ($h\nu$ = 1253.6 eV) was used as the exciting radiation. The instrument was calibrated using standard samples using the lines Au4f (84.0 eV), Ag3d (368.3 eV), Cu2p (932.7 eV), and CuLMM (918.7 eV).

Spectra of powders of modified iron and compound **4d** were recorded *in vacuo* (~10^{-8} Pa) at room temperature.

The spectra were processed, including smoothening, subtraction of the background, quantitative analysis, and decomposition of complicated peaks to particular spectral components, using the Spectra Presenter program. Recharge of samples was taken into account by the carbon component with the lowest bond energy (285.0 eV).

All experiments under the static and dynamic conditions were carried out at room temperature. Experiments on synthesis of IDTs in the absence of O_2 were conducted with freshly reduced iron without contact with O_2. Oxygen was preliminarily removed from the reactants and solvents.

Thiols **1b—e** and disulfide **3a** were purity grade, Fe (carbonyl iron) was special-purity grade 6-2, Fe (metallic reduced iron) and FeO were purity grade, and Fe_2O_3 was special-purity grade 2-4. Thiols **1b—e** and disulfide **3a** were purified by fractional distillation prior to use. Disulfides **3c—e** were synthesized by described procedures.[8]

To conduct some experiments in quartz ampules, iron was synthesized by the reduction of Fe_2O_3 with hydrogen at 600—610 °C. Hydrogen was purified from an admixture of H_2O vapor by passing over Mg chips at 600 °C.

Formation of IDTs under the static conditions in the absence of O_2. An Fe powder (2.00 g, 0.36 g-at.) was placed in a 15-mL quartz ampule and additionally reduced with hydrogen. Then argon-saturated thiol **1b—e** or disulfide **3a** (4.0 mL) was added to the ampule under an argon atmosphere, and the ampule was sealed off *in vacuo* (~0.5 Torr). The formation of IDT was visually monitored by the appearance of color. When experiments were carried out in the presence of H_2O, 0.09 g of H_2O was introduced into the ampule containing the reaction mixture, after which the contents of the ampule was degassed, and the ampule was sealed off *in vacuo*.

Formation of IDTs under the static conditions in the presence of atmospheric O_2. Ampules (15 mL) with mixtures of carbonyl Fe (2.00 g, 0.36 g-at.) and thiol **1d** or **1e** (4.0 mL) were sealed off in air. After 9 months, 7.8% **1d** and 53.0% **1e** reacted with Fe, which corresponds to the formation of 3.9% **2d** and 26.5% **2e**.

Mechanochemical synthesis of IDTs in argon. Three steel balls 12.7 mm in diameter and three steel balls 7.9 mm in diameter, reduced Fe (purity grade) (2.00 g, 0.36 g-at.), thiol **1b—e** or disulfide **3a** in the individual state (10.0 mL), or disulfide **3c—e** (0.01 mol) in purified heptane (10.0 mL) were placed in a steel reactor. The reactor was purged with argon and hermetically closed. After mechanical activation of the reaction for 3 h, the iron powder was repeatedly washed with hexane by decantation, filtered off, and dried *in vacuo*. X-ray photoelectronic spectra were recorded after several days.

Mechanochemical synthesis of IDTs in the absence of O_2. Unlike experiments under the static conditions, five quartz balls 6—7 mm in diameter were placed into the ampule before the additional reduction of the Fe powder (2.00 g, 0.36 g-at.). After Fe was reduced, degassed and argon-saturated thiol **1b—e** or disulfide **3a** (4.0 mL) was added to the ampule under an argon atmosphere, the contents of the ampules were degassed, and the ampules were sealed off *in vacuo*. The duration of mechanical activation of the reaction was 1 h. In experiments with disulfide **3a**, H_2O (0.09 g) was introduced into the ampule. The reaction mixture was degassed, and the ampule was sealed off. The duration of mechanical activation was 1 h.

Reaction of thiols 1b with iron oxides. ***A.*** A mixture of FeO or Fe_2O_3 (0.10 g) and thiol **1b** (2.0 mL) in 15-mL ampules *in vacuo* were degassed by freezing—thawing out in liquid nitrogen, and the ampules were sealed off. After 8 or 10 days, respectively, a brown color appeared, which turned green upon contact with air.

B. Water (0.04 g) was introduced into an ampule containing a mixture of Fe_2O_3 (0.40 g) and thiol **1b** (2.0 mL). The content of the ampule was degassed, and the ampule was sealed off *in vacuo*. After 1 h, the ampule was shaken several times, after which thiol **1b** turned brown; it turned then green upon contact with air.

Synthesis of O-containing thiolate 4d. A degassed and argon-saturated solution of thiol **1d** (2.0 mL, 17 mmol) and Et_3N (1.5 mL, 10.8 mmol) in acetonitrile (25 mL) was added with stirring to a degassed solution of $FeCl_2 \cdot 4H_2O$ (0.30 g, 1.5 mmol) and Bn_2S_2 (1.0 g, 4 mmol) in acetonitrile (25 mL). Acetonitrile immediately turned brown, and an amorphous precipitate of the same color was formed.

The reaction mixture was magnetically stirred for 3 h under argon and then in air until MeCN became completely colorless. A dark green precipitate was filtered off on a porous glass filter suitable for separation of volatile solvents by pressing-out with gas, washed with ether (4×15 mL), and dried *in vacuo*. The yield of compound **4d** was 0.55 g (77.5%). Found (%): C, 53.25; H, 5.05; Fe, 13.06; S, 20.40. $C_{21}H_{21}FeO_2S_3$. Calculated (%): C, 53.28; H, 4.47; Fe, 11.80; S, 20.32. The elemental composition of compound **4d** depends on the duration of contact of dithiolate **2d** with O_2 in organic solvents. The substance is insoluble in organic solvents, and in the solid state in air it keeps for unrestrictedly long time. In the individual state IDT **2d** in air is oxidized with heating to red heat.

Qualitative determination of IDTs. The reaction mixture containing IDTs contacted with air O_2. In this case, IDTs containing *n*-alkyl or phenylmethyl substituents instantly changed the brown color to green forming a bulky amorphous dark green color.[9]

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