Reactions of thiols and organic sulfides with hydrogen in the presence of iron powder

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Previously unknown reduction of thiols to hydrocarbons and H_2S with hydrogen formed by the interaction of powdered iron with dilute HCl was found.

Key words: thiols, organic sulfides, disulfides, trisulfides, hydrogen, iron.

Organic disulfides in a mixture of chlorohydrocarbons are efficient additives to mineral oils that decrease friction and attrition wear of steel surfaces. As a result of the boundary friction they decompose to evolve H_2S and HCl, respectively, and the mobile hydrogen atom in hydrocarbons reacts with air oxygen to form H_2O. Therefore, it was of interest to reveal whether thiols and organic sulfides, disulfides, and trisulfides can be reduced to H_2S with hydrogen formed by the reaction of HCl with iron.

In the present work, we studied the reduction of thiols (RSH) **1a—e**, sulfides (R_2S) **2d,e**, disulfides (R_2S_2) **3a—e**, trisulfides (R_2S_3) **4a,b** (R = Bu (**a**), Bu^t (**b**), Dd (dodecyl, **c**), Bn (**d**), and Ph (**e**)), and O-containing iron thiolates $C_{10}H_{24}Fe_2O_6S$ (**5**) and $C_{14}H_{16}Fe_3O_7S_2$ (**6**) with hydrogen.

Results and Discussion

The results of quantitative determination of H_2S are presented in Table 1. It is seen that monosulfides **2d,e** and sterically hindered disulfide **3b** are not reduced with hydrogen to H_2S. For the reduction of sterically hindered trisulfide **4b**, the yield of H_2S is by 15 times lower than that for the reduction of trisulfide **4a** (*cf.* entries *5* and *10*) containing unbranched butyl radicals. Upon the addition of pentane, the yield of H_2S during the reduction of thiols **1a,b** decreases, which is caused, most likely, by the removal of thiols with volatile pentane from the reaction mixture. The improvement of conditions for contact of powdered iron with reduced compounds in a pentane solution exerts virtually no effect on the yield of H_2S during the reduction of thiols **1c—e** and disulfide **3a** (*cf.* entries *12* and *13*, *17* and *18*, *24* and *25, 3* and *4*). For the reduction of disulfide **3d** and trisulfides **4a** and **4b**, the yield of H_2S increases by 5.8, 2.1, and 3 times, respectively (*cf.* entries *21* and *22*, *5* and *6*, *10* and *11*). When thiol **1c** is reduced, the increase in the Fe : **1c** ratio by 3 times increased the yield of H_2S by 2.8 times (*cf.* entries *12* and *14*). When thiol **1d** is reduced with the iron powder preliminarily wetted with water, the yield of H_2S decreases by 3.5 times (*cf.* entries *18* and *19*).

Unlike disulfide **3a** containing *n*-butyl radicals, sterically hindered disulfide **3b** is not reduced with hydrogen, and wetting Fe with water decreases the yield of H_2S in the case of reduction of thiol **1d**. Therefore, it can be assumed that only the molecules adsorbed on the Fe surface are reduced. In this case, organic disulfides are reduced with hydrogen to thiols, which then interact with the Fe surface purified from oxides using the chemical method. In fact, the formation of so-called "self-assembled monolayers" of Fe thiolates already at 100—150 K was found in numerous works (see, *e.g.*, Refs 1 and 2) on the interaction of thiols with the surface of Fe single crystals under ultrahigh-vacuum conditions. At 256—298 K iron thiolates decompose to form FeS and the corresponding saturated or unsaturated hydrocarbons.

In the previous work,[3] we have shown that in the reaction with the powder of reduced iron thiols **1d**,**e** form iron dithiolates (IDT) at room temperature, and thiol **1e** exceeds thiol **1d** in reactivity, which is undoubtedly related to a higher acidity of thiol **1e** compared to thiol **1d**. It is found in the present work that these thiols, when reduced with hydrogen, form mostly H_2S (*cf.* entries *17*, *18*, *24*, and *25*); however, thiol **1d** exceeds thiol **1e** in reactivity, which is caused, most likely, by the higher nucleophilicity of thiol **1d** compared to thiol **1e** (see Ref. 4).

To compare amenability of hydrogen reduction of the C—S bond in IDT and disulfides, we synthesized and reduced O-containing thiolates **5** and **6**.

The IDT samples are very sensitive to O_2. In the individual state some of them are reduced with ignition and, hence, O-containing thiolates **5** and **6**, which are more stable in open air, were used for reduction with hydrogen.

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Table 1. Yields of H_2S in the reduction of organosulfur compounds (OSC)

Entry	OSC	m_{OSC} /g	Conditions[a]	V^b /mL	Yield of H_2S (%)
1	BuSH (**1a**)[c]	0.1076	+	2.3	1.0
2	**1a**	0.1021	–	4.1	1.8
3	Bu_2S_2 (**3a**)	0.1028	+	1.1	0.5
4	**3a**	0.1020	–	1.4	0.6
5	Bu_2S_3 (**4a**)	0.1015	+	26.3	9.1
6	**4a**	0.1001	–	12.4	4.3
7	Bu^tSH (**1b**)[c]	0.1009	+	0.6	0.3
8	**1b**	0.1000	–	3.5	1.6
9	$Bu^t{}_2S_2$ (**3b**)	0.1011	+	0.0	0.0
10	$Bu^t{}_2S_3$ (**4b**)	0.1002	+	1.8	0.6
11	**4b**	0.1005	–	0.7	0.2
12	DdSH (**1c**)	0.0997	+	1.8	1.9
13	**1c**	0.1011	–	1.9	1.9
14	**1c**[d]	0.1051	+	5.6	5.4
15	Dd_2S_2 (**3c**)	0.1013	+	1.6	1.6
16	**5**	0.1017	–	4.4	8.3
17	BnSH (**1d**)	0.1003	+	59.8	37.1
18	**1d**	0.1022	–	57.5	35.8
19	**1d**[e]	0.1001	–	16.9	10.5
20	Bn_2S (**2d**)	0.0979	+	0.0	0.0
21	Bn_2S_2 (**3d**)	0.1014	+	6.8	4.1
22	**3d**	0.0993	–	1.2	0.7
23	**6**	0.1010	–	29.4	36.7
24	PhSH (**1e**)	0.1011	+	10.6	5.9
25	**1e**	0.1108	–	10.7	5.4
26	Ph_2S (**2e**)	0.1009	–	0.0	0.0
27	Ph_2S_2 (**3e**)	0.0999	+	5.3	2.9

[a] Sign "+" means that the solvent (pentane) was preliminarily added to the reaction mixture and then evaporated *in vacuo*; "–" indicates that no solvent was added.

[b] Volume of a 0.01 *M* solution of I_2.

[c] Pentane was not evaporated *in vacuo.*

[d] A weighed sample of the Fe powder was 3 g; in all other entries, 1 g.

[e] Water (1 mL) was first added to the Fe powder, then the reduced compound was added, and finally dilute HCl was added.

As can be seen from the data in Table 1, O-containing thiolates **5** and **6** form more H_2S than disulfides **3c,d** (*cf.* entries *15* and *16*, *22* and *23*) containing similar radicals.

The reduction of thiols with hydrogen formed by the interaction of the iron powder with dilute HCl can be presented, most likely, by the following schemes:

$$\mathrm{Fe + 2\,HCl \longrightarrow FeCl_2 + H_2,}$$

$$\mathrm{R{-}SH + (Fe)_{\mathit{n}} \longrightarrow R{-}S{-}(Fe)_{\mathit{n}}{-}H,}$$

$$\mathrm{R{-}S{-}(Fe)_{\mathit{n}}{-}H + H_2 \xrightarrow{Fe} (Fe)_{\mathit{n}} + R{-}H + H_2S}$$

or, taking into account published data,[2]

$$\mathrm{R{-}S{-}(Fe)_{\mathit{n}}{-}H \longrightarrow FeS + (Fe)_{\mathit{n}-1} + R{-}H,}$$

$$\mathrm{FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S,}$$

where R = Alk, Bn, or Ph; $(Fe)_n$ is the Fe powder on which thiols are chemisorbed. When thiol **1d** is reduced with hydrogen evolved upon the interaction of Na with anhydrous EtOH, H_2S and dibenzyl[5] are formed, indicating a possibility of another reduction mechanism.

The quantitative determination of H_2S formed by the reduction of thiols and disulfides with hydrogen showed that the reduction of compounds **1a,b,d,e** and **3a,d** begins already at room temperature, and the initial reduction of compounds **1c** and **3c,e** is observed only after heating the initial mixture of the reactants.

The formation of hydrocarbons, in particular, toluene upon the reduction of thiol **1d**, was confirmed by GLC.

Thus, the earlier unknown reaction of reduction of thiols to hydrocarbons and H_2S with hydrogen formed upon the interaction of dilute HCl with the Fe powder was found.

Experimental

Identification of $PhCH_3$ formed upon the formation of compound **1d** was carried out on a «Chrom-4 chromatograph (glass column 2.5 m×3 mm, Chromaton N-AW + 15% Apieson L, 160 °C, carrier gas He).

The FT-IR spectrum of O-containing thiolate **6** was recorded on a Magna-750 instrument (Nicolet).

Compounds **1a—e**, **2d,e**, and **3a** (high-purity grade) were additionally purified by fractional distillation using Fe (special purity grade 6-2). Reactants **3b—e** and **4a,b** were synthesized by known methods.[6]

Reduction of compounds 1a—e, 2d—e, 3a—e, and 4a,b. The reaction was carried out in a device consisting of a 100-mL conic flask equipped with a reflux condenser, a dropping funnel, and tubes for gas supply and removal. The H_2S that formed was displaced with argon and absorbed by a 10% solution of $CdCl_2$.

Powdered Fe (1.00 g), a compound under study (0.1 g), and pentane (1 mL) were placed in the flask. The mixture was slightly stirred for 1—2 min, the solvent (except for experiments with thiols **1a,b**) was evaporated *in vacuo*, after which the flask was connected to the reflux condenser, and argon was passed through the device (50 mL min^{-1}). Hydrochloric acid (40 mL) diluted with water (1 : 1) was added to the dropping funnel, and in 10 min the rate of passing argon was decreased to 10—15 gas bubbles per min, after which the acid was added to the flask. Hydrogen began to evolve at room temperature but the reaction mixture was slightly heated to accelerate the evolution. After all the Fe dissolved, the flask content was heated to boiling (2—3 min). Heating was stopped, the rate of bubbled argon was increased, and the gas was continued to pass for 30 min more. A precipitate of CdS was separated by filtration through a folded paper filter and washed first with distilled water and then with EtOH. The amount of evolved H_2S in the decomposition of CdS with concentrated HCl was determined iodometrically using titrated 0.01 *N* solutions of I_2 and $Na_2S_2O_3$ (see Ref. 7).

O-Containing thiolate 5. Weighed samples of $FeCl_2 \cdot 2H_2O$ (0.30 g, 1.8 mmol), compound **1c** (1.00 g, 4.9 mmol), and Et_3N (0.7 mL, 5.0 mmol) were dissolved in 25, 15, and 10 mL of EtOH, respectively. Each solution was refluxed under Ar atmosphere and sealed. All the three solutions were placed in a box filled with Ar and mixed in a 100-mL flask, which was hermetically closed. The reaction mixture was magnetically stirred for 1 h. Next day iron bis(dodecanethiolate) that formed was filtered off in air with suction through a porous glass filter. The precipitate was washed with EtOH and benzene and dried *in vacuo*. A dark green oxygen-containing amorphous substance was obtained. Found (%): C, 29.90; H, 6.14; Fe, 31.97; S, 8.03. $C_{10}H_{24}Fe_2O_6S$. Calculated (%): C, 31.27; H, 6.30; Fe, 29.08; S, 8.35. The oxygen content depends on the duration of filtration and washing. Dry O-containing thiolate **5** in open air is oxidized within several days to disulfide **3c** and Fe_2O_3 and turns brown.

O-Containing thiolate 6 was synthesized similarly to thiolate **5**. Its element composition is variable. Being in the dry state in open air and in water, the substance remains unchanged without color change for many years. Found (%): C, 30.75; H, 3.20; Fe, 31.57; S, 12.25. $C_{14}H_{16}Fe_3O_7S_2$. Calculated (%): C, 31.85; H, 3.05; Fe, 31.73; S, 12.14. FT-IR, ν/cm^{-1}: 258, 324, 340, 478, 697, 764, 915, 1029, 1066, 1193, 1216, 1419, 1452, 1494, 1599, 2853, 2923, 3026, 3060, 3083, 3383. When anhydrous $FeCl_2$ and absolute EtOH are used for the synthesis of **6**, the spectrum contains no broad absorption band at 3383 cm^{-1}.

Thermal decomposition of O-containing thiolates 5 and 6. Wet compound **5** (0.2 g) or dry compound **6** (0.10 g) was placed in a device for sublimation and gradually heated to 300 °C in a vacuum <1 Torr. Several drops of dilute (1 : 1) HCl were added to the residue after decomposition, which was placed in a 10-mL tube. A filter paper wetted with a 1% solution of $AgNO_3$ was introduced into the tube. In both experiments, the filter paper blackened immediately, indicating that compounds **5** and **6** contain the Fe—SDd and Fe—SBn thiolate bonds.

Procedure of qualitative reaction to H_2S. Two—three drops of the liquid (or 0.02 g of solid) tested substance were placed in a narrow tube. In the latter case, several drops of pentane were added to the mixture. The mixture was stirred, the solvent was evaporated *in vacuo*, several drops of dilute (1 : 1) HCl was added to the residue, and a filter paper wetted with a 1% aqueous solution of $AgNO_3$ was immediately introduced. If hydrogen did not begin to evolve at room temperature, the mixture was heated. The indicator paper became dark brown or black in 5—10 s. The indicator paper placed in a gaseous medium of two—three drops of thiols **1b**, **1d**, and **1e** gains light pink, light brown, and light yellow colors, respectively. Thiol **1a** and disulfides impart no color to the indicator paper. (The filter paper that was not stored in open air under laboratory conditions should be used in the experiments).

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