

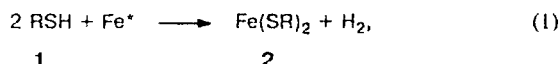
Letters to the Editor

A new mechanochemical reaction of thiols with iron metal

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In this work, we observed a new mechanochemical reaction of substitution of the H atom in the functional group of thiols by Fe. The reaction is accompanied by the formation of iron(II) dithiolates (IDT)



where R = Bu (**a**); Bu^t (**b**); dodecyl (**c**); 1-adamantyl (**d**); PhCH₂ (**e**); and Ph (**f**); Fe* is iron metal activated mechanically. FeS is formed along with IDT, and in the case of **1a** and **1e**, H₂S traces are additionally formed.

Under standard conditions, thiols do not react with metallic Fe. For example, octanethiol and **1f** do not react with Fe powder on heating at 150 °C for 24 h,¹ and **1c** sulfidizes Fe at 200 °C.² The known methods for the preparation of IDT are based on the substitution of chlorine anions in FeCl₂ or FeCl₃ by thiolate anions (RS⁻).^{3–8} Since IDT are readily oxidized by oxygen, they are usually obtained under anaerobic conditions and, as a rule, are not isolated in the individual state but are used for the preparation of derivatives.^{6–8} They were not obtained in the analytically pure state and were not characterized by spectral methods.

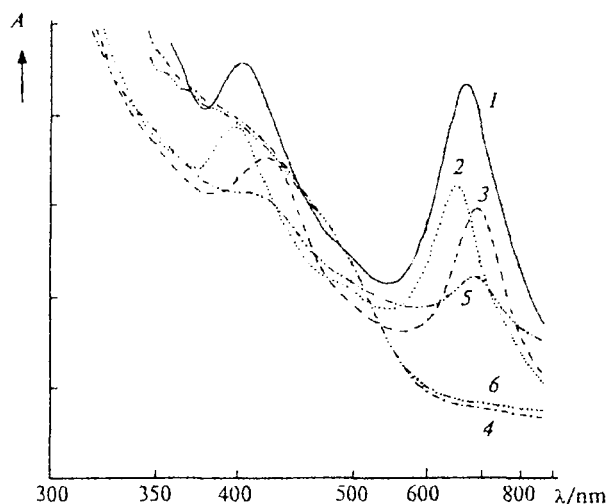
In this work, the reactions of organosulfur compounds with Fe were studied using an M35L vibrational mill (the amplitude of vibrations was ~4 mm, the frequency was 48 Hz, and the electric motor power was 1.7 kW). The deoxygenated organosulfur compound (10.0 mL) or its 30% solution in octane, reduced Fe

powder (2.0 g), three steel balls 12.7 cm in diameter, and three balls 8.9 cm in diameter were placed in an Ar atmosphere into a steel cylindrical ~60-cm³ reactor with a water jacket and a cap with two pipe connections for gas inlet and outlet. The reactor was thermostatted at 20 °C, and the vibrational mill was switched on. The experiment at a specified temperature lasted for 3 h. After the end of the experiment, the presence of H₂S was determined in the reactor gas. Liquid organosulfur compounds were used in the individual state, and solid compounds (**1d** and Ph₂S₂) were used as solutions in octane. The volume of gases in the reactor was measured volumetrically.

The IDT **2a**, **2c**, and **2e** formed in reaction (1) were primarily brown-colored and existed in the solution. After contact with O₂, they became green and formed a bulky amorphous precipitate which occupied, in some cases, up to 1/3 of the thiol volume. The yields of **2a**, **2c**, and **2e** after contact with O₂ were ~0.06%. In the solid state these compounds are amorphous and dark-green-colored, they are insoluble in organic solvents and are only strongly swollen, which likely indicates their polymeric structure.

Iron bis(benzenethiolate) (**2f**) formed in a solution of **1f** is reddish-brown and does not change color on contact with O₂ but precipitates as well.

The chemical composition of **2a,c,e,f** was confirmed by the positive qualitative reaction for Fe²⁺ with potassium hexacyanoferrate(III) and identification by TLC of compounds **1c** and **1e** in the products of decomposition



of compounds **2c** and **2e** isolated in the solid state by hydrochloric acid.

No release of H_2 (~0.4 mL) during interaction of **1a**, **1c**, and **1f** with Fe was observed volumetrically, probably due to dissolution of H_2 in the metal.

The electronic absorption spectra of solutions of **2a,c,e,f** in the starting thiols after the mechanochemical reaction (Fig. 1) were recorded on a Specord M40 spectrophotometer in sealed 0.5-cm cells.

After the mechanochemical interaction with Fe, sulfides Bu_2S and Ph_2S and disulfides Pr_2S_2 , Bu_2S_2 , and Ph_2S_2 gain no color characteristic of IDT, which contradicts the assumption^{2,9,10} about their formation in the reaction with metallic Fe. According to our data, all organic sulfides and disulfides studied form only FeS during the mechanochemical interaction with Fe.

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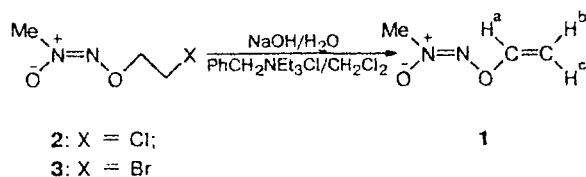
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Synthesis of vinyloxy-NNO-azoxymethane

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Previously unknown vinyloxy-NNO-azoxy methane (1), the first alkoxy-NNO-azoxyalkane (AAZA) with the double C=C bond at the oxygen atom, was synthesized by the dehydrohalogenation of AAZA 2 and 3¹ under phase transfer catalysis conditions.



Four AAZA with the double C=C bond at the N atom (4–7)^{2,3} and two triazenes 8⁴ and 9⁵ close in structure to 1 are described in the literature.

