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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Mechanochemical Reactions of Elementary Sulfur and Iron Sulfides with Hydrogen, Oxygen, and Water

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Abstract—Mechanochemical reactions of elementary sulfur and iron sulfides with hydrogen, oxygen, and water were studied. Three reactions were discovered: (1) between elementary sulfur and dihydrogen, (2) between pyrite and dihydrogen, and (3) between elementary sulfur and water; these reactions are accompanied by hydrogen sulfide evolution. Mechanochemical synthesis of iron sulfide from the constituent elements in water involves hydrogen sulfide, which is generated by the reaction of elementary sulfur with water. We show that elementary sulfur is generated during pyrite oxidation by dioxygen during or after dispersion. In an oxygen-free medium, pyrite is more reactive to water than iron sulfide. Pyrite reacts with dihydrogen and water in an oxygen-free medium directly, avoiding the dissociation stage.

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There is abundant literature on the thermochemical reduction of S_8 and iron sulfides by dihydrogen and the reactions of S_8 with water. The same reactions with mechanochemical activation have not been addressed in periodicals.

This work studies mechanochemical reactions of S_8 and iron sulfides with dihydrogen and water and elucidates the reasons for S_8 formation during dispersion of iron sulfides.

EXPERIMENTAL

The starting commercial chemicals were as follows: iron(III) oxide (high purity grade os.ch. 2–4) and elementary sulfur (high purity grade os.ch. 16–5).

Metallic iron was synthesized by Fe_2O_3 reduction with hydrogen at 600–610°C. Hydrogen was passed over magnesium shavings at 600°C to purify it from water vapor.

Native pyrite was used.

FeS synthesis. To a quartz ampoule 160 mL in capacity, S_8 (48.10 g, 1.5 g/at) was placed and fused in vacuo; the ampoule was then filled with argon and cooled. Then, reduced iron (83.7 g, 1.5 g/at) was added, the ampoule evacuated, filled with argon (three times), and sealed in vacuum (~66.7 Pa). The ampoule was placed, in a horizontal position, into a furnace, and the reagent mixture was heated at 1°C/min. At ~300°C, the mixture heated to redness. The furnace temperature was elevated to 800°C, and heating continued for another 30 h.

Mechanochemical syntheses. Experiments were carried out on an M35L vibration mill (vibration amplitude: ~4 mm; frequency: 48 Hz; electric motor power: 1.7 kW) inside quartz ampoules and a steel reactor. Quartz ampoules 15 mL in capacity and a cylindrical steel reactor (35 mm high, 46 mm in diameter) were mounted in a vertical position. The ampoules and reactor performed near-circular motion without rotating around their axis in the horizontal plane. The working body was 10 quartz balls with diameters of 6.3–6.6 mm (their total weight was ~3 g) in quartz ampoules and three steel balls 7.9 mm in diameter and three steel balls 12.7 mm in diameter (their total weight was ~31 g, steel ShKh-15) in the steel reactor. Before mechanochemical experiments in the reactor, it was purged with the proper gas for a long time. Before mechanochemical experiments in quartz ampoules with liquids, they were repeatedly degassed by freezing and thawing out in vacuum, then sealed in vacuum (~66.7 Pa) or at the atmospheric pressure (when experiments were carried out in argon, hydrogen, or air atmosphere). The steel reactor was air-tightened with a steel cover equipped with two nipples for entering and leaving gases. Experiments in quartz ampoules were carried out at room temperature; in the steel reactor equipped with a water jacket, at 20°C.

After activation was over, ampoules were unsealed, and a filter paper strip wetted with 1% aqueous $AgNO_3$ solution was rapidly inserted into the neck of an ampoule. In the presence of H_2S, indicator paper darkened in 5–10 s.

In runs 10, 18, and 26 (table), gases were passed through the reactor at ~40 mL/min. Before entering the reactor, hydrogen passed a Drexel bottle filled with glass wool and P_2O_5. Leaving gases passed through a Drexel bottle filled with 10% aqueous $CdCl_2$ solution.

Qualitative and quantitative analyses of products of mechanochemical reactions

Sample no.	Starting reagents; the amount of solids (g) and liquids and gases (mL) is parenthesized	Atmosphere	Reactor material	Reaction time, h	Reaction products; yield in % of calcd.			
					H_2S	S_8	FeS	$FeSO_4$
1	$S_8(2.00) + H_2(14.0)$	H_2	Quartz	2	+[a]			
2	$S_8(0.64) + H_2O(3.0)$	Vacuum	Quartz	1	+			
3	$S_8(0.64) + H_2O(3.0)$	Ar	Quartz	1	+			
4	$S_8(0.64) + H_2O(3.0)$	Air	Quartz	1	+			
5	$Fe(5.00) + S_8(3.21)$	Ar	Steel	2			+	–
6	$Fe(5.00) + S_8(3.21) + EtOH(5.0)$	Ar	Steel	2			+	–
7	$Fe(5.00) + S_8(3.21) + C_6H_6(5.0)$	Ar	Steel	2			+	–
8	$Fe(5.00) + S_8(3.21) + H_2O(5.0)$	Ar	Steel	2			9.80	1.78
9	FeS(5.10)	Ar	Steel	5		0.02		–
10	$FeS(5.01) + H_2$	H_2	Steel	1	–			
11	$FeS(5.09) + O_2(49.4)$	O_2	Steel	5		0.13		0.61
12	$FeS(5.11) + H_2O(0.20)$	Ar	Steel	5		1.79		
13	$FeS(5.02) + H_2O(0.20)$	Ar	Steel	1	–			
14	$FeS(3.00) + H_2O(0.50)$	Vacuum	Quartz	2	–			
15	$FeS(3.00) + H_2O(5.00)$	Vacuum	Quartz	2	–			Traces
16	$FeS(5.14) + O_2(118.8) + H_2O(0.20)$	O_2	Steel	5		3.64		0.47
17	$FeS_2(5.10)$	Ar	Steel	5		0.02	2.36[b]	0.91
18	$FeS_2(5.10) + H_2$	H_2	Steel	5	0.11		4.54[b]	0.90
19	$FeS_2(3.60) + Fe(1.68)$	Ar	Steel	5			18.80	
20	$FeS_2(5.10) + O_2(92.3)$	O_2	Steel	5		0.79	2.36[b]	3.49
21	$FeS_2(5.11) + H_2O(0.20)$	Ar	Steel	5		0.18	0.58[b]	
22	$FeS_2(5.02) + H_2O(0.50)$	Ar	Steel	1	+			
23	$FeS_2(3.00) + H_2O(0.40)$	Vacuum	Quartz	2	+			
24	$FeS_2(3.00) + H_2O(5.00)$	Vacuum	Quartz	2	–	0.00		Plenty
25	$FeS_2(5.00) + O_2(125.4) + H_2O(0.20)$	O_2	Steel	5		0.91	0.004[b]	3.99
26	$Fe_2O_3(2.80) + H_2S$	H_2S	Steel	2			78.57	

[a] "+" means a positive qualitative test; "–"means a negative test. [b] Activated pyrite or its impurity.

The presence of H_2S was indicated by the appearance of a yellow CdS precipitate.

In oxidation of iron sulfides in runs 11, 16, 20, and 25, the reactor was purged with oxygen; after the vibration mill was switched on, oxygen was fed from a burette with a leveling bottle.

Quantitative determination of S_8. A sample (1–4 g) of the product of mechanochemical reaction was extracted with benzene in an argon atmosphere for 3 h in a Soxhlet apparatus (250 cycles of solvent pouring in/off the extractor). Elementary sulfur was determined gravimetrically. Benzene was distilled off in vacuum; the residue was weighed.

Quantitative determination of FeS and activated pyrite. The analytical device consisted of a conical flask 100 mL in capacity equipped with a refluxer. On top, the refluxer was hermetically connected to a dropping funnel adapted to operate under a small pressure, a feed gas pipe passing through the refluxer to its lower end, and a leaving gas pipe with one end connected to the top of the refluxer and the other to a U-shaped pipe cooled to –50°C. The U-shaped pipe was connected to a Drexel bottle that contained about 100 mL of 10% $CdCl_2$ solution in water.

To the conical flask, a test sample (1–4 g) was placed; the flask was connected to the refluxer, and argon was fed through the device at 50 mL/min. After 10 min, the argon flowing rate was decreased to 10–15 bubbles/min, after which dilute HCl (1 : 1) was added to the flask (10 mL of acid per 1 g of the sample) and refluxed for 10 min. Heating was stopped, and the argon flow rate increased; the gas was fed for another 30 min. CdS was collected on a folded paper filter and washed with distilled water. The amount of H_2S released as a result of CdS digestion by concentrated HCl was determined iodometrically using titrated 0.1 or 0.01 N solutions of I_2 and $Na_2S_2O_3$ [1].

Inasmuch as atomic hydrogen generated by the reaction of metallic iron with hydrochloric acid reduces S_8 to H_2S [2], FeS in runs 5–8 was quantified only after S_8 was removed by benzene extraction in a Soxhlet apparatus.

In the hydrochloric acid solution resulting from FeS or activated pyrite determination, $FeSO_4$ was determined gravimetrically in the form of $BaSO_4$.

Qualitative analysis of anions and quantitative analysis of hydrogen degenerated during FeS and pyrite dispersion with water. After FeS was dispersed with excess water (run 15), the ampoule was centrifuged, unsealed in an argon atmosphere, and a filter paper strip wetted with $AgNO_3$ solution was inserted into the neck of the ampoule. H_2S was not detected. The aqueous solution gave negative tests with $AgNO_3$, $K_3[Fe(CN)_6]$, and $K_4[Fe(CN)_6]$. After the test with $BaCl_2$, the solution clouded faintly.

After pyrite dispersion with excess water (run 24), the ampoule was centrifuged, unsealed in an argon atmosphere, and a filter paper strip wetted with $AgNO_3$ solution was inserted into the neck of the ampoule. H_2S was not detected. The aqueous solution was separated by centrifugation or suck-filtering in an argon atmosphere. The hydrogen index of the solution was ~4. Tables XIV and XV from [3] were used in qualitative analysis for anions.

To a 0.5-mL portion of the test solution, excess $AgNO_3$ solution was added. The resulting gray precipitate was separated, and water was added. The precipitate did not dissolve during heating; therefore, SO_3^{2-} and $S_2O_3^{2-}$ anions could be present. The precipitate was separated, treated with dilute HNO_3, and heated. The precipitate dissolved; therefore, SO_3^{2-} and $S_2O_3^{2-}$ were present. To the solution, dilute aqueous ammonium was dropped so that two layers formed. No white ring appeared; therefore, SO_3^{2-} was absent.

To a 0.5-mL portion of the test solution, excess $BaCl_2$ solution was added; the precipitate centrifuged, treated with dilute HNO_3, and heated. The precipitate did not dissolve; therefore, SO_4^{2-} was present. The precipitate was separated, and aqueous NaOH was added to the solution in dilute HNO_3. A precipitate appeared; therefore, $S_2O_3^{2-}$ was present.

To a 0.5-mL portion of the test solution, excess $Pb(CH_3COO)_2$ solution was added. The nascent precipitate dissolved in aqueous $Na_2S_2O_3$ solution; therefore, $S_2O_3^{2-}$ was present.

Drop tests of the test solution with $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ were positive; therefore, Fe^{2+} and Fe^{3+} were present.

After the aqueous solution was suck-filtered in an argon atmosphere, the residue was dried in vacuum at room temperature and extracted by hot deoxygenated and argon-saturated benzene several times in an argon atmosphere. Benzene was filtered off and distilled off in vacuum. To a 0.0007-g portion of the residue, pyridine (1 mL) and 2 N NaOH (1–2 drops) were added. Pyridine did not turn blue; therefore, S_8 was absent.

After pyrite was dispersed in excess water, the ampoule neck was cut, and the ampoule was placed, with its mouth down, into water boiled and cooled under argon; after this, the ampoule was unsealed. The gas collected in the upper part of the ampoule was analyzed on a Khrom-F 3700 chromatograph equipped with a katharometer detector; the carrier gas was nitrogen (20 mL/min), the steel column was 2.5 m long and 3 mm in inner diameter, and the solid phase was carbon SKT. The column temperature was 100°C; the detector temperature was 110°C.

The table displays the results of mechanochemical reactions.

RESULTS AND DISCUSSION

Reduction reactions. Mechanically activated sulfur is reduced at room temperature not only by hydrogen to hydrogen sulfide, but also by water (table, runs 1–4):

$$S + H_2 \longrightarrow H_2S, \quad (1)$$

$$S + H_2O \longrightarrow H_2S + O. \quad (2)$$

The enthalpy of S_8 reduction by water is positive (214.5 kJ/mol) [4]; therefore, the reaction must not occur under the STP. However, by analogy with other mechanochemical reactions that do not occur under the STP, it was suggested that mechanical activation would make this reaction possible. In particular, in the reaction of heavy metals with S_8 in the presence of water, sulfide formation can occur as a result of H_2S participation. To check this suggestion, we studied the effect of various solvents on FeS yield. The reaction of iron with S_8 in a solid state and in the presence of organic solvents produced trace FeS amounts; the presence of water abruptly increased FeS yield (runs 5–8). This fact, as well as H_2S formation by scheme (2), proves that FeS is not generated by a direct reaction between S_8 and iron during mechanochemical activation in the presence of water, but with participation of H_2S, which verifies the suggestion made in [4].

Mechanically activated FeS, unlike pyrite, is not reduced by dihydrogen to H_2S. We should note that during thermochemical reduction FeS also has lower reactivity than pyrite [5]. FeS is reduced starting at ~900°C by the scheme

$$FeS + H_2 \longrightarrow Fe + H_2S, \tag{3}$$

FeS_2 reduction starts at 440°C:

$$FeS_2 + H_2 \longrightarrow FeS + H_2S. \tag{4}$$

Thus, the fact that FeS is not reduced mechanochemically at room temperature (run 10) is quite natural.

Because thermochemical reduction of pyrite by dihydrogen [5] and its thermochemical dissociation to FeS and S_8 in an inert atmosphere [6] occur roughly at the same temperature (500°C), we may assume that the mechanochemical reduction of pyrite by dihydrogen follows the scheme

$$FeS_2 \longrightarrow FeS + S \tag{5}$$

and, then, scheme (1). However, another reduction mechanism is possible: dihydrogen directly reacts with activated pyrite. It was shown earlier [7] that pyrite reacts with metallic iron in this way. We managed to determine which mechanism is implemented in the mechanochemical reduction of pyrite by dihydrogen only after determining the conditions under which FeS and pyrite generate S_8.

Oxidation reactions. S_8 evolution upon oxidation of wet FeS by atmospheric oxygen was discovered by Berzelius in 1826 [8].

By our observations, FeS and pyrite activated in a vibration mill oxidize even at room temperature, as shown by a steady increase in the sample weight. There is warning in [9] that fine milling of pyrite induces small sulfur loss in the form of SO_2 and noticeable $FeSO_4$ generation. However, other researchers report different data. For example, when the initial pressure is 13.3 Pa, FeS oxidizes to $FeSO_4$ at 50°C. The reaction rate becomes negligibly low when a $FeSO_4$ monolayer is formed. Within 50–150°C, oxidation does not generate SO_2 or SO_3 [10].

High-temperature X-ray diffraction discovered that pyrite milled in a planetary mill oxidizes starting at ~300°C, and pyrite pestled in a mortar, at temperatures 120°C higher. In oxidation of activated pyrite, sulfate formation dominates over iron oxide formation [11]. Apparently, Samgunov et al. [11] did not know that pyrite after pestling oxidizes even at room temperature [9].

Buckley and Woods [12] studied the pyrite surface exposed to air by X-ray photoelectron spectroscopy. $FeSO_4$ was detected on the surface in the first minutes; its amount increased with exposure time. After long exposure, iron oxide was detected; however, S_8 was not.

In mechanochemical pyrite synthesis from the constituent elements in air, $FeSO_4$ formation prevails [13].

Jiang et al. [14] showed that mechanochemically prepared pyrite is oxidized by atmospheric oxygen to $FeSO_4$, whereas FeS particles are only coated by a thin $FeSO_4$ layer.

By our data, only 0.02% S_8 is formed upon FeS and pyrite activation in argon (runs 9, 17); activation in an oxygen atmosphere abruptly increases its yield (runs 11, 20). Evidently, S_8 is formed upon FeS and pyrite dispersion in an argon atmosphere due to oxygen adsorbed on the surface of iron sulfides and reactor walls. In our opinion, S_8 formation during mechanical pyrite activation observed in [15, 16] was due to the oxygen ambience.

The oxidation mechanism of activated iron sulfides likely consists in that oxygen can attack both an iron atom,

$$FeS + 1/2O_2 \longrightarrow FeO + S, \tag{6}$$

$$FeS_2 + 1/2O_2 \longrightarrow FeO + S_2, \tag{7}$$

and a sulfur atom,

$$FeS + 2O_2 \longrightarrow FeSO_4, \tag{8}$$

$$FeS_2 + O_2 \longrightarrow FeS + SO_2. \tag{9}$$

The fact that S_8 is not formed during pyrite activation in the absence of oxygen implies that hydrogen directly reacts with pyrite by scheme (4) during mechanochemical reduction of pyrite by dihydrogen. FeS yield in pyrite reduction by hydrogen is 5.6 times lower than in pyrite reaction with iron (runs 18, 19). This is certainly because iron is solid and hydrogen is in a gaseous state. In view of the fact that pyrite does not dissociate by scheme (5) during mechanical dispersion, the question appears: why is H_2S evolution observed in the reaction of mechanically activated pyrite with hydrochloric acid? We think that this results from an increase in dispersivity (entropy) of pyrite. For example, it is known that monolithic pyrite does not oxidize in air, whereas ultrafine pyrite ignites spontaneously [17].

Jiang et al., in their work [14] on mechanochemical synthesis of iron sulfides from the constituent elements, characterized reaction products by X-ray diffraction, Mössbauer spectroscopy, and scanning electron microscopy. The 100% yield of pyrite FeS_2 is achieved by activating the reaction between iron and S_8 with 1 : 2 stoichiometry in a high-energy planetary mill for 110 h in an argon atmosphere. When the reaction stoichiometry is 1 : 1, near 100% FeS yield is achieved after 67 h. Thus, Jiang et al. support our inference that pyrite does not dissociate during dispersion in argon.

Lin et al. [18] studied the structure of iron sulfides generated by mechanochemical activation of iron and S_8 powders in a ball mill, using X-ray diffraction, extended X-ray absorption fine structure (EXAFS), and X-ray absorption near-edge structure (XANES) spectroscopy. An FeS_2 phase appeared after 3 h of mechanical alloying of $Fe_{50}S_{50}$ powders. During mechanical alloying of $Fe_{33}S_{67}$ powders, an $Fe_{1-x}S$ phase appeared after 15 h, but pyrite formation was not observed. This fact is not at variance with the results obtained by Jiang et al. [14]: our synthesis was performed in a low-energy ball mill and for a short time.

Reactions with water. Dispersion of iron sulfides in aqueous media were studied in several works. For example, Molchanov and Arkhipenko [19] report that FeS reacts with water by the scheme

$$FeS + H_2O \longrightarrow FeO + H_2S, \qquad (10)$$

$$3FeO + H_2O \longrightarrow Fe_3O_4 + H_2. \qquad (11)$$

Mechanical activation of the reaction was carried out in a copper reactor with copper shot. Because the atmosphere in the reaction was not specified, we must believe that experiments were carried out in air. In our opinion, H_2S formation by the above scheme is impossible: the rate of the reaction between iron oxides and H_2S is very high as judged from FeS yield (run 26), whereas the rate of the reaction between FeS and water is null (runs 13, 14).

Bocharov et al. [20] studied pyrite oxidation in metallic and porcelain mills with free excess of air in the presence of water at various pHs, which were controlled with CaO, NaOH, and H_2SO_4. During pyrite dispersion in 1.06 N aqueous NaOH in a porcelain mill, quantitative chemical analysis determined the following anions (concentrations in equiv/L are parenthesized): S^{2-} (1.23×10^{-2}), SO_3^{2-} (2.34×10^{-3}), $S_2O_3^{2-}$ (9.14×10^{-3}), and $S_nO_6^{2-}$ (4.14×10^{-3}). During pyrite dispersion in a metallic mill, $S_3O_6^{2-}$ (6.25×10^{-4}equiv/L) was found in addition to the aforementioned anions.

Selezneva and Molchanov [21] mechanically activated pyrite in a planetary mill in water, aqueous NaCl, $NaNO_3$, and NaOH with MnO_2 addition. We can only guess that the experiments in water were carried out in air. Selezneva and Molchanov suggested that the mechanochemical reaction of pyrite with water is accompanied by the formation of iron sulfide and sulfur in an active state:

$$FeS_2 \longrightarrow FeS^{\bullet} + S^{\bullet}, \qquad (12)$$

$$2FeS^{\bullet} + 10H_2O \longrightarrow 2Fe[SO_4][OH] + 9H_2. \qquad (13)$$

Because the product of the mechanochemical reaction of pyrite with water was filtered, washed, and dried in air, S_8 was formed during oxidation of activated pyrite by atmospheric oxygen, but not as a result of pyrite dissociation by scheme (12).

Kulebyakin [22] studied alteration of pyrrhotite and pyrite in various activation regimes in a high-energy centrifugal planetary mill using X-ray powder diffraction. After pyrrhotite and pyrite were dispersed in air for 7 min and disaggregated in water, the following compounds were detected:

$$\begin{gathered}Fe_7S_8 \longrightarrow Fe_7S_8 + FeSO_4 \cdot 4H_2O \\ + 4Fe_2(SO_4)_3 \cdot 5Fe_2O_3 \cdot 27H_2O + S,\end{gathered} \qquad (14)$$

$$\begin{gathered}FeS_2 \longrightarrow FeS_2 + FeSO_4 \cdot H_2O \\ + 3Fe_2O_3 \cdot 8SO_3 \cdot 2H_2O + \delta\text{-}FeOOH.\end{gathered} \qquad (15)$$

After dispersion in water for 30 min,

$$\begin{gathered}Fe_7S_8 \longrightarrow Fe_7S_8 + FeSO_4 \cdot 4H_2O \\ + 4Fe_2(SO_4)_3 \cdot 5Fe_2O_3 \cdot 27H_2O + S,\end{gathered} \qquad (16)$$

$$\begin{gathered}FeS_2 \longrightarrow FeS_2 + FeSO_4 \cdot 4H_2O \\ 4Fe_2(SO_4)_3 \cdot 5Fe_2O_3 \cdot 27H_2O + Fe_3O_4 + S.\end{gathered} \qquad (17)$$

We should note that ~500 mL of air was contained in a 600-mL reactor during pyrrhotite and pyrite dispersion. Apart from this, Kulebyakin observed active oxidation in periods after dispersion and before X-ray spectra were recorded. Thus, both pyrrhotite and pyrite were oxidized by dioxygen during dispersion in air or water and after this; we think that S_8 was generated in this way.

X-ray photoelectron spectroscopy did not detect S_8 on the surface of water-exposed pyrite [12].

In our experiments, FeS mechanochemical oxidation in the presence of water drastically increases S_8 yield as compared to yield in the absence of water (runs 11, 16). In pyrite oxidation under similar conditions, S_8 yield increased only insignificantly (runs 20, 25), likely, because of the strong thickening of the reaction mixture.

All mechanochemical reactions of iron sulfides with water were studied in the presence of dioxygen. We have not found studies on the reaction of iron sulfides with water in deoxygenated media. In order to elucidate the effect of dioxygen on mechanochemical reactions of iron sulfides with water, we studied these reactions in a deoxygenated medium.

We did not found H_2S when FeS was reacted with deficient water in either a steel reactor or quartz ampoules (runs 13, 14). Pyrite under similar conditions generated H_2S (runs 22, 23). However, because adsorbate oxygen could be present in the reactor and H_2S was generated by consecutive reactions of scheme (5) and (2) or as a result of FeS_2 reduction by atomic hydrogen generated by the reaction of water with the reactor material, runs were replicated in evacuated quartz ampoules. These replica runs yielded smaller amounts of hydrogen sulfide, likely, because lighter quartz balls created a lower energy load on pyrite than steel balls. In a steel reactor, H_2S and S_8 were detected in the reaction of pyrite with deficient water; S_8 could result from oxidation of activated pyrite after depressurizing the reactor or during extraction of wet pyrite with benzene.

From the results of qualitative analysis of the aqueous solution produced by FeS dispersion in excess water, it follows that FeS virtually did not react with water in an deoxygenated medium (run 15). After mechanochemical reaction of pyrite with water (run 24) under similar conditions, the solution contained the following compounds: H_2 (0.02 mL or 0.4 vol %), Fe^{2+} (plenty), Fe^{3+} (traces), SO_4^{2-} (plenty), and $S_2O_3^{2-}$ (little). Elementary sulfur and H_2S were not detected. This means that pyrite reacts with water directly, as with iron [7] and hydrogen.

Gusev and Molchanov [23] studied the products of dispersion of iron sulfides in water by means of a planetary mill inside a copper reactor with copper shot, apparently, in an air atmosphere. They believed that oxidation of sulfide sulfur can be described as follows:

$$\begin{aligned} 6FeS + 29H_2O &\longrightarrow 2Fe_3O_4 \\ &+ 3H_2SO_3 + 3H_2SO_4 + 23H_2, \end{aligned} \tag{18}$$

$$\begin{aligned} 3FeS_2 + 25H_2O &\longrightarrow Fe_3O_4 \\ &+ 3H_2SO_3 + 3H_2SO_4 + 19H_2. \end{aligned} \tag{19}$$

X-ray powder showed that magnetite was the major component of the solid phase. After 30-min dispersion of FeS and pyrite in water, 21.52 and 5.65 vol % hydrogen were, respectively, found in the reactor atmosphere. After FeS dispersion, filtrate contained 0.024 g/L SO_4^{2-} ; after pyrite dispersion, it contained 0.0074 g/L SO_3^{2-} and 0.032 g/L SO_4^{2-} were found. The hydrogen index of these filtrates was definitely acidic.

Thus, a distinctive feature of mechanochemical dispersion of iron sulfides in degassed water in quartz ampoules (runs 15 and 24) is that FeS, unlike pyrite, virtually does not react with water. Possibly, this is because of the lower energy load on quartz balls as compared to the energy load created by copper shot in a copper reactor. It is noteworthy that FeS in thermochemical interaction with water vapor was also less reactive than pyrite [5]. For example, FeS starts to react with water vapor at ~900 °C by the following scenario:

$$3FeS + 4H_2O \longrightarrow Fe_3O_4 + 3H_2S + H_2, \tag{20}$$

FeS_2 reacts at 380°C:

$$3FeS_2 + 2H_2O \longrightarrow 2FeS + 2H_2S + SO_2. \tag{21}$$

Another distinctive feature of mechanochemical reaction of pyrite with water in a quartz ampoule (run 24) is the absence of SO_3^{2-} in filtrate.

To summarize, having studied mechanochemical reactions of S_8 and iron sulfides with hydrogen, oxygen, and water, we discovered three new reactions occurring at room temperature in which H_2S is generated by schemes (1), (2), and (4). We have shown that H_2S participates in mechanochemical synthesis of FeS from the constituent elements in water. We have also shown that S_8 is formed during mechanochemical oxidation of pyrite by dioxygen during or after dispersion. Pyrite reacts with water even in the absence of oxygen. FeS virtually does not react with water under similar conditions. Pyrite reacts with dihydrogen and water in deoxygenated media directly, avoiding dissociation by scheme (5) or (12).

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