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Publisher Taylor & Francis

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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

A Contribution to the Thermochemical Reduction of SO_4^{2-} in the Presence of S^{2-} and Organic Compounds

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To cite this Article Steinfatt, Ingeborg and Hoffmann, Gerhard Georg(1993) 'A Contribution to the Thermochemical Reduction of SO_4^{2-} in the Presence of S^{2-} and Organic Compounds', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 74: 1, 431 – 433

To link to this Article: DOI: 10.1080/10426509308038150

URL: <http://dx.doi.org/10.1080/10426509308038150>

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A CONTRIBUTION TO THE THERMOCHEMICAL REDUCTION OF SO_4^{2-} IN THE PRESENCE OF S^{2-} AND ORGANIC COMPOUNDS

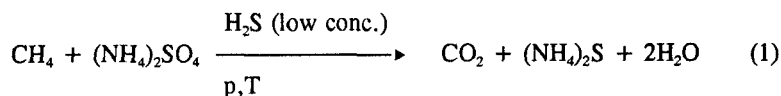
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Abstract The thermochemical reduction of sulfate in the presence of sulfide is discussed. Organic compounds are oxidized to carboxylic acids under these conditions. At higher temperatures CH_2 -degraded hydrocarbons and CO_2 are formed.

INTRODUCTION

The reaction of sulfate with sulfide is strongly pH-dependent and the oxidation potential of sulfate in the neutral pH-region is very low. At atmospheric pressure and temperatures as high as the boiling points of the inorganic and organic media (water, alkanes, alkylsubstituted arenes) no reaction takes place within 100 hrs and even longer reaction periods. However, the reaction may proceed very slowly over a very long time (e.g. geochemical time periods) and is subject of discussion of geochemists¹.



There are only two interesting papers concerning the redox reactions between sulfate and organic compounds in the presence of small amounts of sulfide as shown for methane in Eq. (1)^{2,3}. These investigations aimed to a technical process for the manufacturing of phthalic acids via xylenes. It is reported that ammonium sulfate reacts with organic compounds in the presence of H_2S under redox conditions, however, not without H_2S . The reactions were run at temperatures in the range of 320°C and starting pressures of 23 bar.

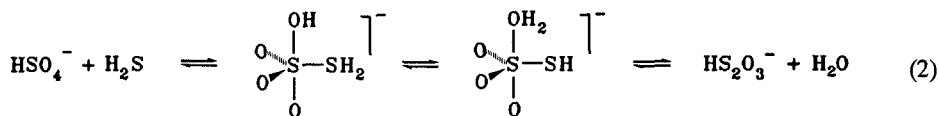
The scope of these investigations has to be seen from another side of practical interest. During some steam flooding processes for oil production huge amounts of H_2S are produced together with CO_2 . At the producing zones the temperatures lie in the range of 250 to 270°C which is significantly below the conditions described in literature^{2,3}. Nevertheless, the H_2S -production rises from 50 ppm to up to 300 000 ppm.

RESULTS

The experiments were carried out in glass cylinders which were installed in stainless steel autoclaves⁴. The starting pressure was either atmospheric pressure or the steel cylinder pressure of H₂S. The starting temperature was RT, reaction pressure, -temperature and -time were in the range of 70 to 180 bar, 270 to 360°C, and 1 to 72 hours, respectively.

To rule out artifacts, it firstly was shown that in aqueous sulfate solutions no reduction of sulfate proceeds. Furthermore it was necessary to prove that the quantitative disproportionation of sulfur to sulfide and sulfate at pH-values around 14 is correct under the chosen conditions and it clearly could be shown that no reaction takes place between aqueous solutions of sulfate and sulfide. The next step was to find out, whether aqueous sulfate solutions react with H₂S under the same conditions and the result was, not surprising, the production of small amounts of elemental sulfur together with reduction of sulfate; the pH value became slightly acidic (pH 5 to 6). The interaction of aqueous sulfate solutions with elemental sulfur was investigated too. Only a small effect in sulfate reduction but a rather high effect in H₂S-production was found. Finally it clearly could be shown that there is no reactivity between aqueous sulfate solutions and toluene. The sulfate was recovered to 100% at the end of the experiments.

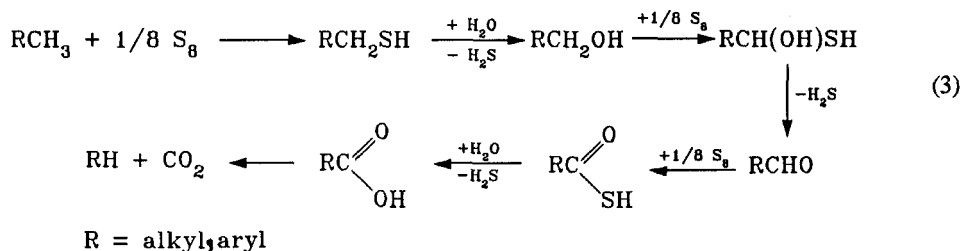
To demonstrate that redox reactions between aqueous sulfate solutions and organic compounds are possible in the presence of H₂S at elevated temperatures and pressures a great bundle of these reactions with different starting conditions (different starting materials in both, the inorganic and the organic part) was performed and it could be shown a sulfate reduction in the range of 6% to 95%.



These reactions can never be one step reactions. In the case of the sulfur atom of the sulfate anion the reaction must run over 8 oxidation numbers, from +VI to -II. The first step on the inorganic side may be formulated as a nucleophilic attack of H₂S on the sulfur atom of the sulfate anion (either S_N2, as formulated in Eq. (2), or S_N1) leading to thiosulfate. This anion is an excellent starting material for all thinkable redox reactions leading for instance to elemental sulfur which itself is a starting material for reactions with the organic compounds⁵. Thiosulfate is one of the inorganic sulfur species detected in the reaction mixtures. We also

could detect sulfite, another good candidate for reactions with organic compounds⁵.

It is not necessary to discuss the whole bundle of reactions which is possible on the organic side, the manifold of possibilities arising is already known⁵. A tentative reaction scheme is shown in Eq. (3). In the case of the reaction with xylene we were able to detect the aldehyde acid besides the various phthalic acids and methylbenzoic acid with the help of high performance liquid chromatography.



To sum up the results one can say that

- redox reactions between sulfate and organic compounds proceed even in the pH-region between pH 5 and pH 9.
- H_2S is necessary to start the reaction and H_2S serves as a catalyst.
- In the presence of ammonium cations the reaction proceeds more easily; it seems that ammonium ions buffer the system. The pH-values of these systems remain around pH 9.
- High temperatures and pressures are necessary to accelerate the reaction, however, there is evidence that these reactions proceed at even lower temperatures.

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