

A Novel Reaction of Metal Sulphides with the Mixed Non-aqueous System Dimethyl Sulphoxide–Sulphur Dioxide

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Several synthetic and naturally occurring metal sulphides react with the system dimethyl sulphoxide–sulphur dioxide to give metal hydrogen sulphates or sulphates, in contrast with the reaction of sulphides with aqueous sulphur dioxide, which yields mainly thiosulphate.

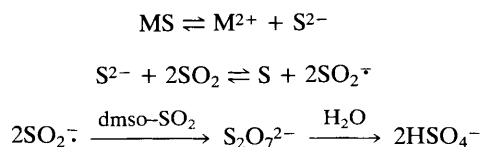
The metal sulphides SnS, SnS₂, As₂S₃, Sb₂S₃, Bi₂S₃, Cr₂S₃, MnS, FeS, FeS₂, CoS, NiS, CuS, Cu₂S, ZnS, CdS, HgS, CuFeS₂, and FeAsS react very slowly at ambient temperature, but quite rapidly at 70 °C, with the mixed non-aqueous system dimethyl sulphoxide (dmsO)–sulphur dioxide to form metal hydrogen sulphate, [M(dmsO)_x]^{y+}(HSO₄)_y (x = 6; x = 5 for M = Sb); the byproducts include dimethyl sulphide and paraformaldehyde. The products were characterised by elemental analysis for sulphur, carbon, and hydrogen and by i.r. spectroscopy. PbS reacts to form PbSO₄.

The sulphides MoS₂ and Ag₂S have so far proved inert to the solvent mixture. Both Cu^I and Cu^{II} sulphides give rise to Cu^{II} hydrogen sulphate and Fe^{II} sulphide forms Fe^{III} hydrogen sulphate.

In contrast with the reaction of metals or metal oxides with dmsO–SO₂,^{1,2,3} which occur at or a little above ambient temperatures, when no solvent decomposition occurs, reactions of metal sulphides with dmsO–SO₂ lead to the formation of hydrogen sulphates rather than disulphates. Dimethyl sulphoxide is known to decompose slowly when refluxed at ordinary pressures, with the formation of many products, including paraformaldehyde, methane thiol, and water.⁴ Mixtures of dimethyl sulphoxide and sulphur dioxide also

decompose on prolonged storage in sealed tubes.⁵ It is thought that the presence of sulphur dioxide catalyses the decomposition of dimethyl sulphoxide at elevated temperatures. There also exists the possibility that adducts formed between dmsO and SO₂⁶ are precursors to decomposition. Dinitrogen tetroxide also forms an adduct with dmsO⁷ and NO₂ is known to catalyse the decomposition in a similar manner above 50 °C.⁸

If the sulphides are dissolved in dmsO–SO₂ at room temperature, crystals of sulphur form as the metal sulphide dissolves over several weeks. In aqueous solutions of SO₂, very small amounts of sulphur form; thiosulphates and polythionates are the major products from the reaction of MnS, FeS, and ZnS with aqueous SO₂.⁹



Scheme 1

The mechanism of the reaction is unknown and the products observed in the non-aqueous system suggest that a mechanism operates which is different from that observed in aqueous solution. Our recent paper¹⁰ has detailed a likely unified mechanistic pathway for all the reactions we have observed in dmsO-SO₂ and we believe that the present reaction follows a similar course after initial generation of the sulphonylate radical anion on reduction of SO₂ by sulphide (Scheme 1). However, we have not observed SO₂^{•-} in the sulphide reactions, probably because at room temperature the reaction is very slow and at higher temperatures SO₂^{•-} is rapidly oxidised by the dmsO. Experimental precautions and the preparation and drying of solvents have been reported previously.¹

Received, 28th January 1988; Com. 8/00311D

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