

THE THERMAL DECOMPOSITION OF DMSO

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DMSO has been reported to be fairly stable toward thermal decomposition; it can be refluxed at its boiling point of 189° with only 3.7% volatile products produced over a 72 hr period.¹ We report here our discovery of conditions which bring about the complete decomposition of DMSO at elevated temperatures.

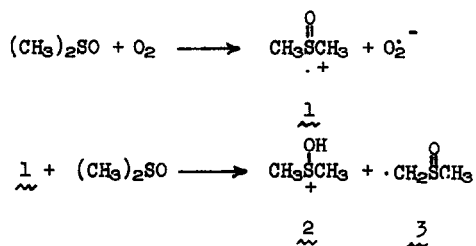
If about 3 ml of purified^{2a} DMSO is sealed in a Carius tube (total volume about 10 ml; previously washed with chromic acid, NH₄OH, distilled water--in that order--and dried in an oven at 180°) under either an atmosphere of air or one enriched in oxygen and heated at 180° for 68 hr,^{2b} the sample separates into two liquid phases: an upper yellowish layer (80% by volume) and a lower colorless layer. A white solid (paraformaldehyde) was often observed to form around the seal and to redissolve in the liquid. Glc analysis (6' x 1/8" Porapak Q, 240°, 25 ml/min) of both layers indicated that no DMSO was present. The upper layer consisted of 42% dimethyl sulfide, 31% bis(methylthio)methane, and 8% methyl disulfide. Numerous other minor peaks from compounds of unknown identity were observed. The lower layer was found to be water. The reproducibility of the results (and those to be described) was confirmed by repeating the experiment numerous times.

If air was carefully removed from a Carius tube containing pure DMSO (by repeated "degassing" on a vacuum line) and replaced with an atmosphere of nitrogen prior to sealing, then heating for 68 hr at 180° resulted in no decomposition. However, dilute DMSO solutions of benzoyl peroxide and tert-butyl peroxide (mole ratio DMSO: peroxide = 42:1) sealed under nitrogen and heated at 180° for 68 hr were completely decomposed (product distribution as quoted above). Also, the addition of one drop 95% methanesulfonic acid to 3 ml DMSO led to total decomposition of DMSO (product distribution as quoted earlier) during a 68 hr period at

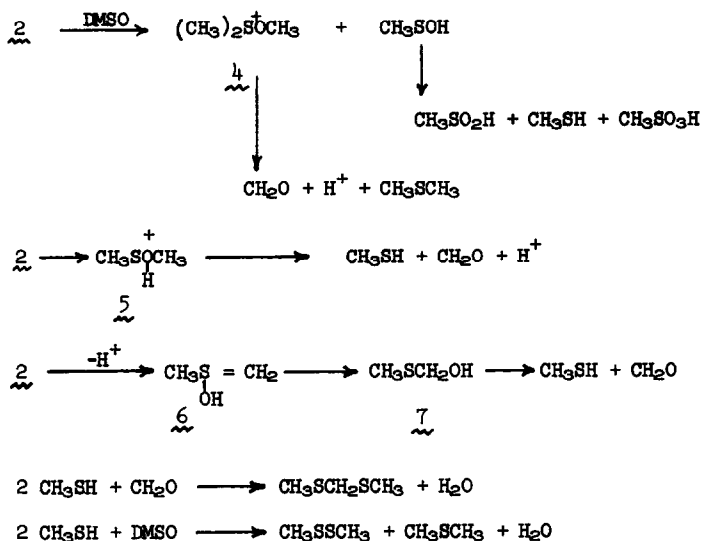
180° in a tube previously freed of air and sealed under nitrogen.

If 3 ml of pure DMSO was added to a Carius tube containing 50 mg anhydrous Na₂CO₃ and the tube sealed under an atmosphere of air or oxygen and heated at 180° for 68 hr, only slight (< 1%) decomposition resulted. Acid production from DMSO seems beyond dispute.¹ We found that DMSO samples heated with air for 3 hr and for 18 hr had pH's of 3.4 and 3.1, respectively; a control solution had a pH of 6.2.

We assume that a key intermediate in the thermal decomposition of DMSO in the presence of oxygen or a radical initiator is the radical cation 1. Radical ions are well known^{3,4} and there are at least two reports of such a cation's formation from DMSO in chemical reactions.^{5,6} This radical cation can then react with another DMSO molecule to produce the dimethyl sulfoxonium cation (2). Similar hydrogen transfer reactions between DMSO and radical cations have been reported.⁷ It is assumed that most of 2 comes from acids formed in subsequent steps; i.e., only a small amount of 2 has to be formed from 1 to initiate the decomposition.



Numerous subsequent reactions of 2 may be considered. For example, reaction of 2 with DMSO may yield 4 plus methane sulfenic acid.⁸ Neither of these products should be stable under the reaction conditions and they could react further as shown. Another possibility is the rearrangement of 2 to a sulfenate ester (5) which would break down to formaldehyde and methyl mercaptan.⁹ Finally, one could assume that conversion of 2 to 7 by a Pummerer-like rearrangement is plausible and may involve 6 as a short-lived intermediate.¹⁰ Since 7 is unstable¹⁰ it would also give rise to formaldehyde and methyl mercaptan. The formation of the other DMSO decomposition products can be rationalized from methyl mercaptan and formaldehyde.



Our present results do not allow us to be more specific about the relative importance of these reactions. What is clear, however, is the very different behavior of DMSO in open and closed containers and the need for oxygen or an initiator to produce an acid necessary for the subsequent decomposition. Additional approaches to the study of this problem will be pursued.

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