

The decomposition of dimethylpolysulfanes in aqueous systems in the absence of solar irradiation: kinetics, products and mechanisms

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Dimethylpolysulfanes (MeS_nMe , DMPS) are formed by the biological methylation of inorganic polysulfides, as well as through the oxidation of sulfur-containing organic molecules. These compounds are formed during the decomposition of algal material, and have a noticeable repulsive odor at concentrations of micrograms per liter, thus extremely decreasing the quality of drinking water.

We measured the kinetics of the decomposition of dimethyldisulfane, dimethyltrisulfane, dimethyltetrasulfane and dimethylpentasulfane and determined the products of these processes. The decomposition rates were measured as a function of temperature, pH and dimethylpolysulfane concentration that allowed us to calculate the reaction rate constants and reaction orders for this complex process.

In aqueous media and in the absence of sunlight, dimethylpolysulfanes with three or more sulfur atoms undergo disproportionation reactions. Two DMPS molecules with n sulfur atoms react to form one molecule with $n+1$ atoms and the other with $n-1$ atoms. Dimethyldisulfane (Me_2S_2) decomposes to methanethiol and methanesulfenic acid. Dimethylpolysulfanes with twelve or more sulfur atoms may decompose into S_8 and dimethylpolysulfanes with a lower number of sulfur atoms.

Results of this research allow an estimation of the residence time of these compounds in oxic aphotic natural aquatic systems. The half-lives of DMPSS were estimated to vary from months for Me_2S_5 to million years for Me_2S_3 at these conditions.