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Kinetics of methanethiol oxidation by oxygen under aqueous conditions

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Methanethiol is one of the most abundant volatile organic sulfur compounds in natural aquatic environments, which is primarily derived from dimethylsulfoniopropionate decomposition. Methanethiol is an important component of the sulfur cycle in marine and freshwater systems, serving as a key intermediate in microbial and chemical processes, a source of energy for certain methanogens, and a contributor to atmospheric sulfate aerosol formation. Despite its significance in sulfur cycling, the rates and mechanisms of methanethiol's chemical oxidation in aqueous media under environmentally relevant conditions have not been previously studied. This study focuses on the kinetic parameters of the reaction of methanethiol and its deprotonated form, methanethiolate, with dissolved oxygen in aqueous solutions at various reactant concentrations, pH, and temperatures. The reaction proceeds through two distinct pathways: slow reaction between protonated methanethiol and oxygen under acidic to neutral conditions, and fast reaction between methanethiolate and oxygen under basic conditions. The reaction order with respect to methanethiol is 2.2 ± 0.4 for the protonated form and 1.6 ± 0.2 for the deprotonated form, while it in both cases is 1.0 ± 0.3 with respect to oxygen. The ratio between the consumption rates of oxygen and methanethiolate was approximately 1:4, while the ratio of oxygen to methanethiol consumption rates was close to 1:2. Dimethyl disulfide was the primary detected product, but oxygen consumption ratios suggest formation additional oxidation products during oxidation of non-dissociated methaenthiol.

The estimated half-life of methanethiol in the oxic marine water column at 25ºC at its typical concentrations of 0.02–2 nM, ranges from 80 to 1200 years. In the surface waters, chemical oxidation occurs at significantly lower rates than photooxidation and degassing, making its overall contribution to the marine methanethiol budget negligible. However, in methanethiol-rich aphotic environments such as hydrothermal and limnic waters, chemical oxidation may play a more prominent role. In systems with methanethiol concentrations exceeding 1 mM, such as bioreactors, chemical oxidation is likely the dominant decomposition pathway, even under low oxygen conditions, surpassing microbial degradation.