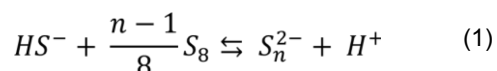


Kinetics and mechanism of polysulfides formation by a reaction between hydrogen sulfide and orthorhombic cyclooctasulfur

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A detailed study of the reaction kinetics between sulfanide (HS^-) and orthorhombic cyclooctasulfur ($\alpha\text{-S}_8$) at environmentally relevant conditions, which results in formation of inorganic polysulfides, was performed [1]. Rates of reaction were measured as a function of pH, temperature and concentrations of S^{2-} and S^0 . Reaction (Eq. 1) was carried out at $[\text{S}^0]/[\text{S}^{2-}] < 0.1$ in order to minimize a contribution of interfering reaction between $\alpha\text{-S}_8$ and polysulfides, which are stronger nucleophiles HS^- .



Reaction was found to follow the first order with respect to concentrations of both HS^- and $\alpha\text{-S}_8$. The reaction activation energy was found to be 69 kJ mol^{-1} . At conditions relevant for sulfidic marine sediments, the characteristic time of the reaction is c.a. 1 year. Relatively high activation energy of the reaction and distribution of polysulfide species testify to formation of polysulfides by a reaction between HS^- and dissolved S_8 rather than by direct nucleophilic dissolution of $\alpha\text{-S}_8$, as was reported for microbially produced and amorphous sulfur.

We suggest that the difference in the mechanism of solubilization for various forms of elemental sulfur in HS^- solutions is caused by low reactivity of $\alpha\text{-S}_8$ as compared to reactivity of colloidal [2] and microbially produced [3] sulfur. As $\alpha\text{-S}_8$ is less prone to nucleophilic attack, its dissolution followed by the reaction with HS^- becomes kinetically favored in reaction.

[1] Avetisyan K., Buchshtav T., Kamyshny A.* (2019) *Geochim. Cosmochim. Ac.*, 247: 96-105. [2] Kafantaris F.C. (2017) Ph.D. Thesis, Indiana University. [3] Kleinjan W.E., de Keizer A., Janssen A.J.H. (2005) *Colloid. Surfaces B*, 43: 228–237.