

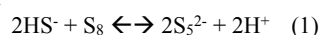
Geochemical kinetics of polysulfide formation

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Sulfur cycling, in particular reactions involving elemental sulfur, sulfide, and polysulfide, is important in many redox active systems.

Elemental sulfur is involved in reactions that cycle S, both biotically and abiotically, and transitions between dissolved elemental sulfur (S_{8aq}, that is sparsely soluble) to metastable elemental sulfur nanoparticles (S_{8nano}) to the thermodynamically most stable form α-S₈. We have found that the coarsening process and the solubility of S_{8aq} are directly influenced by temperature and surfactants (sourced from microbial exudates and/or other sources of natural organic matter). Elemental sulfur is also reactive with other sulfur species, especially sulfide, to undergo nucleophilic dissolution and form polysulfide ions, according to the following reaction.



We have characterized the factors that influence the kinetics of this forward reaction (1) and determined the kinetic rate law for both S_{8weimarn} and S_{8raffo}, which represent the hydrophobic and hydrophilic endmembers of S_{8nano}, respectively. The factors controlling the kinetic rate law of both forms of S_{8nano} include the surface area of S_{8nano}, as well as the physical-chemical parameters of temperature, pH, sulfide concentration, and the ionic strength of the aqueous media. Furthermore, the surface character of S_{8nano} (as affected by the degree of hydrophobicity controlled by precipitation mechanisms and surfactants) significantly affects the reactivity of the nanoparticles. The kinetic rate law for both forms of S_{8nano} takes the form:

$$\frac{-d[\text{S}_8]}{dt} = k[\text{SA}_{\text{S}_8}]^n[\text{HS}^-]^n[\text{H}^+]^{n*} I^{*T}$$

The kinetics of the forward reaction 1, in conjunction with the kinetics of the reverse reaction 1 allow for a small pool of polysulfides to exist and contribute to “cryptic” cycling of intermediate sulfur species. This small, but quickly replenished pool of polysulfide may be key in metabolic reactions, pyritization, organic matter sulfurization, and cycling of S in ancient and modern settings.