

Kinetic parameters of thiocyanate formation by the reaction of cyanide and sulfur specious

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Reactions between cyanide and reduced sulfur compounds in aqueous media result in formation of thiocyanate. While the main source of SCN⁻ in environment is industrial waste waters, thiocyanate was found in non-polluted natural systems where it can be produced by abiotic pathways and during biological cyanide detoxification. The present study was designed to clarify fates as well as mechanisms and rates of transformations of sulfide oxidation intermediates and hydrogen cyanide in natural aquatic systems.

Rate of thiocyanate formation was measured in phosphate buffer solutions at a broad range of reactant concentrations and pH. Calculation of rate constants and reaction orders were performed according to the van't Hoff differential method. Activation energy of reactions was estimated at temperature range 25-80°C.

Rate of thiocyanate formations as well as activation energies strongly depend on pH. Observed experimental data may be explained by a combination of two individual reactions: a) relatively fast reaction of the sulfur species with cyanide anion; and b) slower reaction between the sulfur species and hydrogen cyanide. The activation energy for the reaction thiosulfate with cyanide is to 84-93 kJ·mol⁻¹ at acidic and neutral solutions (pH=5.3-7.0). At pH 12.0 the activation energy was found to be lower, 37 kJ·mol⁻¹. The activation energy for the reaction dimethyl trisulfide with cyanide is 100 kJ·mol⁻¹ at pH=9.0 and ~2 times lower at pH=7.0

Rate of the reaction of thiosulfate with hexacyanoferrate(II) and hexacyanoferrate(III) complexes were significantly slower than the rates of reaction of thiosulfate with hydrogen cyanide and cyanide anion. Calculations based on reaction rates and stability of the iron-cyanide complexes show that direct reaction between complexed cyanide and thiosulfate leads to the formation of thiocyanate, rather than reactions with free cyanide which exists in equilibrium with complexes. Rate of the reaction dimethyl trisulfide with iron-cyanide complexes was found to be slower than rate of dimethyl trisulfide decomposition.