Formation of Carbonyl Sulfide by the Reaction of Carbon Monoxide and Inorganic Polysulfides

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OCS formation by the reaction of inorganic polysulfides with carbon monoxide, which are both abundant in natural aquatic systems, was studied as a model abiotic route for OCS formation in the dark. The net OCS accumulation rate was a function of a bimolecular formation reaction and simultaneous OCS hydrolysis kinetics. The reaction of polysulfides with CO in the dark was found to be first order with respect to CO concentration and first order with respect to the molar sum of the polysulfide species generated by the disproportionation of the dissolved polysulfide precursors. The pH dependence of the OCS production rate was controlled by the pH-dependent disproportionation of polysulfide precursors. Lower temperatures, intermediate redox potentials, and moderately basic pH conditions increase the steady-state concentration of OCS. The speciation of polysulfides in aqueous solutions is still disputed. Some authors claim that hexa-sulfide is one of the dominant species while others believe that pentasulfide is the largest sulfide species in aqueous systems. Despite the disagreement between different models for speciation of polysulfides, the proposed reaction law agreed very well with the thermodynamic data based on four and on five polysulfide species, with only minor differences in the preexponential kinetic coefficients.

Introduction

The reaction of inorganic polysulfides with carbon monoxide was investigated as a model for inorganic polysulfide reactivity and as an abiotic route for OCS formation in aquatic systems.

OCS is the most abundant sulfur gas in the atmosphere. Because of its oxidation resistance (1) it can reach the stratosphere, where it is oxidized to sulfate aerosol. Thus, OCS contributes to stratospheric sulfate formation and thereby influences the stratospheric ozone concentration, earth’s radiation budget, and its climate (2). From 20% to more than one-third (3–5) of the atmospheric OCS is generated in aquatic sources, but until now, the mechanism of OCS production in aquatic systems was not fully understood, though solar radiation is probably very significant for OCS production (6, 7). Flöck et al. (8) demonstrated that OCS is produced from a large variety of dissolved organosulfur compounds under solar radiation. They postulated that OCS production proceeds via the reaction between carbonyl-containing organic compounds (e.g., glutathione, cysteine, or humic acids) and thyl radicals. The exact nature of the coreactants, the sensitization pathway, and the detailed mechanism of the reaction remain obscure. Dark production of OCS was first inferred in the middle 1990s from modeling studies (9). Preiswerk and Najjar (10) later presented a thorough model of the global open ocean source, including dark production and hydrolysis. Recently, Von Hobe et al. (11) also demonstrated that carbonyl sulfide formation in the dark plays a significant role in the overall OCS budget in the oceans. As far as we know, OCS production in freshwater was never modeled. Abiotic pathways for OCS formation in the dark are still unknown. In this paper, we examine a route for the production of OCS in the dark, taking the reaction of polysulfides and carbon monoxide as a model reaction.

Inorganic polysulfides are among the least researched reduced sulfur species in aquatic systems. This set of compounds, which have oxidation numbers spanning the range between hydrogen sulfide and elemental sulfur, are important intermediates during the oxidation of hydrogen sulfide in near-neutral and basic aqueous systems. Polysulfides exhibit redox reactivity as well as high nucleophilicity, so despite their low concentration in aquatic systems, they may play a significant role in the sulfur cycle. Our knowledge of the speciation of inorganic polysulfides in aquatic systems relies exclusively on complex deconvolution of the light absorption spectra of their mixtures, which leaves many aspects of polysulfide speciation unresolved. Indeed, Boulegue and Michard (12) claimed that hexasulfide is one of the dominant polysulfide species, while others (13, 14) believe that pentasulfide is the largest sulfide species in aquatic systems. Likewise only limited data are available on the reactivity of polysulfides in aquatic systems. The reactions of polysulfides and aldehydes and ketones were reviewed by Aizenshtat et al. (15). Our laboratory has recently established the presence of inorganic polysulfides inoxic natural waters and associated them with the formation of dimethyl disulfide and dimethyl polysulfides in freshwater and in the ocean (16).

CO was selected as a coreactant in the current studies for several reasons. CO is abundant in natural—freshwater as well as marine—aquatic systems; its concentration ranges from 0.1 to 8.5 nmol/L (17, 18). CO is a very stable compound, gives no side reactions, and does not participate in acid–base transformations. This makes it a very good model compound for studies of polysulfide reactivity, since the observed pH-dependent OCS production reflects polysulfides’ speciation and reactivity rather than CO transformations. Additionally, there is experimental evidence for a correlation between CO and OCS levels in natural waters that can be due to coupled production or common substrate (19) but can also reflect a reactant–product relationship.

Experimental Section

Materials. Pure 97.5% OCS and cumene were purchased from Aldrich (Milwaukee, WI). Toluene, NaPO₄·12H₂O, and Na₂HPO₄·12H₂O were from Riedel-de Haën (Seelze, Germany). Absolute ethanol was purchased from J. T. Baker (Deventer, Holland) and dried on molecular sieves for 2 days before use. The 85% H₃PO₄ (CP grade) and NaOH were purchased from Frutarom (Haifa, Israel). Alkali metals (sodium and potassium) were purchased from BDH (Poole, England). The 99.97% CO was purchased from Scott Specialty Gases (Plumsteadville, PA). NaH₂PO₄·H₂O was purchased from Mallinckrodt (Paris, Kentucky). The 98% pure Na₂S·9H₂O was purchased from Sigma (St. Louis, MO). Elemental sulfur was
were used unless otherwise stated.

### Polysulfide Synthesis

- **Synthesis of Na₂S₂**: Solution of EtOK in dry ethanol was obtained by dissolution of 2.0 g of potassium in 30 mL of absolute ethanol in a 150-mL flask equipped with a drying tube on its reflux outlet. After the potassium was totally dissolved, highly dry H₂S was bubbled to the solution for a time period sufficient for conversion of all potassium ethylate to potassium hydrosulfide (KHS). Then, 3.28 g of pure, fine powder of sulfur was added to the solution. The reaction mixture was boiled in a water bath for 1 h under nitrogen atmosphere. Orange-red K₂S₂ precipitated during this time. K₂S₂ was then quickly vacuum-filtered under nitrogen and dried in a vacuum desiccator above P₂O₅. K₂S₂ yield was usually 7–8 g.

- **Synthesis of Na₂S₄**: Synthesis of Na₂S₄ was performed following the K₂S₅ protocol. The only differences were that sodium was taken instead of potassium, 4.17 g of sulfur was used, and the solution was evaporated to 5-mL volume before vacuum filtration. Na₂S₄ yield was usually 5–6 g.

- **Synthesis of K₂S₅**: Solution of EtOK in dry ethanol was obtained by dissolving 5.0 g of potassium in 72 mL of absolute ethanol in a 150-mL flask equipped with a CaCl₂ drying tube. After the potassium was dissolved, half of the solution was removed from the flask, and dry H₂S was bubbled to the solution through the gas inlet in order to convert all the potassium ethylate to potassium hydrosulfide. Then the solution was boiled for a short time to remove excess of H₂S. The two solutions were mixed together. Then 4.1 g of pure fine powdered sulfur was added, and the reaction mixture was boiled on a water bath for 30 min under nitrogen. Orange-red K₂S₅ crystals precipitated. The K₂S₅ grains were vacuum-filtered immediately under nitrogen flow and dried in a vacuum desiccator above P₂O₅. K₂S₅ yield was usually 6–7 g.

- **Synthesis of Na₂S₆**: Synthesis of Na₂S₆ in absolute ethanol was prepared as described above. Then 4 g of Na₂S₅ was added to the solution under a nitrogen blanket. The reaction mixture was boiled in a water bath for 30 min under nitrogen. The pale-yellow Na₂S₆ precipitate was vacuum-filtered under nitrogen and dried in a vacuum desiccator above P₂O₅. Na₂S₆ yield was usually 7–8 g.

Each of the polysulfide salts was characterized by X-ray diffraction and found to have the reported diffraction pattern (25). Reported and observed X-ray diffraction data are depicted in the Supporting Information.

The exact composition was found by elemental analysis, which showed that the synthesized compounds have alkali metal-to-sulfur ratios that are very close to the theoretical ones, namely, Na₂S₅₋₂, K₂S₇₋₂, Na₂S₇₋₁, and K₂S₈₋₁.

### Preparation of Polysulfide Solutions

Polysulfide solutions were prepared by dissolving desirable weights of polysulfides in 50 mM aqueous phosphate buffer followed by pH adjustment with sodium phosphate, phosphoric acid, or NaOH solutions and addition of distilled water to the precise volume. This solution was thermostated for at least 12 h to reach equilibrium and, when the solution was supersaturated with sulfur, to allow sulfur precipitation and sedimentation.

**Preparation of CO Solutions**. CO-saturated stock solution was prepared by sparger bubbling CO gas in 50 mM aqueous phosphate buffer until equilibrium was reached. This gives 892 μM CO at 30 °C. This solution was transferred to 5-mL thermostatted vials with zero headspace.

**CO Quantification**. We prepared the test samples from CO-saturated solutions. The stock solutions were prepared by sparger stripping with N₂ followed by sparger bubbling of CO for 3 min. Preparation was carried out under CO atmosphere in a glovebox. The samples were closed with septa-sealed screw caps under CO atmosphere. CO concentration in the saturated solutions was determined using a Dohrman DC-80 automated laboratory TOC analyzer.

**OCS Calibration**. Commercial reference materials for OCS are unavailable, and therefore, we used two types of reference materials for OCS calibration, 1-atm saturated water and saturated toluene solutions. Saturated solutions of OCS were prepared by sparger bubbling of gaseous OCS in toluene or water for 3 min, which was found sufficient to reach saturation. Concentrations of saturated OCS solutions were reported to be 0.024 mol/L in water (calculated from ref 26) and 0.67 mol/L in toluene at 22 °C (calculated from ref 27).

**OCS Production**. OCS production tests were conducted in 5-mL glass vials filled with CO solution. Prior to each test, 2.5 mL of aqueous CO solution was taken from the vial with a syringe and 2.5 mL of polysulfide solution was added. The vial was closed with a cap equipped with rubber septa and thermostated for the required reaction period. Then, 0.5 mL of the solution was taken out by a syringe through the septum, and 0.5 mL of cumene was injected in the same way. The mixture was shaken for extraction and allowed to set for 1–2 min to separate the layers. A 1-μL aliquot of cumene solution was taken through the septum with a gastight GC syringe and analyzed by GC–MS operated in SIM mode.

### Results

To quantify OCS formation, one has to take into account the hydrolysis of OCS in water. Several research groups (28–33) studied the kinetics of OCS hydrolysis in buffered solutions that is usually described as a sum of two contributing mechanisms (28):

**reaction with water**

\[
\text{H}_2\text{O} + \text{OCS} \rightarrow \text{H}_2\text{S} + \text{CO}_2 \quad (1)
\]

**and reaction with hydroxyl anion**

\[
\text{OH}^- + \text{OCS} \rightarrow \text{HS}^- + \text{CO}_2 \quad (3)
\]

The overall hydrolysis coefficient is derived from eqs 2 and 4:

\[
d\text{[OCS]}/dt = \text{-}k_{\text{h,tot}}\text{[OCS]} \quad (5)
\]

\[
k_{\text{h,tot}} = k_{\text{h,1}} + k_{\text{h,2}}\text{[OH}^- \text{]} \quad (6)
\]

The rate law of eq 5 depends very little on the ionic strength up to 0.5 M NaCl (31). However, since there was significant variability between the values obtained by different experimentalists (28–31), we derived \( k_{\text{h,tot}} \) independently using the same experimental setup and experimental conditions used in the OCS formation tests.
Conditions: 0.446 mM CO, 50 mM phosphate buffer. (A) T = 30 °C (lines correspond to pH 6.12, 6.72, 7.17, 7.50, 7.89, 8.25, and 9.00 in order of increasing slope). (B) Temperature 5 °C (lines correspond to pH 5.9, 7.15, 7.95, and 8.75 in order of increasing slope). Each data point represents the average of five different tests.

**Rate of OCS Hydrolysis.** OCS hydrolysis tests were performed at seven different pH levels in the range 6.0–9.0 at 30 °C. Each test was repeated five times under the same conditions, and at least five different exposure durations were used to evaluate each kinetic coefficient. Figure 1 depicts typical graphs demonstrating the time course of OCS hydrolysis at different pH and temperatures.

k_{h,tot} was obtained according to eq 5 from the slope of the curve of the natural logarithm of the ratio [OCS]_0/[OCS] versus time. The kinetic coefficients, k_{h1} and k_{h2}, for water and OH^- stimulated hydrolysis were calculated by linear regression. Best fits were obtained for $k_{h1} = (4.37 \pm 0.28) \times 10^{-5}$ s$^{-1}$ and $k_{h2} = 34.5 \pm 2.2$ s$^{-1}$ M$^{-1}$, respectively. To determine the activation energies, the hydrolysis rate was measured at 5 °C for pH values. $k_{h1} = (1.25 \pm 0.10) \times 10^{-6}$ s$^{-1}$ and $k_{h2} = 1.11 \pm 0.09$ s$^{-1}$ M$^{-1}$ were obtained for 5 °C. Based on total of 11 data points at two temperatures, the Arrhenius expression for $k_{h,tot}$ was evaluated: $k_{h,tot} = (4.19 \pm 0.34) \times 10^{12} e^{-1210/T} + (1.41 \pm 0.11) \times 10^{13} e^{-11580/T} [OH^-]$ s$^{-1}$ (T, in kelvin). These correspond to activation energies of 98.5 and 96.3 kJ/mol for the water and hydroxyl-dependent hydrolyses terms.

The report of Elliott et al. (31) is probably still the most comprehensive article on OCS hydrolysis, since it accounts for OCS hydrolysis over a large pH and temperature ranges. Most other sources report OCS hydrolysis rate only under particular temperature or pH conditions. We compared the OCS overall hydrolysis rate constant for 20 °C and pH 8.03. Under these conditions, Uher and Andreae (32) computed the following rate coefficients based on experimental data provided by their tests and different other sources: $k_{h,tot} = (1.93 \pm 0.19) \times 10^{-5}$ s$^{-1}$, based on their tests; $(1.82 \pm 0.08) \times 10^{-5}$ s$^{-1}$, based on ref 32; $k_{h,tot} = (1.91 \pm 0.44) \times 10^{-5}$ s$^{-1}$, based on ref 33. Additionally, from values calculated by Elliott et al. (30), based on previous works of Thompson et al. (28) and Phillip and Dautzenberg (29) at two extreme pH regimes, we computed $k_{h,tot} = 1.8 \times 10^{-5}$ s$^{-1}$. Under the same pH and temperature, we derived, based on eq 6, $k_{h,tot} = (2.1 \pm 0.2) \times 10^{-5}$ s$^{-1}$. Thus, at least under these conditions, our calculated hydrolysis rate agrees well with previously reported values (± the respective standard deviation).

**Determination of OCS Production Rate.** In this set of experiments, the rate of carbonyl sulfide production from inorganic polysulfides and carbon monoxide was studied at 30 and 5 °C. The samples were prepared as described in the Experimental Section, and the level of OCS in the samples was determined by GC-MS analysis. The hydrolysis rate was added to the observed accumulation rate of OCS in the batch studies to obtain the overall OCS production rate as calculated from eq 7.

$\frac{d[OCS]}{dt}_{\text{produced}} = \frac{d[OCS]}{dt}_{\text{observed}} + k_{h,tot}[OCS]$ (7)

The time derivatives represent the measured accumulation rate of OCS in a batch test and the overall, actual rate of OCS formation. It is permissible to use eq 7 since CO and polysulfide levels were taken at large excess compared to OCS formation.

Typical raw results of the accumulated OCS and overall production of OCS (as of eq 7) from 4.6 mM K$_2$S$_5$ + 446 μM CO solutions for three pH levels (8, 9, 10) are presented in Figure 2. Each point in this figure represents the average of five different tests. The difference between the overall...
formation rate and the observed concentration becomes more significant at high pH. In fact, at pH 10, near steady state was attained in less than 30 min.

**Dependence of OCS Formation on CO Concentration.**
The dependence of OCS production rate on CO concentration was studied for K₂S₅ samples containing 20 mM K₂S₅, corresponding to total sulfur concentration, TSC = 100 mM at 30 °C, pH 9. The production rate – CO dependence was studied for one pH only, since CO does not participate in acid–base reactions. The levels of CO and polysulfide concentration were at least 2 orders of magnitude larger than the OCS produced during the kinetic studies. For example, total OCS production (which was much higher than accumulated OCS) was equal to or less than 4 μM, while CO concentration was 446 mM and polysulfide concentration was more than 4 mM. The experiments showed that the reaction between CO and polysulfides at 30 °C is first order relative to carbon monoxide concentration with correlation coefficient $R^2 = 0.9996$ (each data point in Figure 3 is the average of five tests). The zero intercept indicates that the same rate law and underlying mechanism holds for the entire CO range.

**Dependence of OCS Formation on the Type of Polysulfide Precursor.**
The dependence of OCS production rate on the pH and the type of polysulfide precursor (i.e., Na₂S₂, K₂S₃, Na₂S₄, or K₂S₅) was studied for the pH range 7–10 at T = 30 °C. In all tests, we used the same level of total sulfur concentration, TSC = 23.0 mmol of S/L (corresponding to 11.50 mM for Na₂S₂, 7.67 mM for K₂S₃, 5.75 mM for Na₂S₄, and 4.60 mM for K₂S₅). The dependence of OCS production on pH was found to be highly nonlinear even after taking into account OCS hydrolysis rate. Additionally, the pH dependence of OCS production changed from polysulfide to polysulfide as depicted in Figure 4A. A similar nonlinear dependence was observed at T = 5 °C. Figure 4B shows the dependence of OCS production rate on pH for K₂S₅ precursor at T = 5 °C and TSC = 23 mM in pH range from 8 to 10. The net production rates at T = 5 and 30 °C (Figure 4A) are apparently very different even after taking OCS hydrolysis rate into account.

**Dependence of OCS Production Rate on Polysulfide Concentration.**
To conclude the phenomenological description of the dependence of OCS production rate on reaction conditions and on the different reactants, we checked the effect of polysulfide concentration on OCS production taking K₂S₅ and K₂S₃ as representative polysulfide precursors. The test was conducted at pH 9. The net production rate was linearly dependent on polysulfide concentration (Figure 5). The correlation coefficients, $R^2$, were 0.994 and 0.998 for the tri- and pentasulfide precursors, respectively. The ratio of the slopes corresponding to K₂S₃ and K₂S₅ precursors was found to be 1.49 ± 0.09.

**Discussion**

Figures 3 and 5 show clearly that OCS formation rate depends linearly on CO and polysulfide concentrations. Thus, these figures agree well with the postulated bimolecular reaction mechanism. The zero intercept of all the dependencies also supports the dominance of the bimolecular reaction mechanism over the entire concentration range. However, the complex dependence of OCS formation rate on the pH
Polysulfides undergo fast disproportionation reactions in aqueous solutions, and thus, the distribution of dissolved polysulfides is pH dependent on the pH-dependent speciation of polysulfides in aqueous solutions.

**Speciation of Polysulfides.** Polysulfides undergo fast disproportionation reactions in aqueous solutions, and thus, the distribution of dissolved polysulfides is pH dependent on the pH-dependent speciation of polysulfides in aqueous solutions. The quantitative distribution of the polysulfides varies considerably between the two thermodynamic sets examined in this study; e.g., Boulegue et al. (12) assumed that S₄ and S₅ are the dominant species in the water solution under environmentally relevant conditions, and Maronny’s data (13) suggest that S₃ and S₆ are the dominant species. Maronny predicted S₃ concentrations that are nearly 2 orders of magnitude higher than those of Boulegue. However, the two thermodynamic sets predict similar qualitative trends of dissolved polysulfides. For all the different polysulfide precursors, PS decreases as the pH goes down, reaching near-zero concentration at pH 7. As pH increases, so does PS until sulfur becomes totally dissolved, and then PS levels off. Saturation level depends on the type of polysulfide used and is lower for longer polysulfides (corresponding to higher redox potentials). Detailed speciation of the polysulfides and their pH dependence are tabulated in the Supporting Information. For explanation of OCS production rate dependence on the polysulfide type and pH, we assumed that the production kinetics depends linearly on the concentration of all dissolved polysulfides, PS, that will result from that action. PS is defined as

\[
PS = \sum_{n} ([H_2S_n^\text{aq}] + [HS_n^\text{aq}] + [S_n^\text{aq}]) \quad \text{for } n = 2-5 \text{ or } 2-6 \quad (12)
\]

The difference between C₅ and PS is equal to the total monosulfide species in the solution (i.e., [H₂S] and [HS⁻]). Sulfur mass balance implies that the sum of the zerovalent sulfur atoms is constant. This can be derived on the basis of sulfur mass balance and the electroneutrality condition.

\[
(m-1)C_{T,Sm} = \sum_{n} (n-1)([S_n^\text{aq}] + [HS_n^\text{aq}] + [H_2S_n^\text{aq}] + [S_{aq}]) \quad \text{for } n = 1-5 \text{ or } 1-6 \quad (13)
\]

If elemental sulfur concentration exceeds the sulfur solubility, then condition 13 is not preserved and it should be replaced by a constant activity condition, given by sulfur solubility equation.

\[
S_S = S_{aq} \quad K_S \quad (14)
\]

This set of equilibrium reactions is translated into a set of equilibrium equations (with the respective equilibrium constants marked in eqs 8–10). Since there is no agreement in the scientific literature about the speciation of polysulfides or even on the number of polysulfides that are actually present in aqueous solutions, we solved the system for two sets of equilibrium coefficients. The first is based on Maronny’s (13) equilibrium coefficients that are derived by assuming that only dimer- to pentasulfide species exist in high-pH solutions. A second set of coefficients is based on Boulegue’s work (12), taking into account the presence of hexasulfide species as well. The two sets of equilibrium coefficients are summarized in Table 1. It should be noted that the thermodynamic constants are based on computation of a set of complex UV-visible spectra, without using isolated reference materials for each polysulfide and also involve an a priori guess of the highest polysulfides present in the solution. The two sets are based on data for 5°C, but Giggenbach (14) demonstrated that speciation depends very little on temperature at T < 150°C. Since both thermodynamic sets are based on rather questionable assumptions, we did not attempt to elaborate on the thermal effect on speciation in the range between 5 and 30°C. Likewise, we ignored ion strength effects on speciation because these were nearly constant in our tests and because these effects are not accounted for in the derivation of the underlying thermodynamics.

This set of 15 or 18 equations was solved subject to electroneutrality and sulfur preservation conditions that hold for closed systems. The electroneutrality is manifested in preservation of the total molar concentration of the sulfide and polysulfide species, which also should be equal to the molar concentrations of polysulfide salt precursors that were introduced into the test beakers.

\[
C_{T,Sm} = \sum_{n} ([S_n^\text{aq}] + [HS_n^-] + [H_2S_n]) \quad \text{for } n = 1-5 \text{ or } 1-6 \quad (11)
\]

where \(m\) denotes the average polysulfide precursor \((K_2S_m)\), i.e., the polysulfide salt that was introduced to the beaker, and \(n\) denotes the chain length of the sulfide or polysulfide present in the solution. \(C_{T,Sm}\) is also the molar concentration of the dissolved polysulfide salt precursor. It should be underscored that the concentration of the polysulfide salt that is introduced into the reaction beaker is different from the total concentration of dissolved polysulfides, PS, that will result from that action. PS is defined as

\[
PS = \sum_{n} ([H_2S_n] + [HS_n^-] + [S_n^\text{aq}]) \quad \text{for } n = 2-5 \text{ or } 2-6 \quad (12)
\]

The difference between \(C_{T,Sm}\) and PS is equal to the total monosulfide species in the solution (i.e., [H₂S] and [HS⁻]). Sulfur mass balance implies that the sum of the zerovalent sulfur atoms is constant. This can be derived on the basis of sulfur mass balance and the electroneutrality condition.

\[
(m-1)C_{T,Sm} = \sum_{n} (n-1)([S_n^\text{aq}] + [HS_n^\text{aq}] + [H_2S_n^\text{aq}] + [S_{aq}]) \quad \text{for } n = 1-5 \text{ or } 1-6 \quad (13)
\]

If elemental sulfur concentration exceeds the sulfur solubility, then condition 13 is not preserved and it should be replaced by a constant activity condition, given by sulfur solubility equation.

\[
S_S = S_{aq} \quad K_S \quad (14)
\]

\(K_s\) was taken as 1.52 × 10⁻⁷ M for calculation of polysulfide speciation according to Boulegue (37) and as 5.00 × 10⁻⁶ M based on Maronny’s (13) set of coefficients.

Figure 6 depicts the total molar concentration of dissolved polysulfides (including disulfide but excluding monosulfide species), PS, based on the two thermodynamic sets of Tables 1. The figure describes only the four polysulfide precursors that were studied in Figure 4 (TSC = 23 mM).

The quantitative distribution of the polysulfides varies considerably between the two thermodynamic sets examined in this study. For examples of OCS production rate dependence on the polysulfide type and pH, we assumed that the production kinetics depends linearly on the concentration of all dissolved polysulfides, PS, and on the concentration of CO.

\[
(d(OCS)/dt)_{\text{produced}} = (d(OCS)/dt)_{\text{observed}} + k_{\text{red}}[OCS] = k_p[CO]PS \quad (15)
\]

Here, \((d(OCS)/dt)_{\text{produced}}\) is the rate of OCS production by reaction of carbon monoxide and dissolved polysulfides and \(k_p\) is the bimolecular rate coefficient.

For quantitative verification of this model, we calculated the dependence of \((d(OCS)/dt)_{\text{produced}}\) at 30°C on PS for the two sets of thermodynamic constants (Table 1). The linear

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curves in include all the experimental data given in Figure 4. Interestingly, despite the quantitative disagreement between the two sets of thermodynamic constants, both explain the observed kinetics very well. This, in fact, was rather disappointing for us, since it implies that the reaction of polysulfides with CO cannot be used for selection of the more accurate thermodynamic set. Boulegue’s set of constants (12) gave somewhat better correlation ($R^2 = 0.972$) than Maronny’s (13) ($R^2 = 0.964$), and therefore, it was used for all further calculations. The slope of OCS formation rate versus PS according to Boulegue’s set is $k_p[CO] = (6.02 \pm 0.14) \times 10^{-7}$ s$^{-1}$. From this value and the known value of [CO] = 4.46 $\mu$M, $k_p$ was calculated to be $(1.35 \pm 0.03) \times 10^{-3}$ mol$^{-1}$ L$^{-1}$ s$^{-1}$. Values of $k_p$ at 30 and 5°C were used for calculation of the activation energy of the reaction giving $E_a$ = 21.3 kJ/mol.

Possible Significance. There are no data in the literature on CO, polysulfides, and OCS levels in the same aquatic system. In fact, there are only few reports on the levels of CO and polysulfides in natural systems. Typical [CO] levels in freshwater are reported, for example, for Constance Lake (38) to be 0–54 nM, and 50–250 nM were reported for Troy Lake (39). Roberts (40) found 84 $\mu$M polysulfides in the anoxic Lower Mystic Lake. Though they pertain to different locations, one can estimate based on the reported CO and polysulfide levels the steady-state OCS concentration (at pH 8; $T = 20$ °C) by the equation

$$\text{[OCS]} = k_p[CO]PS/k_{h,tot}$$

Calculated OCS level falls in the range from 0 to 1.0 nM. For comparison, Richards’ (41) comprehensive survey of OCS in Canadian lakes show that OCS falls in the range 0.55–7.6 nM. So the reported and calculated OCS levels fall within the same orders of magnitude, particularly after taking into account the fact that dark OCS production is only a fraction (9, 10, 32) of the total (phonic and dark) OCS production.
here is a few orders lower than the level that will affect OCS production in marine water.
Solar photogeneration of OCS that is based on similar experimental tests and polysulfide speciation data will be presented elsewhere.

**Acknowledgments**

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**Supporting Information Available**

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

**Glossary**

- **C_{T,S,r}** molar concentration of the polysulfide salt (K_2S_{2n^-}, Na_2S_{2n}) that was introduced into the test beakers (M)
- **k_{1h}** OCS hydrolysis rate coefficient by reaction with water (s^{-1})
- **k_{2h}** OCS hydrolysis rate coefficient by the reaction with OH^{-} (s^{-1} M^{-1})
- **k_{h,tot}** OCS hydrolysis rate coefficient by the reaction with H_2O and OH^{-} (k_{h,tot} = k_{1h} + k_{a1} [OH^{-}])
- **k_{p}** bimolecular OCS production rate constant by the dark reaction of CO and polysulfides
- **k_{a1,n}** first acid dissociation constant of H_2S_n
- **k_{a2,n}** acid dissociation constant of HS^{-}
- **K_n^{1+}** equilibrium constant of the disproportionation reaction H_2S_n + S_{aq} = H_2S_{n+1} (M)
- **K_S** solubility constant of elemental sulfur
- **PS** total molar concentration of dissolved polysulfides (see eq 12) (moles of dissolved polysulfides / L)
- **TSC** total polysulfide and monosulfide concentration expressed as sulfur. TSC = mC_{T,S,r} (mol of S / L)

**Literature Cited**

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