Formation of Polysulfides in an Oxygen Rich Freshwater Lake and Their Role in the Production of Volatile Sulfur Compounds in Aquatic Systems

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We present the first observations on the occurrence of inorganic polysulfides in an oxygen rich aquatic system. Inorganic polysulfides were found both in the hypolimnion and the epilimnion of a freshwater lake—Lake Kinneret. The presence of these compounds inoxic systems resolves the enigma concerning the mechanism of formation of dimethyl disulfide, dimethyltrisulfide, and dimethyltetrasulfide in oxygen rich aquatic systems and marine water. The abundance of low molecular weight organic and inorganic polysulfides relative to the a priori postulated dominance of the pentasulfide family is explained by the low level of polysulfides in oxygen rich aquatic systems. Thermodynamic calculations show that for trace levels of reduced sulfur compounds, dimethyl disulfide becomes the dominant polysulfide form.

Introduction

Volatile sulfur compounds (VSCs) are important for the understanding of the global sulfur cycle and its influence on global warming, ozone hole formation and cloud nucleation (1, 2). The most abundant VSCs are dimethyl sulfide (DMS), methanethiol, hydrogen sulfide, dimethyl disulfide (DMDS), dimethyltrisulfide (DMTS), dimethyltetrasulfide (DMTeS), carbonyl sulfide, and carbon disulfide. Currently only the mechanisms for the formation of the first three compounds in oxygen rich aquatic systems are understood, while the formation mechanisms of the other five VSCs remain unclear. When the formation mechanism of a set of related compounds is unknown, then one may suspect the existence of yet another missing piece of the puzzle that will shed light on a common latent source for these compounds. In this manuscript, we present evidence for the occurrence of another set of volatile sulfur species in oxic aqueous systems—polysulfanes (HnSx) and their corresponding polysulfide (Sn−) and hydropolysulfide (HnSx−) forms. These compounds are important in their own right as an integral part of the sulfur cycle and we believe that their presence is vital for the understanding of the formation mechanisms of the other VSCs. We claim that polysulfides are direct precursors for dimethyl disulfide, dimethyltrisulfide, and dimethyltetrasulfide, and they probably participate in the formation of carbonyl sulfide as well. This does not preclude other parallel formation mechanisms such as the oxidative dimerization of methanethiol to give DMDS.

Recently, we have demonstrated the abundance of a number of VSCs including (dimethylsulfiniopropionate, DMSP derived -) dimethyl sulfide (3, 4), and dimethylpolysulfides (DMOS) (3) in the epilimnion of a freshwater system—Lake Kinneret. Based on a combination of algal and bacterial culture studies and measurements of the concentration distribution of DMOS in Lake Kinneret we postulated that “...the mechanism of formation of the dimethyl sulfides probably involves biogenic production of inorganic sulfides, which are then methylated by organic methyl donors to give dimethylpolysulfides” (5). The objective of this paper is to provide evidence for the presence of inorganic polysulfide intermediates in an oxygen rich natural aquatic system, and thus to confirm the proposed mechanism. Inorganic polysulfides have never been reported before in any oxygen rich natural aquatic system.

Lake Kinneret, the subject of the current study, is a 168 square km lake; its average and maximum depths are 20 and 90 m, respectively. The lake collects the inflowing Jordan River as well as winter surface floods and supplies half of the drinking water of the state of Israel. The chemical and biological characteristics of the lake are well-studied (6, 7). As far as we know, the chemical composition of the lake water does not exhibit site specific properties relevant to this study. The average August concentrations in the epilimnion over the period 1969–1998 were as follows (8): alkalinity, 105 mg/L; calcium, 50 mg/L; chloride, 225 mg/L; ammonia, 0.03 mg/L; nitrate, 0.03 mg/L; nitrite < 0.01 mg/L; organic nitrogen, 0.5 mg/L; oxygen, 8 mg/L; pH 8.5; total dissolved phosphorus 0.01 mg/L; silica 6.5 mg/L; sulfate 52 mg/L; total suspended solids, 3.0 mg/L; turbidity, 2 NTU.) The lake is stratified between May and October. We have monitored the level of DMOS in Lake Kinneret over a three-year period and found that it ranged between 0 and 1 nM, peaking in the epilimnion during spring season. A bloom of Peridinium gatunense—a dinoflagelate—dominates the algal population of the lake in the spring. During that period the dissolved organic carbon (DOC) doubles compared to its yearly average level and reaches up to 10 mg/L. The level of DMOS in the hypolimnion is rarely above detection level (3).

Our hypothesis that inorganic polysulfides are the precursors for organic polysulfides was based on the formation of inorganic polysulfides by six bacteria strain cultures (including an obligatory aerobe strain—Acinetobacter lwoffi) that were isolated from Lake Kinneret and fed on organosulfur compounds under oxygen rich conditions. Organosulfur methyl donor nutrients (e.g., d3-methionine and methionine) gave both inorganic and organic polysulfides, while compounds that had no transferable methyl group (e.g., cysteine) yielded only the inorganic polysulfides. Additionally, our field observations demonstrated that DMOS are formed even in an oxygen rich unstratified lake, which confirmed that the entire formation process in the lake occurs under oxic conditions. However, until now, there was no direct unequivocal evidence for the occurrence of inorganic polysulfides in natural oxic systems.

Experimental Section

Materials. Dimethyl sulfide, dimethyl disulfide, d3-methylidioxide, allyl bromide, carbon monoxide, and sodium tetrasulfide were obtained from Aldrich. COS was supplied by EMC Special Gases, U.K. Dimethyltrisulfide and dimethyltetrasulfide were synthesized as previously reported (5) according to recently published synthesis procedure (9).
Analytical Methods. Currently, there is still no accepted or validated analytical method for the determination of inorganic polysulfides at the relevant concentration range. Therefore, we based our analysis on the conversion of the inorganic sulfides to $d_6$-DMDS and conventional chromatographic determination of the DMDS and the deuterated polysulfides. Derivatization of the inorganic polysulfides was carried out by mixing the sample with $d_3$-methyliodide (0.5 g/L) in ambient conditions for 24 h. Then the volatiles were concentrated by a closed loop stripping apparatus (CLSA) and quantitated by a GC/mass selective detector (GC/MSD) operated in electron impact, selected ion monitoring (EI/SIM) mode. In the configuration and flow rates used in the current study the CLSA-GC/MSD/EI/SIM exhibited 40% and 50% recoveries and 0.25 and 0.2 pM minimum detection limits (MDL) for DMDS and DMTS, respectively. The MDL for dimethyltetrasulfide was approximately 20 pM. The method was inappropriate for detection of dimethylpentasil sulfide because of its lower volatility. To confirm the presence of the inorganic polysulfides by an independent method we derivatized the polysulfides also by allylbromide (by adding 100 mg of allylbromide to 1-L sample and mixing for 60 min at 21 °C). Allylbromide forms active radical cations (12) in aqueous solutions which readily react with strong nucleophiles such as polysulfides and hydro polysulfides. CLSA is inappropriate for the preconcentration of diallyl polysulfides but aextraction with 60 mL of 1:1 (v) methyltertbutyl ether: pentane and vacuum concentration (to 1 mL) we could determine the diallyl polysulfides using a GC/MSD/EI/SIM analysis. The method is less accurate compared with $d_3$-methylation, but for >100 pM range it confirmed the presence of the inorganic polysulfides in the samples.

COS was determined by Cutter's method (13, 14) with a few changes. We used a GC equipped with a Chrompack-silicaPLOT 30 m × 0.32 mm ID capillary column and a MSD/EI for quantitation. Oven temperature was kept constant at 35 °C.

A HP5890 gas chromatograph equipped with a temperature programmable on-column injector and an electron ionization (EI) mass selective detector (HP5971 MSD) was used for quantitation. The capillary column for polysulfide determination was 30 m × 0.32 mm ID RTX-1 with 1-micrometer film thickness.

The light intensity (for the range 400–2800 nm) was measured by Epply PSP piranometer. Chlorophyll a, DOC, and hydrogen sulfide measurements were conducted according to reported procedures (3, 11). Dissolved oxygen was determined by the Winkler method (11).

Sampling. Samples were collected from station A—the deepest point of Lake Kinneret, located at its center—by the sampling boat of the Yigal Alon Limnological Laboratory. Field sampling protocol was reported earlier (3).

Results To test the hypothesis that inorganic polysulfides are abundant in oxic aquatic systems we acquired three concentration profiles of the relevant chemical compounds in Lake Kinneret during late spring and summer of 1999. Samples were collected from different depths at station A. Figure 1 presents the concentration profiles of dimethyl disulfide, dimethyltrisulfide, dimethyl tetrasulfide, and dimethyltrisulfide (marked as $d_6$-DMDS and $d_6$-DMTS in the figure), temperature, dissolved oxygen, pH, hydrogen sulfide, dissolved organic carbon, and chlorophyll a at station A. Algae analysis in the water column did not reveal any dominant algae species. A large number of different algae populated the water column including cyanophyta (Aphanothece and Oscillatoria), chloro-
TABLE 1. Lake Kinneret Concentration Profiles (May, 1999)

<table>
<thead>
<tr>
<th>depth (m)</th>
<th>T (°C)</th>
<th>O₂ (mM)</th>
<th>pH</th>
<th>H₂S² (μM)</th>
<th>DOC (mg/L)</th>
<th>DMTS</th>
<th>DMSO</th>
<th>trisulfide</th>
<th>disulfide</th>
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<tbody>
<tr>
<td>0</td>
<td>23.71</td>
<td>0.384</td>
<td>9.03</td>
<td>0</td>
<td>4.6</td>
<td>16.6</td>
<td>9.6</td>
<td>413.3</td>
<td>230.7</td>
</tr>
<tr>
<td>5</td>
<td>23.28</td>
<td>0.416</td>
<td>9.05</td>
<td>0</td>
<td>4.4</td>
<td>137.6</td>
<td>108.6</td>
<td>305.5</td>
<td>192.3</td>
</tr>
<tr>
<td>10</td>
<td>20.99</td>
<td>0.353</td>
<td>8.82</td>
<td>0</td>
<td>4.5</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>15</td>
<td>18.95</td>
<td>0.341</td>
<td>8.28</td>
<td>0.735</td>
<td>4.4</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>20</td>
<td>17.85</td>
<td>0.175</td>
<td>7.75</td>
<td>2.941</td>
<td>3.7</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>30</td>
<td>16.87</td>
<td>0.006</td>
<td>7.7</td>
<td>7.353</td>
<td>2.9</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>38</td>
<td>16.59</td>
<td>0</td>
<td>7.55</td>
<td>7.353</td>
<td>3.8</td>
<td>0.01</td>
<td>0.3</td>
<td>670.0</td>
<td>420.0</td>
</tr>
</tbody>
</table>

*Not measured. ²H₂S = [H₂S₅] + [HS⁻].

Rhophyta ( Crucigenia, Scenedesmus, Cosmarium, Pedastrum, Coelastrum, Oocystis, Closterium, Chlorococcum, Tetracoccus, Selenastrum and Pedastrum), and pyprophyta (Peridinium). The alga inhabitants are rather typical for the summer population of Lake Kinneret (6). Inspection of the depth-concentration profiles of the inorganic and organic polysulfides reveals two different dependencies for the epilimnion (<18 m deep) and for the hypolimnion of the lake. For the oxygen rich epilimnion, we found positive dependence between the dissolved oxygen level and the inorganic polysulfides. Moreover, the level of the inorganic polysulfides increased as the sampling point approached the water surface (further away from the hydrogen sulfide rich locations). The dimethylpolysulfides obeyed the same depth-concentration dependence at all locations except for the sampling point near the surface. There the concentration was much lower probably due to evaporation. In contradistinction, negative dependence between the inorganic and organic polysulfides was found in the oxygen-poor hypolimnion (> 18 m). The concentration of polysulfides was larger at deeper locations, exhibiting a strong positive correlation with the level of dissolved bisulfide.

A positive correlation between inorganic and organic polysulfides in the epilimnion is consistent with our laboratory studies, which showed that inorganic sulfides are intermediates for dimethylpolysulfide production (5). The negative correlation between inorganic and organic polysulfides in the hypolimnion shows that the inorganic polysulfides are not the limiting reactants for DMOS formation in the hypolimnion; the presence of methyl donors is at least as important. Indeed, inorganic polysulfides correlate well (correlation coefficient, R = 0.94, n = 9) with the level of chlorophyll a which is intuitively associated with the level of methyl donors. There was no significant correlation between the DOC level and the organic polysulfides, probably since DOC is a measure of the total organic carbon which includes a large fraction of undegradable organic substances that cannot donate methyl groups.

The trends of Figure 1 are also observed in Table 1 which shows the profiles of the sampling trip in May (2.5.99). The lake was stratified and the thermocline was at 17 m. Although during this sampling we collected only a few data points we can still observe a significant increase of the inorganic polysulfides closer to the water surface level. The levels of inorganic and organic polysulfides in the epilimnion and the DOC level in May were much higher compared to August.

In May we did not obtain the level of chlorophyll a, which is a better indicator for algal activity than DOC. However we can deduce that the algal activity was higher in May than in August from the levels of the dissolved oxygen and pH in the epilimnion.

Polysulfide levels and other relevant concentrations for the field test in July (11.7.99) are given in Figure 2A,B. The algae population of the lake was dominated by chlorophyta (mainly Pedastrum, Coelastrum and Ankistrodesmus); some cyanophyta were also present (mainly Microcystis). Peridinium gatunense was observed at low concentrations in this period, as seen in Figure 2. The lack of correlation between the distributions of Peridinium and chlorophyll a shows that the Peridinium was not the dominant algae at this date. The levels of hydrogen sulfide and inorganic polysulfides were especially high at the hypolimnion for the July sampling trip. The polysulfide trends in the epilimnion and the deep hypolimnion sections in July agree very well with the general trends of Figure 1 and Table 1. The trends observed in July (as well as in all other sampling dates) are as follows: (1) larger concentrations of inorganic polysulfides at higher locations in the epilimnion; (2) larger concentrations of DMOS at higher locations in the epilimnion; (3) larger concentrations of inorganic polysulfides and lower concentrations of DMOS at deeper points in the hypolimnion; (4) positive correlations between inorganic polysulfides and DMOS in the epilimnion; and (5) negative correspondence between the inorganic and organic polysulfides in the hypolimnion. However, in July, the concentrations of the DMOS were abnormally high for depth levels of 20 and 25 m, corresponding to hypolimnion points close to the thermocline. We attribute this maximum to local mixing effects that brought together inorganic polysulfides from the hypolimnion and organic methyl donors from the epilimnion. It should be noted that during early July there were anomalous fish death episodes in the lake. It is possible that the same local mixing phenomenon is responsible for the fish death episode and to the anomalous increase of the DMOS below the thermocline.

**Discussion**

The presence of polysulfides in the oxygen rich epilimnion and the concentration profile of both organic and inorganic polysulfides agree well with our prior field studies in Lake Kinneret and our laboratory studies, which indicated polysulfide production during bacterial assimilation of organosulfur compounds (3, 4).

Previous research on the speciation of polysulfides showed that the pentasulfide species (i.e., [H₂S₅] + [HS⁻] + [S⁻]) are the dominant inorganic polysulfide forms (15, 16). It therefore seems surprising that we did not find higher polysulfides in our studies, even after allylbromide derivatization. A similar question may be raised for dimethylpolysulfide abundance in marine water. If indeed DMOS are formed by methylation of inorganic polysulfides then why dimethylsulfides was never reported and DMTeS was so rarely found? Theoretically, the distribution of polysulfides can be explained by solar radiation induced disproportionation of higher organic polysulfides. Indeed, previous research showed that higher polysulfides, especially those having an odd number of catenated sulfur atoms, disproportionate to give lower polysulfides under UV irradiation (17, 18). However, this mechanism cannot explain the predominance of low molecular weight inorganic polysulfides that was observed in this study. To explain the seemingly anomalous polysulfide distribution we conducted thermodynamic calculations of the speciation of polysulfides as a function of pH and the concentration of reduced sulfur species.
The following set of equations and equilibrium constants define polysulfide reactions in aqueous systems:

Acid dissociation:

\[ \text{H}_2\text{S}_n \rightleftharpoons \text{HS}_n^- + \text{H}^+ \quad K_{a1,n} \quad (1) \]
\[ \text{HS}_n^- \rightleftharpoons \text{S}_n + \text{H}^+ \quad K_{a2,n} \quad (2) \]

for \( n = 1, 2, 3, 4, 5, 6 \)

Disproportionation:

\[ \text{HS}^- + (n/8)\text{S}_8(aq) \rightleftharpoons \text{S}_{n+1} \quad K_n \quad (3) \]

for \( n = 1, 2, 3, 4, 5 \)

Elementary sulfur dissolution:

\[ 1/8\text{S}_8(aq) \rightleftharpoons 1/8\text{S}_8(aq) \quad K_s \quad (4) \]

Hydrogen sulfide dissolution:

\[ \text{H}_2\text{S}(aq) \rightleftharpoons \text{H}_2\text{S}(g) \quad K_H \quad (5) \]

Equations 1–3 represent 17 equilibrium equations. These can be solved using constraints imposed on the system by adjacent phases. In analogy with the carbonate system, four ideal systems can be classified, depending on the presence/absence of sulfur precipitate and the presence/absence of gaseous phase that determine the level of the dissolved hydrogen sulfide.

The current discussion involves only systems without a gas phase (closed system) and without a separate sulfur phase. The solubility of orthorhombic sulfur precipitate is still disputed. Reported values range between \( 2 \times 10^{-8} \) and \( 5 \times 10^{-6} \) M (16, 19, 20). However, even the upper value is rather low and sulfur colloid formation can easily remain unnoticed in natural aquatic systems. The equilibrium constants of eqs 1–3 are also still disputed. In fact, even the mere existence of hexasulfane species in aqueous systems is still disputed (15, 16, 21). The calculations below were made with the set of equilibrium values of Table 2 and references therein. The choice of this specific data set influences only the absolute predicted concentrations but not the general observed trends. Thermodynamically, thiosulfate and sulfite dominate over the polysulfides in the high pH range, while in natural systems the polysulfides are more abundant in the high pH range than in lower ones as a result of kinetic considerations. Since the rate of the disproportionation reactions is rather fast we assume that the equilibrium trends will be similar or at least influence the actual relative distribution of polysulfides in the lake.

Based on eqs 1–4 it is possible to calculate the distribution of dissolved reduced sulfur species \( (C_{S_n} = [\text{H}_2\text{S}_n] + [\text{HS}_n^-] + [\text{S}_n]) \) for \( n = 1–6 \) and the solubility of total reduced sulfur compounds expressed as \( \text{S}_\text{TSCS} \) as a function of two variables, pH, and the relative concentration of divalent sulfur (RDS). The second variable corresponds to the redox potential of the solution which is true for high sulfur concentrations.
percentage, is defined as 100 concentration of each of the polysulfides, expressed in mole of the polysulfides for pH 8 and RDS of TSCS. Figures 3 shows the relative concentration of each 

ance to exclusive existence of the disulfide species. The 

shifts from pentahydrosulfide and hexahydrosulfide domi-

TSCS is lowered, the distribution of the polysulfide species 

reversed compared to that of a saturated solution. As the 

polysulfides for low levels of dissolved sulfur species is 

(25 °C)\(^a\)

<table>
<thead>
<tr>
<th>name</th>
<th>notation</th>
<th>value</th>
<th>calcd from ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfur solubility constant</td>
<td>pK_s</td>
<td>7.72</td>
<td>(21)</td>
</tr>
<tr>
<td>First and Second Acid Dissociation Constants (Eqs 1 and 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrogen sulfide</td>
<td>pK_{a,1,1}; pK_{a,2,1}</td>
<td>7;17</td>
<td>(21, 15)</td>
</tr>
<tr>
<td>hydrogen disulfide</td>
<td>pK_{a,1,2}; pK_{a,2,2}</td>
<td>5;9.7</td>
<td>(21)</td>
</tr>
<tr>
<td>hydrogen trisulfide</td>
<td>pK_{a,1,3}; pK_{a,2,3}</td>
<td>4.2; 7.5</td>
<td>(21)</td>
</tr>
<tr>
<td>hydrogen tetrasulfide</td>
<td>pK_{a,1,4}; pK_{a,2,4}</td>
<td>3.8; 6.3</td>
<td>(21)</td>
</tr>
<tr>
<td>hydrogen pentasulfide</td>
<td>pK_{a,1,5}; pK_{a,2,5}</td>
<td>3.5; 5.7</td>
<td>(21)</td>
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<tr>
<td>hydrogen hexasulfide</td>
<td>pK_{a,1,6}; pK_{a,2,6}</td>
<td>3.2; 5.2</td>
<td>(22)</td>
</tr>
<tr>
<td>Disproportionation (Eq 3)</td>
<td>pK_3</td>
<td>9.52</td>
<td>(23)</td>
</tr>
<tr>
<td>hydrogen sulfide/sulfide</td>
<td>pK_4</td>
<td>9.41</td>
<td>(23)</td>
</tr>
<tr>
<td>hydrogen disulfide/trisulfide</td>
<td>pK_5</td>
<td>9.62</td>
<td>(23)</td>
</tr>
</tbody>
</table>

\(^a\) The data were used by Williamson and Rimstidt (24).

We calculated the distribution of polysulfides as a function of TSCS. Figures 3 shows the relative concentration of each of the polysulfides for pH 8 and RDS = 0.5. The relative concentration of each of the polysulfides, expressed in mole percentage, is defined as 100 \(\times (\sum_{i=0}^{n} [\text{H}_2\text{S}_n^-]) / \sum_{i=0}^{n} [\text{H}_2\text{S}_n^-])\) (for \(n = 2 – 6\)). The distribution of the different polysulfides for low levels of dissolved sulfur species is reversed compared to that of a saturated solution. As the TSCS is lowered, the distribution of the polysulfide species shifts from pentahydrosulfide and hexahydrosulfide dominance to exclusive existence of the disulfide species. The numerical solution of polysulfide speciation shows that disulfide is the dominant species also for all other RDS values at low dissolved sulfur concentrations.

Since all prior laboratory studies of polysulfide research were carried out under exceedingly high polysulfide concentrations, researchers correctly observed that the pentasulfide species were the dominant polysulfide forms. This is not true for natural, oxygen-rich aquatic systems where only trace sulfide concentrations are present. The shift in polysulfide speciation as a function of TSCS was indeed verified by laboratory experiments with dissolved commercial sodium tetrasulfide at pH 9.2. A shift of polysulfide distribution (determined as diallylpolysulfide) was observed when the amount of sodium tetrasulfide was lowered. For 10 mg/L sodium tetrasulfide the polysulfide forms were the dominant species, while for 0.05 mg/L Na₂S₄ only disulfide was found.

Details of the speciation studies and their deviation from the reported thermodynamic predictions will be presented elsewhere.

We believe that the importance of polysulfanes and their deprotonated forms in aquatic systems goes beyond being yet another abundant class of semivolatile sulfur species. First, their presence gives a simple mechanistic explanation for the occurrence of dimethylpolysulfides in aqueous systems. Second, this mechanism and the shift in polysulfide distribution for low concentrations of reduced sulfur explains why lower dimethylpolysulfides are always found when the higher polysulfides are present in oceans and other aquatic systems (i.e. DMDS is always found when DMTS is reported and DMTS and DMDS are always found when DMTES is reported).

Finally, polysulfides are strong nucleophiles (much stronger than hydrogen sulfide), and they also easily form thyl radicals (S₄⁻) under solar radiation. It is therefore easy to outline the formation of COS and possibly even CS₂ from polysulfides and these react to give COS. Note that the formation of COS from CO and S⁻ (eq 8) has a very large
TABLE 3. Experimental Conditions and COS Yield by the Reaction of CO and Reduced Sulfur Species.

<table>
<thead>
<tr>
<th>test no.</th>
<th>reactants</th>
<th>incident solar radiation (Kcal/m² h)</th>
<th>COS (pM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.6 μM CO + 57.5 μM Na₂S₄</td>
<td>660</td>
<td>3400</td>
</tr>
<tr>
<td>2</td>
<td>3.6 μM CO + 57.5 μM Na₂S₄</td>
<td>0 (dark)</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>3.6 μM CO + 62.5 μM sulfur (as S)</td>
<td>572</td>
<td>nd²</td>
</tr>
<tr>
<td>4</td>
<td>3.6 μM CO + 69.3 μM Na₂S</td>
<td>735</td>
<td>nd²</td>
</tr>
</tbody>
</table>

*a nd, not detected (i.e., <5 pM). Reaction duration was 1 h (tests 3 and 4 were repeated for 3 h with identical results), pH 8.

Energetic driving force:

\[
\text{CO} + S_2^{2-} + H^+ \rightarrow \text{COS} + HS^- \quad \Delta G^0 = -26.7 \text{ kcal/mol (8)}
\]

Even for low levels of the reactants, reaction 8 is driven to the right. For example, for \( pCO = 10, pH = 8, pS^{2-} = 11 \), and \( pH^+ = 7 \) the predicted COS equilibrium level is ca. 3.8 mM.

To show that COS can be produced from CO and polysulfides we conducted the following comparative test. Three 1-L Pyrex bottles containing distilled water and (1) CO and sodium tetrasulfide, (2) CO and hydrogen sulfide, and (3) CO and elemental sulfur were exposed to solar irradiation for 1 h, after which COS concentration was determined. The pH in all cases was set to pH 8 through addition of HCl or sodium tetrasulfide, (3) CO and elemental sulfur were exposed to solar irradiation and sodium tetrasulfide, (2) CO and hydrogen sulfide, and (2) CO and polysulfides. In fact, a considerable concentration of COS was formed even when the reaction contained CO and polysulfides. In fact, a considerable concentration of COS was formed even when the reaction between the CO and the polysulfides was carried out in the dark.

In this article we did not address the formation mechanism of the inorganic polysulfides. It is possible that these are formed by the oxidation of hydrogen sulfide. Cutter (13) has already demonstrated hydrogen sulfide abundance in the ocean. In a recent review of atmospheric sources of H₂S from the ocean D. Shooter (28) concluded that “In recent years H₂S has played a decreasing role in the global sulfur budget ...”. It is possible that the current research signals a comeback for hydrogen sulfide and the other inorganic sulfides stimulated by recognition of their central role in the formation of VSCs.

Acknowledgments

Temperature, DOC, pH, dissolved oxygen, and hydrogen sulfide data were supplied by the Yigal Alon Limnological Laboratory, J. Gun and I. Shkrob thank the financial support of the Water Technology Program of the BMBF, Germany, and MOS Israel.

Literature Cited

(1) Pham, M.; Muller, J. F.; Brasseur, G. P.; Granier C.; Megie, G. J. Geophysical Res. – Atmospheres 1995, 100, 26061.
(2) Charlson, R. J.; Lovelock, J. E.; Andreae, M. O.; Warren, S. P. Nature 1987, 326, 655.
(8) Yigal Alon Limnological Laboratory: Annual activity report; The Yigal Alon Limnological Laboratory: Tiberias (in Hebrew), 1999.
(23) Boulegue, J.; Michand, G. Hydrog. 1978, 9, 27.

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