

On the Autoxidation of Aqueous Sodium Polysulfide [1]

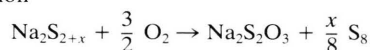
Ralf Steudel*, Gabriele Holdt, and Regine Nagorka

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Sekr. C2, D-1000 Berlin 12, F.R.G.

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Aqueous sodium polysulfide of composition in the range $\text{Na}_2\text{S}_{2.0}$ to $\text{Na}_2\text{S}_{4.6}$ undergoes autoxidation by either air or pure oxygen at temperatures of between 23 and 40 °C according to the equation



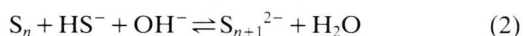
Iodometric determination, vibrational spectra and ion-pair chromatography showed that neither sulfate, sulfite nor polythionates are formed and that the sulfur precipitated consists of S_8 ($\geq 99\%$).

Introduction

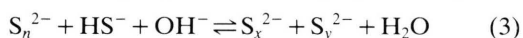
Aqueous sodium sulfide is strongly alkaline because of hydrolysis due to the extremely low value of the dissociation constant of the HS^- ion:



At pH values between 7 and 12.5, HS^- is the dominating sulfide species. These solutions dissolve elemental sulfur with formation of polysulfide anions; according to Teder [4] the maximum sulfur content obtained corresponds to the formula $\text{Na}_2\text{S}_{4.5}$ at 25 °C and $\text{Na}_2\text{S}_{5.0}$ at 80 °C, respectively:



Anions of different chain-length are in an equilibrium which is rapidly established ($x+y = n+1$):



At pH = 10–13 neither S^{2-} nor HS_n^- are present in noticeable concentration, and on addition of acid elemental sulfur is precipitated (back reaction (2)) [4].

The maximum chain length of the anions present in the yellow to orange solutions is uncertain but most observations can be rationalized assuming species with up to 6 sulfur atoms [4–7]. However, crystalline polysulfides with up to 8 sulfur atoms have been isolated (sometimes from non-aqueous solutions) and partly characterized by X-ray structural analysis [8–21].

It has been repeatedly observed that aqueous polysulfide is subject to autoxidation when exposed to

air, but no systematic study of this reaction has been reported. Only the autoxidation of aqueous monosulfide (containing H_2S , HS^- , S^{2-} in pH dependent equilibrium) has been investigated by several authors. Bowers *et al.* [22] using H_2S and O_2 at constant partial pressures of between 100 and 500 Torr (no further details were reported) found (a) that for $[\text{HS}^-] < 2 \cdot 10^{-3}$ mol/l the autoxidation was very slow and the product was elemental sulfur, (b) for $2 \cdot 10^{-3} < [\text{HS}^-] < 3 \cdot 10^{-2}$ mol/l yellow polysulfides built up to a steady state concentration prior to precipitation of sulfur, and (c) for $[\text{HS}^-] > 3 \cdot 10^{-2}$ mol/l oxygen uptake was very fast and a clear solution of unidentified sulfur-oxygen anions resulted. For conditions (b) the activation energy for the rate of sulfur formation was determined to be 250 kJ/mol (below 27 °C) and as 31 kJ/mol (above 27 °C), respectively. Polysulfide ions were found to be much more susceptible to autoxidation than hydrogen sulfide ions and to catalyze the oxidation of monosulfide [22].

Avrahami and Golding [23] observed thiosulfate as the first product of the autoxidation of HS^- at temperatures between 25 and 55 °C (pH = 11–13; $c_{\text{HS}^-} = 10^{-4} \dots 10^{-3}$ mol/l). After longer reaction times sulfate was formed in addition, but neither polysulfides nor other intermediates were observed, although sulfite was assumed to be a primary product rapidly oxidized to give sulfate. Occasionally colloidal sulfur was formed as concluded from a milkiness of the solutions.

These results were basically confirmed by Cline and Richards [24], who studied the autoxidation of HS^- in sterilized sea-water at pH = 7.5–7.8 and a temperature of 9.8 °C. The major reaction products

* Reprint requests to Prof. Dr. R. Steudel.

were thiosulfate and sulfate, with small concentrations of sulfite occurring as an unstable, but fairly long lived intermediate. Elemental sulfur and polysulfides were never detected in the reaction mixture. In a very detailed and careful study, Chen and Morris [25] found that HS^- is oxidized by O_2 at 25 °C to give polysulfides (at pH near 7), elemental sulfur (at high sulfide-to-oxygen ratios), thiosulfate (which is the principal product at $\text{pH} > 8.5$ regardless of the sulfide-to-oxygen ratio), and some sulfite (which is slowly oxidized to sulfate and is absent in the final solutions). The reaction rate strongly depends on the pH, and is largest for $\text{pH} = 8$ and 11, respectively. An induction period of between 0.5 h and several hours has also been observed for the first time.

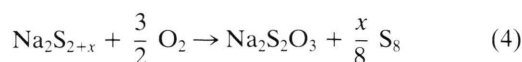
In yet another investigation of the "oxygenation" of sulfide in aqueous solution, O'Brien and Birkner reported that thiosulfate and sulfite, but neither sulfur nor polysulfides were formed when "reduced sulfur species" (H_2S , HS^-) were treated with O_2 at a pH of 4, 7.55 or 10 and a temperature of 25 °C; since the sum of $\text{S}_2\text{O}_3^{2-}$ and SO_3^{2-} was less than the sulfide consumed, it was assumed that SO_4^{2-} was also formed in this reaction [26]. However, both Chiu and Meehan [27] as well as Almgren and Hagström [28] observed the precipitation of sulfur as a sol when oxygen was bubbled into aqueous H_2S solutions at pH values between 3 and 8.5.

The above survey shows that polysulfides are intermediates in the oxidation of sulfide, and this holds even for the enzymatic anaerobic sulfide oxidation by certain sulfur bacteria [29]. We have therefore studied the reaction products obtained by oxidation of aqueous sodium polysulfide of composition Na_2S_2 to $\text{Na}_2\text{S}_{4.6}$ with oxygen, at temperatures of between 23 and 40 °C and pH values in the range 9–13.5.

Results and Discussion

When oxygen gas was bubbled through a glass sinter frit into an aqueous polysulfides solution at 23 ± 3 °C, the yellow to brown-red solution (depending on the sulfur content) finally became colorless.

Any precipitated sulfur was then isolated and weighed. Aliquots of the aqueous phase were analysed for sulfur-oxyanions by ion-pair chromatography [30], iodometric titration and (after evaporation to dryness) by infrared and Raman spectroscopy. Experimental details are given in Table I and in the Experimental Part. Six experiments of this type have been carried out and the results can be summarized as in eq. (4):



Elemental sulfur precipitated only when the sulfur content of the solution was higher than for disulfide. This sulfur dissolved almost completely in carbon disulfide and the soluble part (>99%) consisted entirely of S_8 . The colorless filtrate contained only sodium thiosulfate, the amount of which was equivalent to the sodium sulfide used to prepare the polysulfide solution. Neither polythionates nor sulfate or sulfite could be detected by any of the techniques mentioned above.

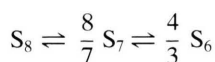
As can be seen from Table I, the time required for the discoloration of the solutions increased with the average chain-length of the polysulfide anions under otherwise identical conditions. This indicates that the reactive species is a short-chain ion like disulfide the concentration of which must be highest at compositions close to Na_2S_2 . If any sulfate or sulfite would have been formed in addition to the thiosulfate, the final pH would be expected to be below 7 due to the lacking sodium cations. The infrared spectrum (200–4000 cm^{-1} ; KBr disc) of the evaporation residue was identical to that of commercial $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ (analytical grade) except for an occasional splitting of $\delta_s(\text{S}_2\text{O}_3^{2-})$ into a doublet (558 and 553 cm^{-1}). In the Raman spectrum a splitting of ν_{ss} (ν_1 of $\text{S}_2\text{O}_3^{2-}$) into two components at 450 and 431 cm^{-1} was observed. Presumably sodium thiosulfate crystallizes as two modifications or hydrates showing slightly different wavenumbers. The ion-pair chromatogram [30] of the oxidized solution did not show even traces of polythionates.

Initial composition	Initial pH	Reaction time	Sulfur precipit. exper.	Sulfur precipit. theoret.	Thiosulfate formed exper.	Thiosulfate formed theoret.	Final pH
$\text{Na}_2\text{S}_{2.21}$	13.16	24 h	0.24 g	0.34 g	8.1 g	7.82 g	7.80
$\text{Na}_2\text{S}_{3.42}$	12.77	48 h	2.19 g	2.24 g	8.1 g	7.82 g	8.28
$\text{Na}_2\text{S}_{4.62}$	11.55	9 d	4.10 g	4.17 g	7.9 g	7.82 g	8.44

Table I. Autoxidation of sodium polysulfide solutions at 23 ± 3 °C [theoretical values calculated from eq. (4)].

If the evaporation residue had contained any sodium sulfate ($635, 612\text{ cm}^{-1}$), sulfite ($965, 630\text{ cm}^{-1}$), polythionates ($1230, 610\text{ cm}^{-1}$) or carbonate (1440 cm^{-1}), infrared absorptions at the wavenumbers given in brackets would have been observed ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ does not absorb in these regions). The autoxidation of aqueous polysulfide according to eq. (4) turned out to be independent of the experimental conditions, as the following examples demonstrate: When 0.5 ml Na_2S_2 solutions (prepared from 283 mg $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 38 mg S_8) and 49.5 ml of cyclohexane were stirred at 40°C in a 50 ml Erlenmeyer flask equipped with a vertical reflux condenser, it took 22 h for the aqueous phase to become colorless. The organic layer was analyzed for elemental sulfur by HPLC [2] and contained only 1 mg of S_8 . Even in a stoppered flask the autoxidation proceeded to completion since diffusion and occasional sampling obviously provided sufficient oxygen. When 2 ml Na_2S_4 solution (prepared from 970 mg $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 388 mg S_8) were stirred with 98 ml cyclohexane at 23°C in a stoppered 100 ml volumetric flask, it took 395 h for discoloration, after which 285 mg elemental sulfur were found by quantitative HPLC analysis [2] in the organic phase (theoretical amount according to eq. (4): 260 mg).

When aqueous Na_2S was stirred at 23°C with a solution of S_8 in cyclohexane in an open or stoppered flask, the sulfur concentration in the organic phase first decreased to a very low value due to the formation of polysulfides. It then increased again due to slow autoxidation provided the average polysulfide chain-length was >2 . The final S_n concentration was in agreement with eq. (4); the species present in the cyclohexane phase were S_8 (99%), S_7 ($\approx 0.7\%$) and S_6 ($\approx 0.3\%$) according to the equilibrium



the establishment of which is catalyzed by nucleophilic reagents and polar solvents [31].

Experimental

Chemicals: S_8 was recrystallized from carbon disulfides; $\text{Na}_2\text{S} \cdot 7-9\text{H}_2\text{O}$ (Merck, analytical grade) was recrystallized from small amount of warm water after filtration followed by cooling. The sulfur content (and hence the water content) was determined by bromine oxidation and titration of the sulfate using barium perchlorate. Elemental sulfur was used as a standard. Oxygen from a steel cylinder was loaded with water vapor before application to the polysulfide solution.

Instruments: Varian 5000 chromatograph with Rheodyne loop injector ($10\text{ }\mu\text{l}$), Varian UV 5 absorbance detector (254 nm for elemental sulfur, 215 nm for thiosulfate and polythionates), C18 bonded phase glass column (Chrompack). Perkin-Elmer 580 B infrared spectrophotometer. Cary 82 Raman spectrometer (Varian) and Raman System U 1000 (Instruments S.A.) with a krypton laser (647.1 nm). The pH values were measured with a glass electrode.

Procedure for the experiments listed in Table I: 71.70 g of freshly recrystallized $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ with 11.04% sulfur content were dissolved in 250 ml demineralized water. 50 ml of this solution were heated with 1.93, 3.88 or 5.76 g S_8 , respectively, to prepare the $\text{Na}_2\text{S}_{2.21}$, $\text{Na}_2\text{S}_{3.42}$ and $\text{Na}_2\text{S}_{4.62}$ solutions listed in Table I. These solutions were freshly prepared prior to use. Water saturated oxygen was then bubbled into the solutions through a glass frit in a wash bottle. After discoloration carbon disulfide was added to dissolve the precipitated sulfur, the two phases were separated, the CS_2 evaporated in a vacuum, and the mass of the sulfur determined by weighing. The aqueous phase was freed from traces of CS_2 in a vacuum, filtered and diluted to a measured volume, from which aliquots were taken for iodometric titration and other investigations.

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