THE REACTION OF AQUEOUS THIOSULFATE WITH FORMALDEHYDE

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The reaction of aqueous thiosulfate with formaldehyde was followed by C-13 NMR and Raman spectroscopy. At pH 7 no reaction was observed. In acidic solution, the only carbon containing compound formed was trithiane. No hydroxymethanesulfonate nor hydroxymethanesulfinate was observed. This indicates that intermediates in the reaction do not include sulfur oxyacids in oxidation states $+2$, $+3$, or $+4$. Therefore, the reaction involves auto-thiolysis of thiosulfate without redox reactions. Raman spectra reveal, in addition to trithiane, an equilibrium mixture of tri- and tetrathionate in a mole ratio corresponding to the overall stoichiometry:

$$6HS_2O_3^- + 3CH_2(OH)_2 = (CH_2S)_3 + 3S_3O_6^{2-} + 6H_2O$$
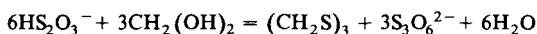
Excess thiosulfate yielded elemental cyclooctasulfur, in addition to the above. Secondary reaction products correspond to those formed during the decomposition of polythionates.

INTRODUCTION

Reports on the reaction between thiosulfate and aqueous formaldehyde have been conflicting. Schmidt[1] reported the formation of $HO-CH_2-S-SO_3H$ in equilibrium with residual reagents, Raschig[2] found that the reaction needed to be initiated by acid and found polythionates among the products, and Vanino[3] used the reaction as a preparative method for the synthesis of trithiane, without mentioning any other products.

It is relevant that all three authors agreed that acid facilitated their reactions, because it is well known that acid causes the auto-decomposition of aqueous thiosulfate, even in the absence of formaldehyde. Thus, while aqueous thiosulfate is stable in neutral solutions for several years and does not readily decompose, even upon heating[4] up to 150°C, acidic solutions rapidly decompose yielding a bewildering number of metastable products that eventually convert to elemental sulfur or sulfate. Aten,[5] Engel,[6] and Steudel[7] found primarily elemental sulfur allotropes among the intermediate products. According to Davis[8] these allotropes are formed by step-wise chain formation involving sulfane–sulfonic acids.[9] This reaction yields one mole of sulfite for each thiosulfate as a biproduct. Feher[10] proposed sulfanes as intermediates; LaMer,[11] Agarwala[12] and Mizoguchi[4] reported the formation of polythionates, and some authors report the smell of hydrogen sulfide or sulfur dioxide, and sometimes both.[13,14] The reaction products, and their yield, depend on pH, temperature and concentration.[15]

We studied this system because formaldehyde reacts with three different oxidation states of sulfur. It quantitatively reacts with sulfur dioxide, bisulfite, and sulfite over a large pH range yielding hydroxymethanesulfonate; it reacts with sulfide yielding trithiane, and with dithionite or with sulfite and reducing agents forming hydroxy

methanesulfinate.[16] All three formaldehyde derivatives have well characterized C-13 NMR and Raman spectra that make it possible to identify them *in situ* in mixtures. Thus, we hoped that formaldehyde might trap intermediates in the reactions of thiosulfate.

RESULTS

We observed neutral mixtures of formaldehyde with thiosulfate in the concentration range from 0.05 M to saturated solutions containing 12 M formaldehyde and 6 M sodium thiosulfate by C-13 NMR and Raman spectroscopy over a period of many weeks. If thiosulfate would interact with formaldehyde, one would expect a fairly strong Raman band in the C—S region between 500 and 800 cm^{-1}, such as in Bunte salts, and C-13 NMR resonances in the 50–85 ppm range. We found no peaks other than those of the reagents. However, when the reagent solutions were acidified, rapid reaction set in.

After initial exploratory experiments, we decided to focus on experiments conducted under conditions that parallel the procedure of Aten[5] and Engel,[6] because this system has been carefully studied and there is fair agreement about the products. Figure 1 shows the Raman spectrum of a solution prepared by rapid mixing of equal volumes of 16N HCl, 37 wt% formalin, and saturated sodium thiosulfate. All three solutions were precooled to −25°C. The resulting mixture is approximately 5N HCl, 2M in thiosulfate, and 4M in formaldehyde. These aqueous formaldehyde solutions contain mainly methyleneglycol in equilibrium with poly-methoxymethyleneglycol, and only negligible concentrations of formaldehyde, because the latter readily hydrolyzes. Raman spectra and thiosulfate concentrations were analyzed by comparison with standard spectra of 1M oxyacid solutions.[14,15]
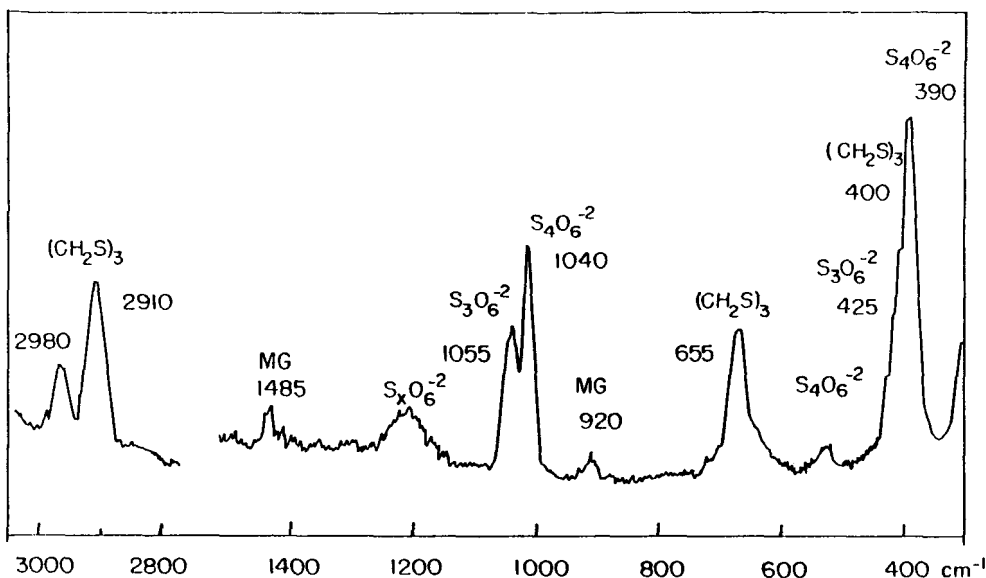

FIGURE 1:   Raman spectrum of thiosulfate formaldehyde reaction products. MG = methyleneglycol oligomers.

The initial Raman spectra, taken ten minutes after mixing when the solution has reached room temperature, still clearly shows the sharp and strong thiosulfate peaks at 1001 cm^{-1} and 451 cm^{-1}, together with the C—S stretch at 670 cm^{-1} of trithiane, and the distinctive peaks of trithionate at 1055, 425, and 264 cm^{-1} and tetrathionate at 1040, 390, and 260 cm^{-1}. The spectrum also shows the distinct peak at 920 cm^{-1}, due to the —C—O—C— vibration of methyleneglycol oligomers, and their CH motions in the 1400 and 2800 cm^{-1} regions. The C—O—C motion is strongly concentration dependent.[16] The solutions show no peaks at 981 cm^{-1} for sulfate, at 1340 and 1144 cm^{-1} for sulfur dioxide, 424 and 235 cm^{-1} for disulfate and bisulfite, nor at 730 cm^{-1} for hydroxymethanesulfonate, even though the corresponding spectral region is free.

Thirty minutes after mixing, the peak at 1001 cm^{-1} due to thiosulfate has vanished, and the spectrum is dominated by tri- and tetrathionate and trithiane, Figure 1. Suprisingly, the strong peak of hydroxymethanesulfonate at 777 cm^{-1} is absent. After about 30 min at room temperature the solution turns opaque and a white solid slowly precipitates and settles within about an hour. The Raman spectrum of the solid is that of trithiane. If the experiment is conducted with a molar excess of thiosulfate, the solid is pale yellow and includes the strong peaks of elemental cyclooctasulfur[13] at 478, 408, 228, 223, 162, and 100 cm^{-1}. The mother liquid continues to be characterized by the strong spectrum of tri- and tetrathionate. Comparison of the scattering intensity of the peaks at 1040 and 1055 cm^{-1} with reference spectra[14,15] shows that the concentrations of tri- and tetrathionates are between 0.5M and 1.0M.

The C-13 NMR spectrum of freshly mixed solutions cannot be rapidly recorded for instrumental reasons. After 30 min, the spectrum in Figure 2 is obtained. The
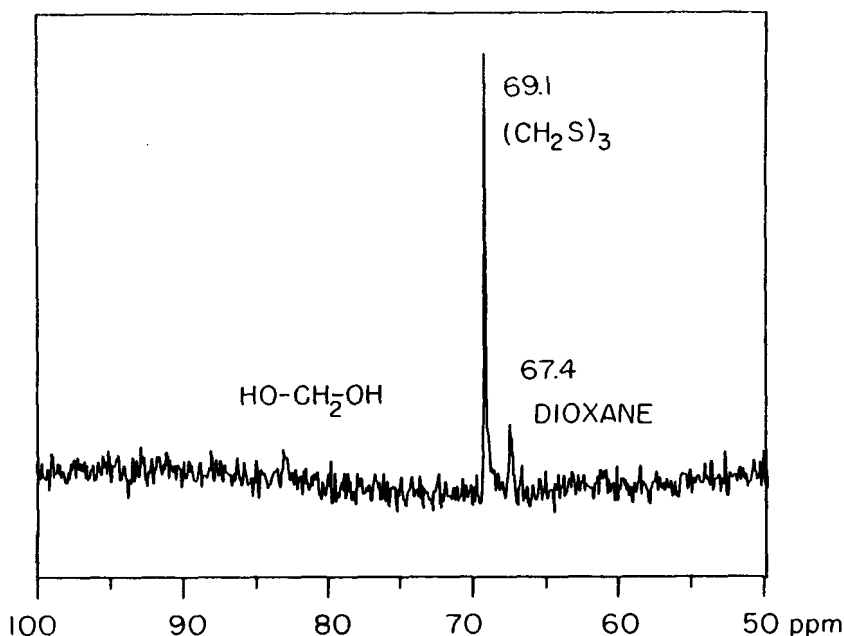

FIGURE 2:   C-13 NMR spectrum of thiosulfate formaldehyde reaction products.

peak at 82.8 ppm is due to residual methylene glycol.[17] The peak at 67.4 ppm is due to dioxane that is added as an internal standard. The strong peak at 69.1 ppm is new. It is assigned to trithiane. This assignment is supported by proton NMR that yields a single peak at 4.18 ppm relative to TMS, where trithiane is known to have its resonance.[18] When the sample is heated the trithiane peak weakens and two new peaks appear, a strong peak at 75.1 ppm corresponding to hydroxymethane-sulfonate, and a very weak peak at 72.7 ppm. This change goes parallel with the decomposition of tri- and tetrathionate that is observed in the Raman spectrum.

DISCUSSION

The C-13 NMR spectrum shows that trithiane is the only primary carbon containing product formed in the acidic reaction of formaldehyde with thiosulfate. The Raman spectrum shows that tri- and tetrathionate are formed parallel with trithiane. Since thiosulfate is known to strongly catalyze conversion[14] between tri- and tetrathionate, it is not necessary that both are primary products of the reaction. In fact, considera-tion of stoichiometry of our reaction suggests a single, balanced equation for the given reaction mixture:

$$6HCl + 6Na_2S_2O_3 + 3CH_2(OH)_2 = (CH_2S)_3 + 3Na_2S_3O_6 + 6NaCl + 6H_2O$$

$$(I)$$
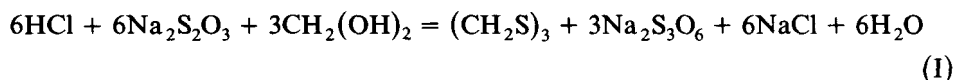
This reaction appears amazingly simple, and it even preserves the nominal oxidation states of all sulfur atoms.[19] Earlier authors[1-3] assumed that the first step in the reaction was the formation of hydroxymethanethiosulfate. As indicated above, this compound should show both a Raman C—S stretch in the 680–800 cm^{-1} region and an NMR resonance in the 60–82 ppm range. However, no peaks are observed other than those of the reagents and products listed in equation I. Thus, no formaldehyde–thiosulfate compound or adduct is present. In fact, the pH depen-dence indicates that the reaction occurs only under conditions where thiosulfate decomposes in the absence of formaldehyde. This indicates that protonation of methyleneglycol is not the reaction inducing step, and that the reaction, if its starts between any isolated reagent pair, would have to begin with two thiosulfate ions. The mechanism of this reaction is discussed below.

Any analysis of possible mechanisms must take into account the high concentra-tion of all reagents. At the beginning the molar ratios of the reagents are approxi-mately $H_2O : H_3O^+ : H_2S_2O_3 : CH_2(OH)_2 = 25 : 3 : 1 : 1$. Thus, three or more solute molecules can readily interact simultaneously. The fact that low temperature greatly enhances[3,5,6] the yield of the two products provides further evidence that the mechanism may involve gradual pre-assembly of reagents into a preferred configura-tion. In any case, the absence of hydroxymethanethiosulfate and the formation of trithionate rather than hydroxymethanesulfonate clearly confirm that the reaction involves more than a thiosulfate–formaldehyde pair.
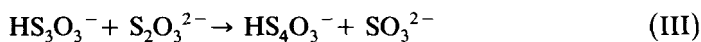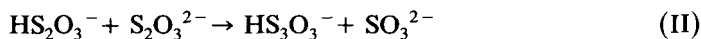
A possible reaction mechanism might involve simultaneous steps such as: protona-tion of methyleneglycol, reaction of the free electron pair of the sulfur atoms at the HS-tail of thiosulfuric acid with the carbon atom, reaction of the free electron pair of HS-sulfur of a second thiosulfate with the sulfonate tail of the first, S—S scission

resulting in trithionate, and, possibly, the simultaneous reaction of the unstable $HO-CH_2-SH$ species with additional methylene glycol, leading to $S(CH_2-OH)_2$, $HO-CH_2(S-CH_2)_n-OH$, and, eventually, to trithiane, tetrathiane or polythiane.

Since C-13 NMR and Raman spectra do not show any initial evidence for hydroxymethanesulfonate, we conclude that bisulfite and sulfur dioxide are not accumulated during the reaction, or that hydroxymethanesulfonate is not stable under our conditions. As to the latter option, however, we did not notice any evolution of sulfur dioxide in the Raman sample tube, and a solution of hydroxy-methanesulfonate acidified with 6M HCl proved stable over many weeks. To test whether nascent sulfur dioxide is capable of forming hydroxymethanesulfonate under our conditions, we added traces of bisulfite to the reaction products and promptly found both the Raman peak at 777 cm^{-1} and the C-13 NMR peak at 75.1 ppm. Finally, we observed that secondary decomposition of polythionate at 42°C yields hydroxymethanesulfonate, and, apparently also consumes some of the tri-thiane. Thus, we conclude that sulfur dioxide and bisulfite are not important products in the initial step of the reaction of formaldehyde with thiosulfate.

The secondary reactions that occur as a consequence of the decomposition of polythionates constitute a separate, complex reaction system[13,14] the discussion of which exceeds the goal of the present paper.

Our results raise the question whether the reaction of formaldehyde with thiosul-fate allows any conclusions about the mechanism of the aqueous auto-decomposition of thiosulfate.[4-12] During recent years interest has focused on two mechanisms. Thode's isotope experiments[12] suggest a bimolecular reaction mechanism, while Davis'[8] work suggests the reaction sequence:

$$HS_2O_3^- + S_2O_3^{2-} \rightarrow HS_3O_3^- + SO_3^{2-} \qquad \text{(II)}$$

$$HS_3O_3^- + S_2O_3^{2-} \rightarrow HS_4O_3^- + SO_3^{2-} \qquad \text{(III)}$$

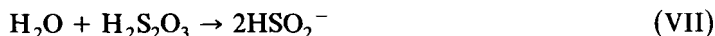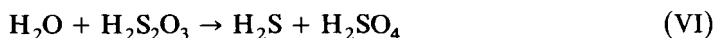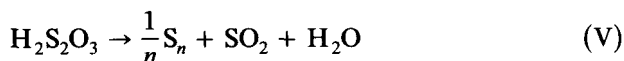$$HS_9O_3^- \rightarrow S_8 + HSO_3^- \qquad \text{(IV)}$$

This step-wise chain build-up in acidic medium is attractive, because it constitutes the reverse of the sulfite degradation[9] of elemental sulfur at high pH. The inter-mediates in this reaction are the sulfane-sulfonic acids[18] that Schmidt[9] succeeded in synthesizing at $-40°C$ in ether. However, the intermediates have not yet been observed in the aqueous system, and one does not observe the vigorous evolution of sulfur dioxide that one would expect if sulfite were formed in 5N HCl.

Our C-13 NMR experiments cannot answer the question whether sulfane–sulfonic acids are present, because one would not expect them to react with formaldehyde if thiosulfate does not react. However, the Raman spectrum should reveal peaks at 2485 cm^{-1} for HS, at 860 cm^{-1} for H—S—S, at 467 and 486 cm^{-1} for S—S—S, and in the 1020 and 1170 cm^{-1} region for the S—O stretches. None have been observed, indicating that sulfane–sulfonates are not formed in significant concentra-tions.

Even though we have not observed sulfur dioxide or sulfane–sulfonates, our work is certainly not able to exclude Davis' mechanism in systems where formaldehyde is absent, because the reaction of formaldehyde with nascent sulfide produced by S—S scission during the thiosulfate–thiosulfate reaction is such a strong driving force that formaldehyde likely would suppress any build-up of sulfane chains, eqs. (II)–(IV).

This raises questions about the intramolecular redox mechanism during decomposition of acidic thiosulfate. Nominally, the scission of the S—S bond may yield three pairs of intermediate oxidation states:

$$H_2S_2O_3 \rightarrow \frac{1}{n}S_n + SO_2 + H_2O \qquad \text{(V)}$$

$$H_2O + H_2S_2O_3 \rightarrow H_2S + H_2SO_4 \qquad \text{(VI)}$$

$$H_2O + H_2S_2O_3 \rightarrow 2HSO_2^- \qquad \text{(VII)}$$

Equation (V) reflects the formation of elemental sulfur according to Aten and Engel according to the Davis mechanism. As stated above, we do not observe the formation of sulfur dioxide or of hydroxymethanesulfonate. Equation (VII) reflects hydrolysis into sulfoxylic acid.[20] This reaction is analogue to the hydrolysis of disulfite. Sulfoxylic acid has been proposed as an intermediate in redox reactions of aqueous sulfur species for almost a hundred and fifty years, but it is extremely unstable and has so far evaded any detection. However, if it would form in our system, formaldehyde would immediately react with it forming hydroxymethanesulfinate, a well characterized compound that can be recognized by its C-13 NMR peak at 84.7 ppm and the Raman peaks at 730, 963, and 1086 cm^{-1}. The latter reaction occurs when hydroxymethanesulfinate forms jointly with hydroxymethanesulfonate during the hydrolysis of dithionite, a process that probably involves both sulfoxylic acid as well as sulfurous acid as intermediates.[22] However, under the acidic conditions of the current work, the situation is more complex, because residual thiosulfate would react with hydroxymethanesulfinate yielding hydroxymethanesulfonate and trithiane.[20] We studied and verified the latter reaction both by Raman and C-13 NMR spectroscopy. Thus, since sulfonate is not among the initial products of the reaction of thiosulfate with formaldehyde, we can exclude equation (VII). This supports formation of products with the sulfur oxidation states shown in equation (VI). However, the presence of high concentrations of thiosulfate in our reaction favors thiolysis of the S—S bond rather than hydrolysis. This leads to the formation of trithionate. Furthermore, due to the presence of formaldehyde, and the high acidity in our system, hydrogen sulfide becomes reactive with methylene glycol, yielding thio-analogues of the oxygen bridged oligomers that are present in formaldehyde solution. The mechanism of the latter reaction is not yet understood, but the reaction is strongly concentration dependent. This fact has puzzled polymer chemists for more than 50 years.[23]

While trithionate is capable of forming 2M solutions, trithiane is poorly soluble and precipitates during the reaction. This explains the otherwise surprising fact that Vanino[3] found thiosulfate a better reagent for the synthesis of trithiane than hydrogen sulfide[21] which is not only unpleasant to handle but has a tendency to yield a mixture of polythianes as biproduct.

EXPERIMENTAL

Materials. Aqueous formaldehyde solutions assayed at 37 wt% were purchased from MCB Reagents and contained 10–15% methanol as a preservative. Reagent grade paraformaldehyde from Mallinckrodt Chemicals was used without further purification. Sodium thiosulfate and sodium bisulfite from Mallinckrodt and Baker, respectively, were of analytical grade.

Instrumental. All C-13 NMR spectra were recorded on a Bruker CXP-200 spectrometer yielding a 50.31 MHz carbon frequency. A sweep width of 15,000 Hz (298.2 ppm), 4 second pulse delays, and 16 K data points were utilized for all spectra. Broad-band heteronuclear decoupling was applied during all acquisitions. Dioxane and D_2O were added to all samples to serve as an internal reference (67.4 ppm) and internal lock, respectively. Spectra were recorded at 290 K unless otherwise noted.

Raman spectra were recorded with a coherent radiation mixed Ar/Kr laser (Model 52M G) coupled with a Spex 1401 monochrometer with slit widths of 100 micron.[14] A 0.10 M perchlorate solution served as a quantitative standard for peak intensity.[14]

^{1}H-NMR spectra were recorded on a Varian 60 spectrometer with $CDCl_4$ as the solvent and chemical shifts in ppm from TMS.

Reaction. In the standard experiment, 20 ml of 12M paraformaldehyde, 20 ml saturated thiosulfate solution, and 20 ml of concentrated HCl were precooled to $-15°C$ and rapidly combined. In some experiments 37 wt% formalin was substituted for paraformaldehyde because the latter dissolves poorly.[16] Formalin contains 10–15 wt% methanol in form of the methyl ether of methyleneglycol. Both Raman and C-13 NMR spectra of the initially clear solution at 290 K were immediately recorded. A pale precipitate formed after the sample was warmed to 315 K, and both Raman and C-13 NMR were again recorded. The precipitate was separated by vacuum filtration and dried at room temperature overnight. The Raman of the solid precipitate and the single proton NMR absorbance at 4.18 ppm are identical to published spectra of pure trithiane.

Spectra. *C-13 NMR* shifts relative to *p*-dioxane were: $CH_2(OH)SO_2^-$: 84.7 ppm; $CH_2(OH)SO_3^-$: 75.1 ppm; $CH_2(OH)OH$: 82.8 ppm, and $(CH_3S)_3$: 69.1 ppm; *p*-NMR 4.18 ppm.

Raman spectra of 1M standard solutions had the following characteristic frequencies. Absolute scattering and intensities are listed in parentheses: Trithiane: 2960 (0.7), 2910 (2), 1370 (1), 1150 (1), 750 (2), 655 (10), 400 (2) and 300 (3). Hydroxymethanesulfonate, $HO-CH_2-SO_3^-$ has its C—S stretch at 777 cm^{-1} (intensity: 0.53); the *S*—O stretches are at 1040 (0.44) and 1090 (0.23). Hydroxymethanesulfinate, $HO-CH_2-SO_2^-$ has its C—S stretch at 720 cm^{-1} (intensity: 0.30), and its S—O stretches at 1085 (0.2) and 945 (0.5). Tetrathionate has peaks at: 1230 (1), 1040 (3.3), 640 (1.3), 522 (1.3), 390 (6.6), 260 (7.0), and Trithionate has Raman peaks at 1247 (0.78), 1055 (1.4), 675 (0.4), 540 (0.3), 425 (1.9) and 264 (3.2). Aqueous solutions of formaldehyde oligomers have Raman scattering peaks at 2990, 2942, 2855, 1485, 1400, 1312, 1260, 1046, 906, and 540, as well as several weaker peaks. The peak at 906 cm^{-1} is due to the CH_2-O-CH_2- bond and its intensity is very concentration dependent. In 1.2M solution its intensity equals that of the 1645 water band.

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