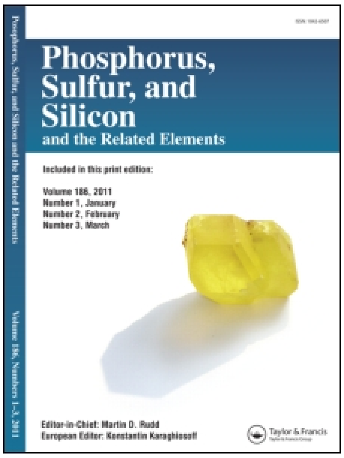


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

RAMAN SPECTROMETRIC STUDY OF THE THERMAL DECOMPOSITION OF AQUEOUS TRI-AND TETRATHIONATE

B. Meyer[ab]; M. Ospina[ab]
[a] Chemistry Department, University of Washington, Seattle, WA [b] Material and Molecular Research Division, Lawrence Berkeley Laboratory University of California, Berkeley, CA

To cite this Article Meyer, B. and Ospina, M.(1982) 'RAMAN SPECTROMETRIC STUDY OF THE THERMAL DECOMPOSITION OF AQUEOUS TRI-AND TETRATHIONATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 14: 1, 23 — 36

To link to this Article: DOI: 10.1080/03086648208073107

URL: http://dx.doi.org/10.1080/03086648208073107

Phosphorus and Sulfur, 1982, Vol. 14, pp. 23–36
0308-664X/82/1401-0023/$06.50/0

RAMAN SPECTROMETRIC STUDY OF THE THERMAL DECOMPOSITION OF AQUEOUS TRI- AND TETRATHIONATE

B. MEYER and M. OSPINA

Chemistry Department, University of Washington, Seattle, WA 98195, and Material and Molecular Research Division, Lawrence Berkeley Laboratory
University of California, Berkeley CA 94720

(*Received May 29, 1982*)

The decomposition of 0.25 M trithionate and 0.5 M tetrathionate was followed at 20, 35, 50 and 70°C. During the reaction tri- and tetrathionate interconvert. Thiosulfate is observed as a prominent intermediate. The end products are elemental sulfur, sulfate, disulfite and bisulfite. The decomposition of trithionate follows a first order reaction with a rate constant of 1.4×10^{-1} at 70°C. In tetrathionate the reaction is preceded by an induction period and is second order, with a rate constant of 4×10^{-3} at 20°C. In both systems sulfate is formed in a first order reaction with a rate constant of 3.1×10^{-3} hrs^{-1} at 20°C. The decomposition mechanism in both systems involves the hydrolysis of trithionate.

INTRODUCTION

Polythionates occur among the intermediates in the acid decomposition of thiosulfate,[1] in Wackenroder's liquid,[2-4] and in almost all systems containing any of the thirteen sulfur oxyacids which are currently known. The polythionates form a homologous series of unbranched chains with the formulae $S_xO_6^{-2}$, and contain sulfur atoms in two or more oxidation states. The structures of tri-, tetra, and pentathionate are shown in Figure 1. At high pH, the polythionates promptly decompose into sulfite and thiosulfate, but in neutral solution and at low pH tri- and tetrathionate are amazingly stable and often serve as metastable aqueous sinks for sulfur, and thus severely interfere with the recovery of sulfur dioxide from flue gas in coal fired power plants.[4]

The polythionates have been known for over 150 years, but despite persistent efforts by many researchers,[1-7] the mechanism of their formation and decomposition is poorly known. One reason for this is that the traditional chemical analysis of mixtures of aqueous sulfur oxyacids is slow and complicated and disturbs the intricate web of interlinked equilibria among the various species.[8] The purpose of the current work is to employ computer aided laser Raman spectroscopy for analyzing the time dependent composition of complex mixtures. The advantage of this method is that measurements can be made *in situ*, and do not affect the equilibria unless the laser light causes photolysis.

RESULTS AND DISCUSSION

Spectral Analysis

The spectral assignment of the Raman bands was straight-forward.[9,10] All sulfur oxyacids have characteristic S—O stretching frequencies in the 950 to 1300 cm^{-1} range.

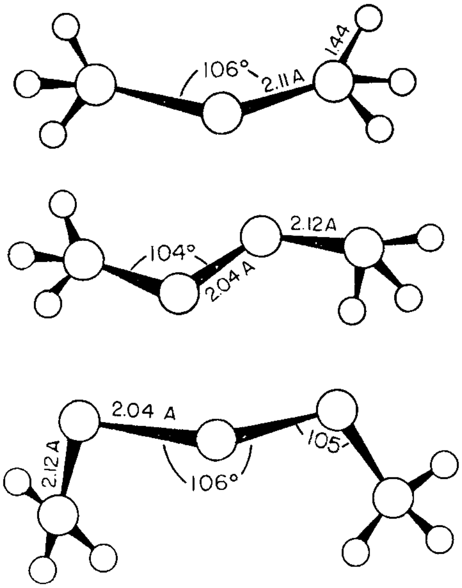


FIGURE 1 The structure of tri-, tetra- and pentathionate (from Ref. 13).

The Raman frequencies, intensities and detection limits of the sulfur oxyacids have been reported earlier.[9,10] Figures 2 and 3 show typical spectra. Figure 2a is the spectrum of a fresh solution of pure 0.25 M trithionate. Figure 2b shows the spectrum after 90 hrs at 35°C. Figure 3c shows the end product of the decomposition, sulfate, bisulfite, disulfite, and elemental sulfur. A series of experiments were made for 0.25 M trithionate and 0.5 M tetrathionate at 20, 35, 50, and 70°C, respectively. Figure 3 shows the spectra of a fresh and a fully decomposed tetrathionate solution.

Trithionate can be recognized in all spectra by a strong and sharp S—O stretch at 1055 cm^{-1} and weaker bands at 1247, 675, 425, and 264 cm^{-1}. The tetrathionate has a strong peak at 1040 cm^{-1}, and weaker peaks at 1233, 651, 532, 390, 310, and 260 cm^{-1}. The pentathionate frequencies are 1036 cm^{-1} for the strong and sharp peak, and 1234, 650, 506, 392 and 287 for the weaker peaks. As the solutions age, the characteristic peaks of sulfate at 982 cm^{-1}, bisulfite and disulfite at 1052, 1021, 655, 424 and 235 cm^{-1} appear, and thiosulfate can be noted at 1001, 450, 1125, 672, 541 and 339 cm^{-1}, as well as the spectrum of elemental sulfur with peaks at 475 cm^{-1} and lower frequencies.[4,11] The latter spectrum often persists in solution, even after the solution has been centrifuged.

If the pH drops during the reaction, the peaks of bisulfate, HSO_4^-, at 1055 cm^{-1} and sulfur dioxide at 1340, 1150 and 540 cm^{-1} also appears. In some systems dithionate, $S_2O_6^{-2}$, can be observed with peaks at 1092, 1206, 710, 550, 320, and 281 cm^{-1}.

The chemical composition of the solution was determined by matching the spectra of the unknown mixtures with the standard spectra of pure 1 M oxyacid solutions. Tri- and tetrathionate have a detection limit of about 0.005 M with our equipment, and their intensity *vs* concentration curves are linear over the entire range from 0.005 M to saturated solutions, within the accuracy of our method. Concentrations can be readily measured to within ±10% for all species. The procedure for determining concentrations is described in the experimental section below.

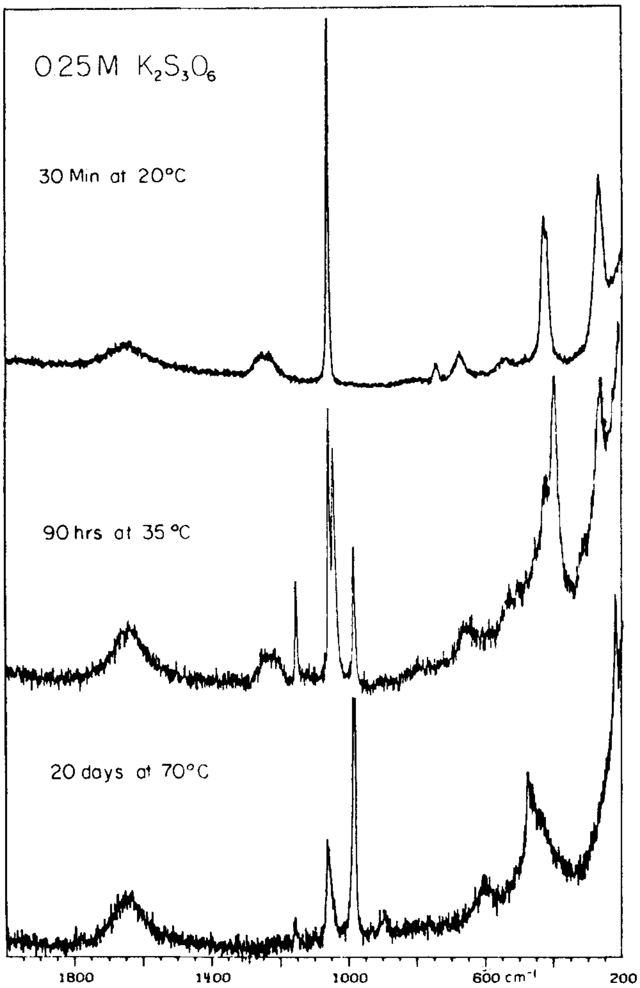


FIGURE 2 Raman spectra of 0.25 M trithionate. (a) Fresh solution at 20°C, (b) after 90 hrs at 35°C, and (c) after 20 days at 70°C.

Since many molecules have similar S—O stretching frequencies and other similar features, their Raman spectra frequently overlap. The deconvolution of complex spectra, Figure 4, proved to be easier than anticipated. We found that empirical curve analysis, even of the most complex observed spectra, always yielded peaks within ±1 cm^{-1} of known oxyacid species. Details of the spectra and the analysis have been reported earlier.[9,10] Since we were mainly interested in the stoichiometry of the reactions, we report here only two significant digits for all concentrations, even though the reproducibility of our work is close to ±5% for most peaks and concentrations. More detail is provided in Ref. 9.

Spectral changes during aging of the solutions are exemplified in Figures 2 and 3. As a fresh solution ages the spectrum of the initial reagent gradually weakens and is replaced by the product spectrum. Since the scattering intensity of each band in each molecule differs, spectral changes do not accurately indicate concentration changes. The disulfite peaks at 1052, 1021, 655, 424, and 235 cm^{-1}, for example, are

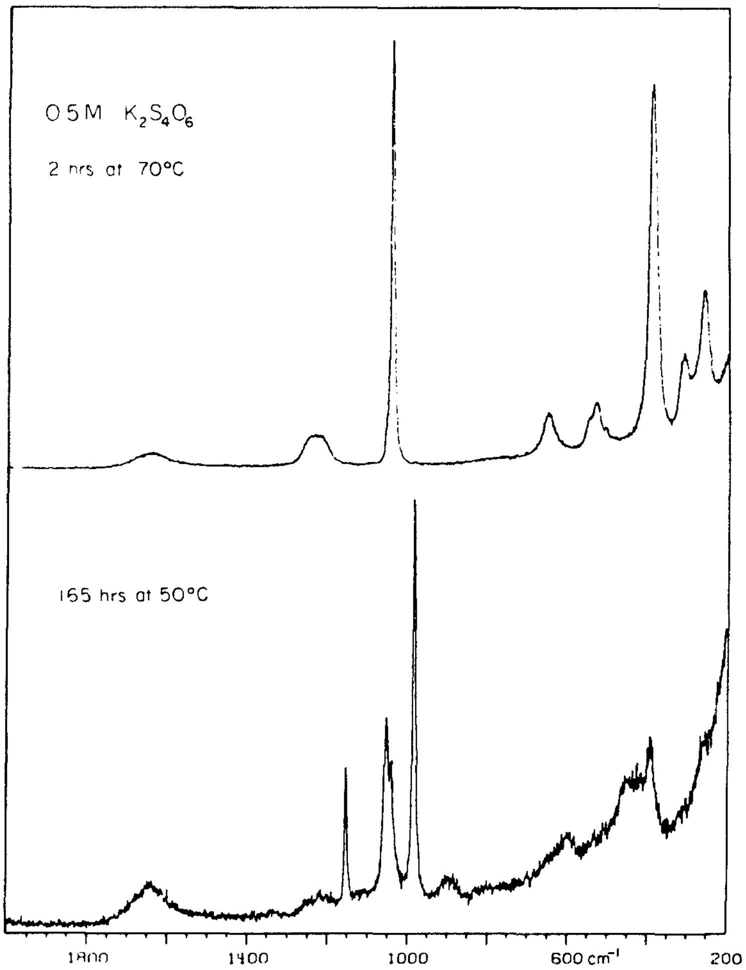


FIGURE 3 Raman spectra of 0.5 M tetrathionate (a) after 2 hrs at 70°C, (b) after 165 hrs at 50°C.

so strong that they tend to dominate a spectrum, even if the concentration of the former amounts to only 5 to 10% of all sulfur species in solution. Another difficulty in the visual interpretation of spectra is that the aqueous concentration of poorly soluble gases or solids does not reflect their presence in other phases. Thus, the concentration of sulfur dioxide and elemental sulfur cannot be directly computed from band intensities.

In the case of 0.25 M trithionate at 20°C, Figures 2 and 6, it took almost ten days before sulfate, the first decomposition product, became noticeable. At the same time tetrathionate and colloidal elemental sulfur also showed. After 27 days tri- and tetrathionate had equal intensities and the peaks at 1001 and 450 cm^{-1} indicated the presence of thiosulfate. Towards the end of the decomposition trithionate appeared merely as a shoulder of the tetrathionate, until it finally faded. At 35°C the sulfate and elemental sulfur peaks were noticeable after 2.5 hrs, jointly with tetrathionate and sulfur dioxide, as well as traces of thiosulfate. After 146 hrs at this temperature tri- and tetrathionate reached equal intensities. At 50°C, Figure 6, it took only 6 hrs for all decomposition products to appear, and at 70°C it took merely 3 hrs. At the

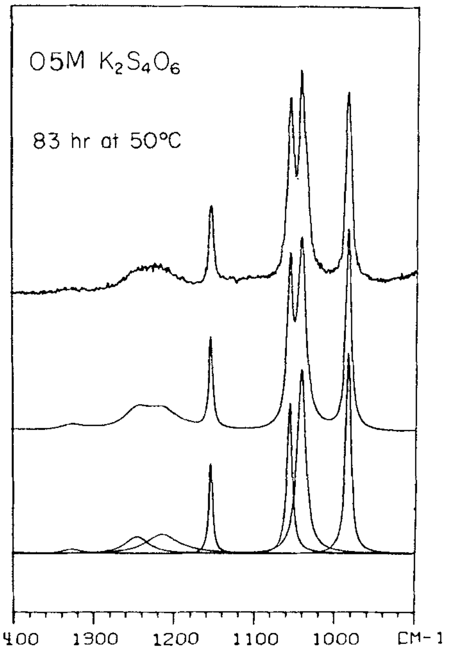


FIGURE 4 Raman spectrum of 0.5 M tetrathionate, after 83 hrs at 50°C. (a) observed spectrum (4 scans), (b) synthesized spectrum, and (c) deconvoluted spectrum, using Lorentzian function.

latter temperature tri- and tetrathionate reached equal intensities after 8.5 hrs, and after 149 hrs the reaction was complete, as evidenced by the fact that only sulfate, bisulfate, sulfur dioxide and elemental sulfur were left.

In the case of 0.5 M tetrathionate at 20°C, Figures 3 and 7, sulfate appeared after 2 days and increased far more rapidly than in the trithionate decomposition. Trithionate, pentathionate and thiosulfate appeared after about 140 hrs. Elemental sulfur appeared after one week. After 26 days tri- and tetrathionate had equal intensity. Bisulfate appeared in the spectrum because the pH dropped to a value of 1.8, Figure 5. The spectrum did not change significantly between 26 and 90 days, except for sulfate. This indicates that the mixture had reached an equilibrium composition among the polythionates. This equilibrium was maintained until all intermediate oxidation states had been consumed and disproportionated into elemental sulfur and sulfate. At 35°C sulfate appeared after 16 hrs and the reaction proceeded similarly, but faster. The pentathionate concentration reached a maximum after 16 days. At 50°C the reaction was the same, but yet faster, and at 70°C, Figure 7b, the decomposition was completed after 80 hrs.

REACTION MECHANISM

The decomposition of tri- and tetrathionate yields elemental sulfur and sulfate as end products.[1,2,4] Thus the reactions can be summarized by the following overall equations:

$$6K_2S_3O_6 + 4H_2O \rightarrow S_8 + 6K_2SO_4 + 4H_2SO_4 \tag{1}$$

$$3K_2S_4O_6 + 2H_2O \rightarrow \tfrac{7}{8}S_8 + 3K_2SO_4 + 2H_2SO_4 \tag{2}$$

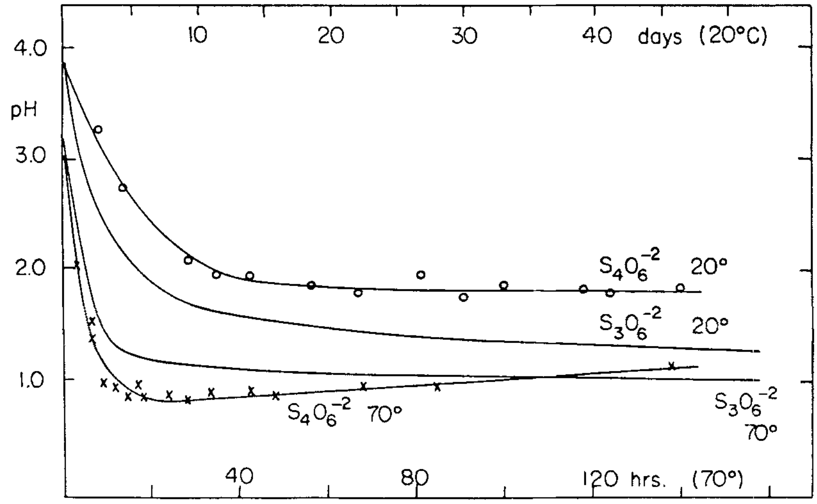


FIGURE 5 pH of 0.25 M trithionate and 0.5 M tetrathionate as a function of time at 20°C and 70°C.

While at least part of the sulfate may be formed directly during the decomposition, elemental sulfur cannot be formed in a one-step reaction, and results only as the end product of a combination of interrelated, parallel reactions. The reaction is further complicated because some intermediates, among the thiosulfate, can catalyze the initial step of the reaction.

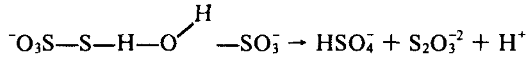
Equations (1) and (2) indicate that the reaction is sensitive to the pH of the solution. At high pH the reaction does not involve redox reactions and merely yields thiosulfate and sulfite.[1,12,13] This paper deals only with the decomposition of unbuffered aqueous solutions prepared by dissolving neutral polythionate salts. Such solutions have an initial pH of 3.5 and 4, respectively. The pH change during decomposition of the solution is shown in Figure 5. The initial decomposition step is most likely either the hydrolysis of the S—S bond, Eq. (3), or a bimolecular reaction among solutes, Eq. (4):

$$^{-}SO_3—S—SO_3^{-} + H_2O \rightarrow HSO_4^{-} + S_2O_3^{-2} + H^{+} \qquad (3)$$

$$S_4O_6^{-2} + S_4O_6^{-2} \rightarrow S_3O_6^{-2} + S_5O_6^{-2} \qquad (4)$$

Unfortunately, the products of these reactions cannot be identified as they are short-lived and are promptly consumed by rapid reaction with the remaining reagents.

The relative speed of reactions (3) and (4) depends on the concentrations, the size of the sulfur chain, the charge distribution within the chain and the relative stability of the potential products. Dithionate, $S_2O_6^{-2}$, for example, the first member of the di-sulfonate series, is far more stable than tri- or tetrathionate[13] because the S—S bond is sterically shielded by the six surrounding oxygen atoms against hydrolysis, and the compound contains only the positively charged sulfonate sulfur atoms in the chain[14] which are resistant to protonation. In contrast, in tri- and tetra- and high polythionates, the sulfur chain contains sulfur links which are both sterically exposed and carry low charges. Thus, in trithionate, for example, the central sulfur atom has a charge of only 0.197, as opposed to the sulfonate charge of +0.312. This charge difference facilitates acid hydrolysis to sulfate and thiosulfate, yielding two stable species:



$$^{-}O_3S{-}S{-}H{-}\overset{H}{O}{-}SO_3^{-} \rightarrow HSO_4^{-} + S_2O_3^{-2} + H^{+} \quad (5)$$

In tetrathionate and higher polythionates the point of hydrolysis is not a priori defined, because both central atoms have the same charge, +0.155;[14] furthermore, symmetrical hydrolysis would not yield stable products. Thus, hydrolysis is more likely at the sulfonate group, yielding sulfate and disulfane-monosulfonate.[12] The latter compound is well known,[15] but all of its homologues, except thiosulfate, are unstable in aqueous solutions. Instead, we observe the formation of other polythionates.

$$^{-}O_3S{-}S_n{-}SO_3^{-} + H_2O \rightarrow {}^{-}O_3S{-}S_n^{-} + HSO_4^{-} + H^{+} \quad (6)$$

Since they appear simultaneously, the polythionates are probably formed by direct bimolecular reaction from the reagent (1):

$$2S_4O_6^{-2} \rightarrow S_3O_6^{-2} + S_5O_6^{-2} \quad (7)$$

Once tetra- and higher polythionates disproportionate to trithionate, the latter readily hydrolyzes to thiosulfate, Eq. (5), as described above. Thus, the latter reaction is expected to dominate all other hydrolysis reactions. Under acidic conditions thiosulfate and polythionates can also catenate and build longer sulfur chains in the form of monosulfane-monosulfonic acids or disulfonic acids, and eventually split of elemental sulfur according to the mechanism proposed by Davis.[16]

$$^{-}S_nSO_3^{-} + S_2O_3^{-2} + H^{+} \rightarrow {}^{-}S_{(n+1)}O_3^{-} + HSO_3^{-} \quad (8)$$

$$^{-}S_mO_3^{-} + H^{+} \rightarrow S_{m-1} + HSO_3^{-} \quad (9)$$

or by other suitable reactions yielding various cyclic elemental sulfur allotropes, such as S_6, S_8, S_{12}, etc.[4]

MASS BALANCE

In order to establish stochiometry of the decomposition reaction of the polythionates and determine whether all intermediates were observed, we computed the mass and redox balance for all species at several points during decomposition. Table I provides an example of how concentrations were determined. It shows the relative integrated areas and the corresponding concentrations of trithionate, tetrathionate, and sulfate as a function of the age of 0.25 M trithionate at 35°C. Similar tables were compiled for all vibrational peaks in this and other systems in solutions at 20, 35, 50 and 70°C for both trithionate and tetrathionate. As indicated above, care was taken to compute elemental sulfur and sulfur dioxide, because elemental sulfur precipitates, and thus evades spectroscopic detection, and, as the pH approaches 2, the value of pK_2 of sulfurous acid, sulfur dioxide forms and is distributed in both the aqueous and the gas phases. Thus, sulfur dioxide does not reflect all sulfur formed in the oxidation state of +4.

Table II shows the observed and the calculated mass and redox balance of a 0.25 M trithionate solution which had been kept at 50°C for 20 hrs. In this case, provided as an example of our calculations, analysis of the balances indicated that thiosulfate was on the threshold of appearing. This accounted for the apparent shortfall of reduced sulfur. The over-all reaction could be represented at this point by:

$$3S_3O_6^{-2} \rightarrow S_4O_6^{-2} + 2SO_4^{-2} + 2SO_2 + \tfrac{1}{8}S_8 \quad (10)$$

TABLE I

Raman intensity ratios and molar concentrations of sulfate, tri- and tetrathionate during the decomposition of 0.25 M trithionate after 83 hrs at 35°C

Time Hrs	$\frac{A_{1050}}{A_{1650}}$[a]	$[S_3O_6^{2-}]$ (M)[b]	$\frac{A_{1040}}{A_{1650}}$[a]	$[S_4O_6^{2-}]$ (M)	$\frac{A_{980}}{A_{1650}}$[a]	$[SO_4^{2-}]$ (M)
0	0.84	0.25	—	—	—	—
5	0.76	0.213	0.071	0.015	0.069	0.04
16.2	0.71	0.19	0.21	0.040	0.076	0.043
18	0.69	0.18	0.23	0.043	0.099	0.053
21.5	0.62	0.152	0.31	0.0580	0.12	0.060
24	0.64	0.16	0.42	0.076	0.13	0.065
30	0.59	0.14	0.36	0.065	0.17	0.081
34.5	0.58	0.137	0.28	0.052	0.16	0.076
36.5	0.51	0.112	0.38	0.069	0.19	0.09
41.5	0.46	0.095	0.42	0.075	0.18	0.088
49.8	0.45	0.092	0.43	0.076	0.24	0.105
55.5	0.50	0.11	0.48	0.085	0.20	0.093
65	0.41	0.078	0.54	0.095	0.25	0.11
68.7	0.36	0.063	0.55	0.097	0.27	0.118
72	0.40	0.077	0.54	0.094	0.23	0.103
78	0.38	0.068	0.55	0.096	0.27	0.115
98.6	0.33	0.054	0.47	0.083	0.28	0.118
117.5	0.30	0.048	0.41	0.073	0.30	0.125
135	0.26	0.0375	0.24	0.046	0.31	0.127

[a] Observed ratio of integrated solute to solvent areas.
[b] Calculated molar concentration ±2.5%.

TABLE II

Mass and redox balance for the decomposition products in 0.25 M trithionate solution after 111 hrs at 35°C

Species	$S_3O_6^{-2}$	$S_4O_6^{-2}$	SO_4^{-2}	SO_2	S_8
Concentration observed		0.07	0.09	0.023	—
Mass balance	3 × 0.06	4 × 0.07	2 × 0.09	2 × 0.032	0.034
Change in oxidation state		−0.8	2.7	0.7	−3.3
Calculated redox balance		−0.8 × 0.28	2.7 × 0.18	0.7 × 0.46	−0.1122
Observed redox balance		−0.224	−0.486	−0.322	−0.112

KINETICS

The concentration of the decomposition products and reagents in the decomposition of 0.25 M trithionate at 20°C is shown in Figure 6a as a function of time. Figure 6b shows the same data for the experiment at 50°C. The decomposition of tetrathionate 0.5 M is shown in Figure 7a at 20°C, and Figure 7b at 70°C. Similar curves were constructed for other temperatures and concentrations. For each system, the concentration of the reagents was then plotted in form of reciprocal concentrations *vs* time, and as the logarithm of the concentration change, log (C_t/C_0), as a function of time, as shown in Figures 8 and 9 for trithionate. The rate constants, calcu-

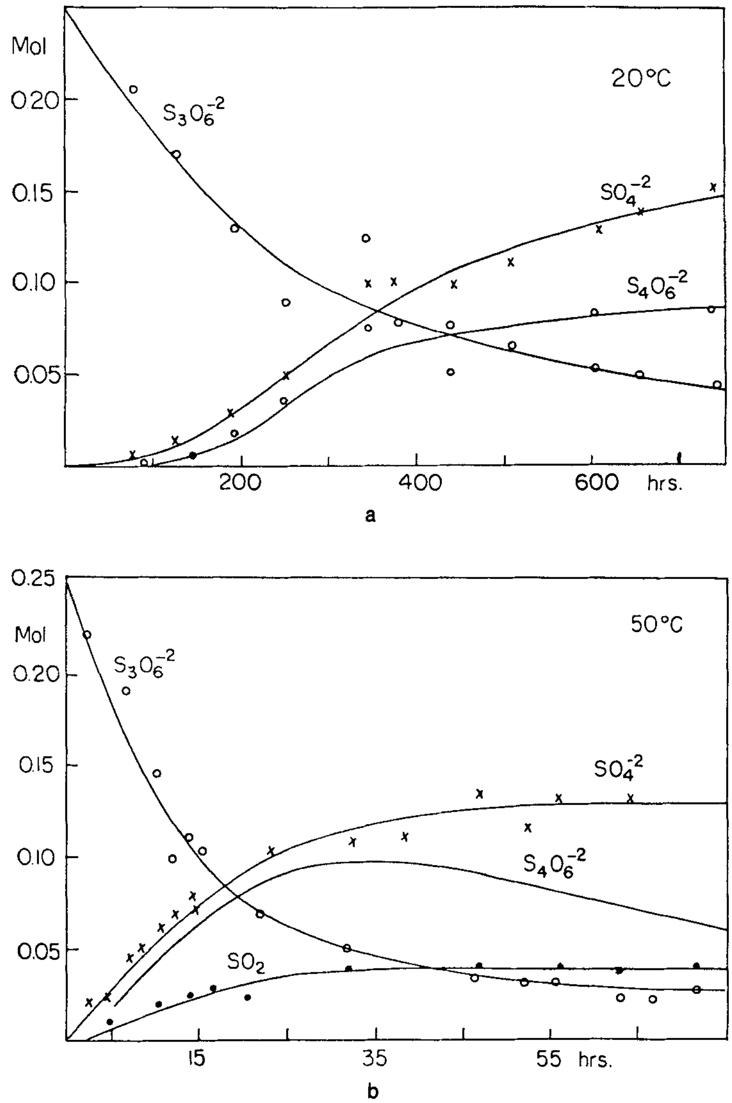


FIGURE 6 Trithionate decomposition products as a function of time. (a) at 20°C, and (b) at 50°C.

lated half-lives and the experimental half-lives, as well as the rate of formation of sulfate are summarized for all four temperatures in Table III for both trithionate and tetrathionate.

The decomposition of trithionate initially follows an exponential decay, Figure 8. Thus, the trithionate decay is first order, and one obtains:

$$d[S_3O_6^{-2}]/dt = k[S_3O_6^{-2}] = 3.22 \times 10^{-3} \tag{11}$$

Towards the end of the reaction, the curve does no longer fit due to competing reactions. We will later see that the onset of accelerated decomposition, i.e. the nonlinear part in Figure 8b, coincides with the build-up of tetrathionate, Figure 6.

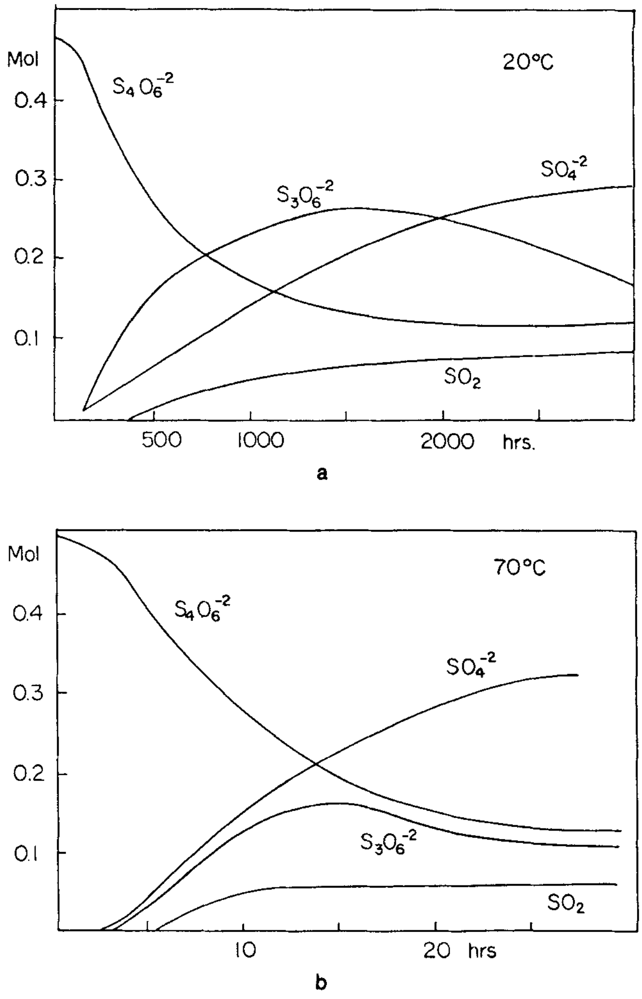
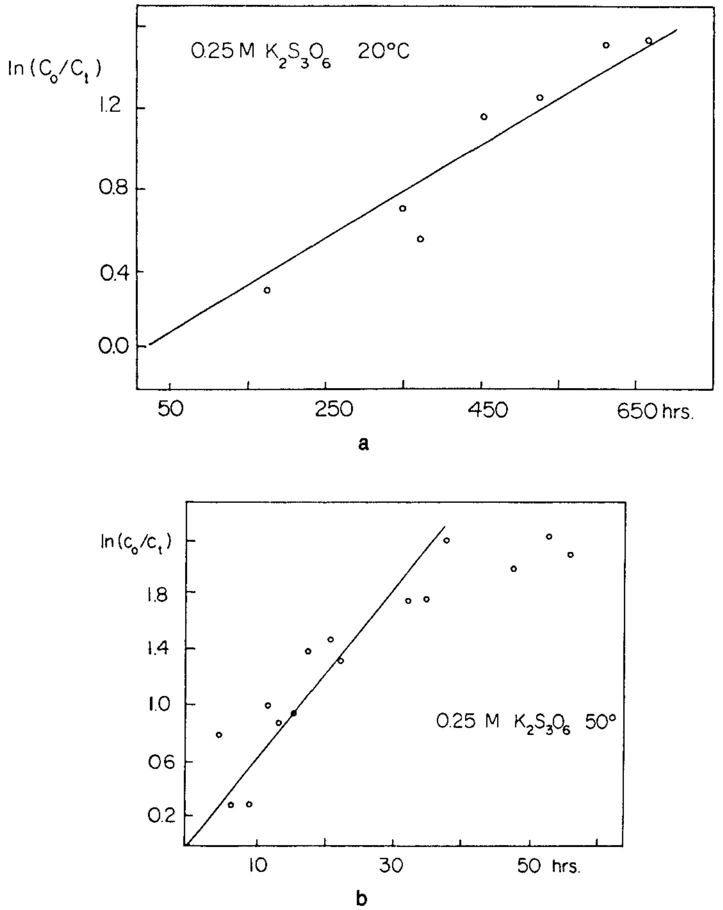


FIGURE 7 Tetrathionate decomposition products as a function of time. (a) 20°C, (b) 70°C.

Comparison of Figures 6 and 7 shows that the decay of trithionate and tetrathionate follow different kinetics, and that trithionate decays more rapidly than tetrathionate. Furthermore, there is a distinct lag between the appearance of sulfate and tetrathionate in the decomposition of trithionate, Figure 6, at all temperatures. This indicates that the tetrathionate is a secondary product. Assuming first order formation of sulfate, following Eq. (3), one obtains:

$$d[SO_4^{-2}]/dt = k[S_3O_6^{-2}] = 3.1 \times 10^{-3} \text{ hrs}^{-1} \ (20°C) \qquad (12)$$

The kinetic data for all solutions is summarized in Table III. At 35°C the decomposition rate of trithionate is about three times higher than at 20°C, and it is about twice the rate of sulfate formation at 35°C. This fact will be further explored below. At 50°C the sulfate formation rate is 2.87×10^{-2}. This corresponds to a value of 3×10^{-2} calculated by Kurtenacker[1] from his data obtained under similar conditions 50 years ago. From the temperature dependence in the range from 20°C to 70°C we obtained an activation energy of 15.2 kcal/mole for Eq. (1).



a

b

FIGURE 8 First order rate constant, log $(C_t/C_0) = f(t)$ for trithionate (a) 20°C, and (b) 50°C.

The decomposition of tetrathionate, Figure 7 shows a distinct induction period for both trithionate and sulfate. In this system sulfate appears simultaneously with the new polythionate. If the slope of the tetrathionate concentration is used to compute a first order rate constant, values between 8×10^{-4} and 14×10^{-4} are obtained, with an average of 10.15×10^{-4}, yielding a half-life of 683 hrs. The corresponding second order rate constant yields a value of 490 hrs. Since the experimental half-life is 520 hrs, we conclude that the reaction follows a second order mechanism:

$$d[S_4O_6^{-2}]/dt = K'[S_4O_6^{-2}] = 4.13\ M^{-1}\ hrs^{-1}\ (20°C) \qquad (13)$$

However, in this system, the sulfate formation rate fits again a first order reaction:

$$d[SO_4^{-2}]/dt = K[S_4O_6^{-2}] = 3.1 \times 10^{-3}\ hrs^{-1}\ (20°C) \qquad (14)$$

This value coincides with that for the sulfate formation from trithionate, Eq. (12). At 35°C the sulfate formation rate constant is 8.6×10^{-3} for tetrathionate and 9.5×10^{-3} for trithionate. At 50°C and 70°C the sulfate formation rate constants agree equally well. Thus, it seems probable that sulfate is formed in both systems by

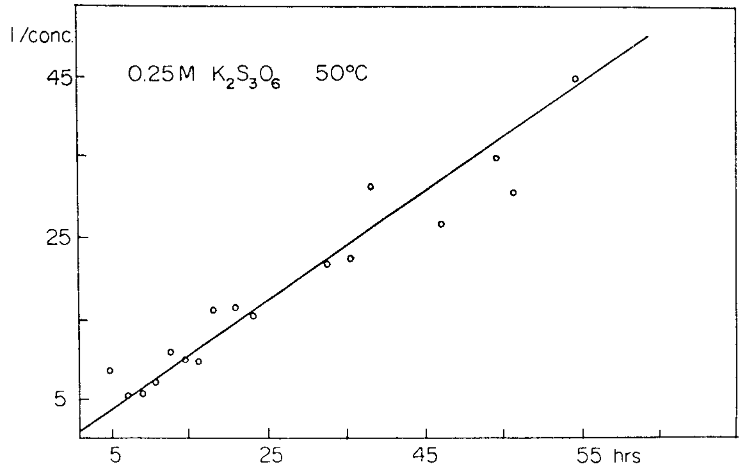


FIGURE 9 Second order rate constant for trithionate at 50°C.

the same mechanism. According to our interpretation, the formation of sulfate is connected in both systems with trithionate, and it is due to the direct hydrolysis of trithionate, Eq. (5). The stochiometry of the sulfate formation in both systems supports this conclusion.

The fate of pentathionate is known from earlier work.[1,2,5,6] It yields tetrathionate and elemental sulfur, and subsequently feeds the trithionate decay channel.

TABLE III

Summary of rate constants for the disappearance of the reagent, the formation of sulfate, and half-lives for tri- and tetrathionate at 20, 35, 50, and 70°C

(a) Trithionate (0.25 M)

T(°C)	$K(n = 1)^a$ hrs^{-1}	$T\frac{1}{2}$(calc) hrs^{-1}	$T\frac{1}{2}$(exp) hrs	$K(n = 1)^b$ hrs^{-1}
20	3.22×10^{-3}	216	207	3.1×10^{-3}
35	1.81×10^{-2}	38.2	36.2	9.5×10^{-3}
50	5.7×10^{-2}	12.2	11.0	2.87×10^{-2}
70	1.38×10^{-1}	5.1	5.7	5.9×10^{-2}

(b) 0.5 M Tetrathionate

T(°C)	$K'(n = 2)^c$ M^{-1} hrs^{-1}	$T'\frac{1}{2}$(calc) hrs	$T\frac{1}{2}$(exp) hrs	$K(n = 1)^b$ hrs^{-1}
20	4.1×10^{-3}	484.6	540	2.29×10^{-3}
35	2.79×10^{-2}	71.68	106	8.66×10^{-3}
50	3.18×10^{-2}	26.9	36	1.49×10^{-2}
70	2.48×10^{-1}	8.01	11.4	8.76×10^{-2}

[a] $\frac{d[S_3O_6^{2-}]}{dt} = K[S_3O_6^{2-}]$.

[b] $\frac{d[SO_4^{2-}]}{dt} = K[S_3O_6^{2-}]$.

[c] $\frac{d[S_4O_6^{2-}]}{dt} = K'[S_4O_6^{2-}]^2$.

The disappearance of thiosulfate is more complex, because thiosulfate can enter several different mechanisms. It is well known that thiosulfate can catalyze the conversion of polythionates:[1]

$$2S_4O_6^{-2} \xrightarrow{S_2O_3^{-2}} S_5O_6^{-2} + S_3O_6^{-2} \qquad (15)$$

It is evident that this reaction will rapidly overwhelm and obscure the original first order decay kinetics of the polythionates. This effect is compounded by the fact that the pH changes during the reactions (1) and (2). In our experiments we did not buffer our solutions to eliminate the pH effect, because all suitable buffers would have interfered with the spectral analysis of the system, and thus, the pH effect limits the accuracy of our kinetic data.

In the acidic decay of polythionate, thiosulfate by itself can build up sulfur chains,[16] as explained in Eqs. (8) and (9), yielding higher polythionates, sulfanemonosulfonates, and eventually, elemental sulfur allotropes, in a reversal of the well known sulfite degradation of elemental sulfur, which prevails at high pH.

CONCLUSIONS

The initial step in the decomposition of tetrathionate is the bimolecular disproportionation of tetrathionate into tri- and pentathionate with a second order rate constant of 4×10^{-3} at 20°C and 2.5×10^{-1} at 70°C. The initial step in the decomposition of trithionate involves hydrolysis yielding sulfate and thiosulfate in a first order reaction with a rate of 3.2×10^{-2} at 20°C and 1.4×10^{-1} at 70°C. Thiosulfate acts as a catalyst in the first reaction, and increases the rank of the sulfur chain, eventually yielding elemental sulfur. The kinetics of the polythionate decay are obscured by secondary reactions, and by the pH change which accompanies the decomposition of polythionates.

The over-all reaction for the decomposition of trithionate can be summarized from the previous reactions as:

$$S_3O_6^{-2} \rightarrow SO_4^{-2} + SO_2 + \tfrac{1}{8}S_8 \qquad (16)$$

Except for the choice of cyclo-octa-sulfur as the stable end allotrope, this reaction is identical with that derived by Debus[2] almost exactly one hundred years ago.

EXPERIMENTAL

Reagents: All chemicals except the polythionates were reagent grade and were used without further purification. Potassium trithionate was prepared by reaction of aqueous disulfite with monosulfur dichloride dissolved in petroleum ether[17,18] at 5°C. Potassium tetrathionate was prepared by reaction of disulfur dichloride in petroleum ether with aqueous disulfite. Potassium pentathionate was synthesized from thiosulfate and concentrated hydrochloric acid in the presence of arsenic trioxide at −10°C. All polythionates were recrystallized and vacuum dried before use. Aqueous solutions were purged with nitrogen and sealed on a vacuum line.

Spectral Equipment: Raman spectra were recorded on a Jobin-Yvon Ramanor double spectrometer, type H6-2. The 488.0 nm line of a Ar-Kr laser Coherent Radiation model Gr-4 was used as light source. The intensities reported in this paper are only valid for this line. Other lines yield different relative intensities.[9,10] Solution samples were sealed in a 6 mm o.d. borosilicate ampule. All spectrometer operations were controlled with a Nicolet NIC-300 Raman interface. The Raman scattering intensity was monitored with a photon counter from which the signals were scaled over a pre-selected dwell period and entered into a digital storage. The spectral resolution was 0.2 cm^{-1}. Normally, four spectral scans were integrated for each spectrum. The spectrum was monitored on a Hewlett-Packard 1304A display oscilloscope and plotted on a Nicolet Zeta digital plotter, and the data were stored on a Control Data "Hawk" dual-platter double density disk drive with a disk capacity of 4.57 megawords.

For evaluation, the spectra were recalled from storage, displayed on the oscilloscope, and the intensity and spectral scale expanded or contracted as desired. The spectrum was smoothed using the Savitsky-Galay least-square method. Spectral regions with overlapping vibrational bands were deconvoluted using a curve analyzer program. For this purpose, each spectral band was individually matched with a synthetic, Lorentzian curve, and the fitting of the resulting synthetic spectra was verified by subtraction from the experimental spectrum. A built-in curve integration program yielded directly numerical values for the area under each curve, and for the relative contribution of each band. Different operators obtained a reproducibility of ±5% in deriving relative integrated areas. The solution spectra were normalized relative to the 1650 cm^{-1} water band or the 937 cm^{-1} band of 0.1 M perchlorate[9,10] which was used as an internal standard. The suitability of the water band for quantitative work was based on earlier work.[9,10]

Kinetic Studies: Solute concentrations were determined as above by comparing the normalized solute scattering intensity with the calibration curves for pure compounds. The reliability of the procedure was tested by preparing synthetic mixtures. The accuracy was always better than ±20%, and usually better than ±10%.

During kinetic studies the sample tubes were kept at 20 ± 2°C or 35 ± 2°C in a Former Scientific Model 2006 water thermostat, or at 50 ± 2°C and 70 ± 2°C in an electric furnace. The pH of the solution was measured in a separate ampule containing 25 ml solution, kept side-by-side in the same thermostat, using a digital Electromak pH analyzer. All spectra were recorded after quenching the samples to room temperature. In early experiments, a large batch of tubes was prepared and each sample was used for only one measurement point. In later experiments, three sample tubes were used for the entire experiment and the spectrum of each tube was followed over the entire duration of the experiment. All experiments proved to be reproducible within ±10%.

ACKNOWLEDGMENT

The early part of this work was performed at the University of Washington with equipment purchased with Departmental NSF funds. The authors wish to thank Prof. J. Macklin for use of his equipment during that period. Final experiments were conducted at the University of California. This work was sponsored by the Office of Fossile Fuel, Morgantown Energy Lab., U.S. Department of Energy, via the Lawrence Berkeley Lab under engineering contract DE-AC03-76SF00098. The authors wish to thank Professors L. Brewer and R. E. Connick for use of their space and equipment, for many valuable discussions, and for continued encouragement. Messrs. K. Koshlap, A. Tini, and K. Ward helped with many experiments and recorded and evaluated many spectra.

REFERENCES

1. A. Kurtenacker, A. Mutschin and F. Stasny, *Z. All. Anorg. Chem.*, **224**, 399 (1935).
2. H. Debus, *J. Chem. Soc.*, **53**, 278 (1888), and *Ann.*, **244**, 76 (1888).
3. H. Wackenroder, *Arch. Pharm.*, **48**, 272 (1846).
4. B. Meyer, *Sulfur, Energy and Environment*, Elsevier, Amsterdam, 1977.
5. M. G. Fiordos, and A. Gelis, *Ann. Chim. Phys.*, **8**, 349 (1843).
6. H. Stamm and M. Goehring, *Z. Anorg. Allg. Chem.*, **250**, 226 (1942).
7. M. Schmidt and G. Talsky, *Ang. Chem.*, **70**, 312 (1958).
8. L. V. Haff, in *Analytical Chemistry of Sulfur Compounds*, J. H. Karchmer, Ed. Interscience-Wiley, New York, 1970. Chapter 4.
9. M. Ospina, PhD thesis, University of Washington, March 1982.
10. B. Meyer, M. Ospina, and L. Peter, *Anal. Chim. Acta.*, **117**, 301 (1980).
11. R. Steudel and H. J. Maeusle, *Z. Anorg. Allg. Chem.*, **448**, 165 (1980).
12. H. Wagner and H. Schreier, *Phosphorus and Sulfur*, **4**, 281 (1978).
13. D. Lyons and G. Nickless, Chapter 14 in *Inorganic Sulphur Chemistry*, G. Nickless ed., Elsevier, Amsterdam, 1968.
14. B. Meyer, L. Peter and K. Spitzer, *Inorg. Chem.*, **16**, 27 (1977).
15. M. Schmidt, *Z. Anorg. and Allg. Chem.*, **289**, 141 (1957).
16. R. E. Davis, *J. Am. Chem. Soc.*, **80**, 3565 (1958).
17. H. Stamm and M. Goehring, *Z. Anorg. Allg. Chem.*, **250**, 226 (1942).
18. F. Martin and L. Metz, *Z. Anorg. Allg. Chem.*, **127**, 83 (1923).