

CHROMATOGRAPHIC STUDIES ON SULPHUR COMPOUNDS
PART IV. THE DECOMPOSITION OF ACIDIFIED THIOSULPHATE AND
POLYTHIONATE SOLUTIONS

F. H. POLLARD, G. NICKLESS AND R. B. GLOVER

*Department of Chemistry,
The University, Bristol (Great Britain)*

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The products formed when an alkaline thiosulphate solution is acidified with mineral acid are very dependent on the conditions, *e.g.* concentration of thiosulphate and acid, rate of mixing and temperature.

With dilute acid, the usual products are sulphur, and sulphur dioxide:



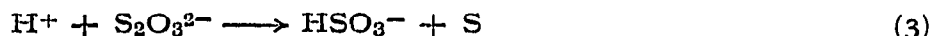
although at higher concentrations of acid, hydrogen sulphide has been detected and the solution is found to contain sulphuric acid and polythionic acids¹⁻⁵, while at medium acidities, sulphur oils are formed. There is often a time lag between the mixing of the solutions and the precipitation of sulphur which was found by LANDOLT⁶ to be directly proportional to the dilution of thiosulphate.

There are numerous postulated mechanisms with the primary intermediate considered to be thiosulphurous acid and sulphylic acid^{7,8}. While many mechanisms have been put forward to account for the observed facts, they all include unlikely intermediates or neglect the condition of acidity in the solution⁹.

SCHMIDT¹⁰ has shown that in non-aqueous solution anhydrous thiosulphuric acid decomposes into sulphur trioxide and hydrogen sulphide:



He assumes this is the primary step in the aqueous solution also:

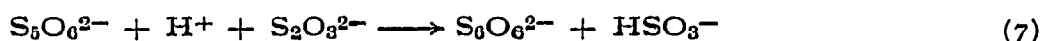
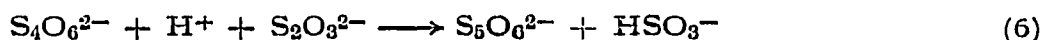
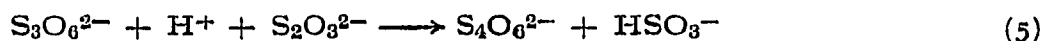


while eqn. (3) explains the formation of sulphite and sulphur.

The polythionates are prepared by the reaction of the products of reaction (2):

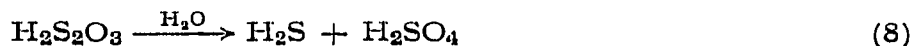


Now in acid solution, trithionate would react with excess thiosulphate to form higher thionates, *viz.*:

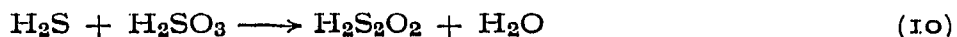


Thus in essence, the production of trithionate as the primary thionate, followed by build-up of higher thionates.

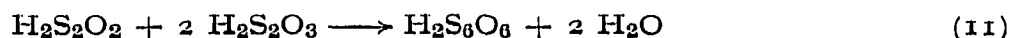
GOEHRING⁷ suggests the formation of thiosulphurous acid as an unstable intermediate:



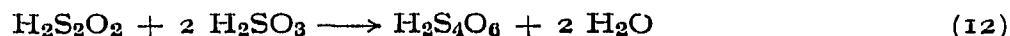
which is then followed by:



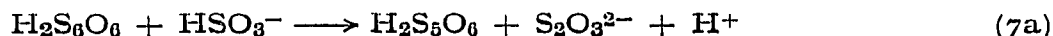
This intermediate immediately reacts with excess thiosulphate to yield $\text{S}_6\text{O}_6^{2-}$ which is then degraded by sulphite to produce the lower polythionates:



also:



then:



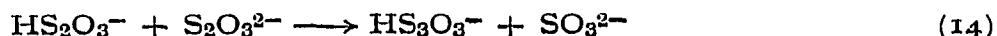
The serious objection to reactions such as (7a), is that it would be expected to move in reverse direction because of the large excess of thiosulphate and acid present.

Thus in this mechanism hexathionate is first formed, which is in contradiction to that of SCHMIDT¹⁰, where trithionate is formed. Thus it can be seen that positive identification of the primary thionate would help to decide which mechanism is most likely.

DAVIS⁹ contributes yet another explanation:



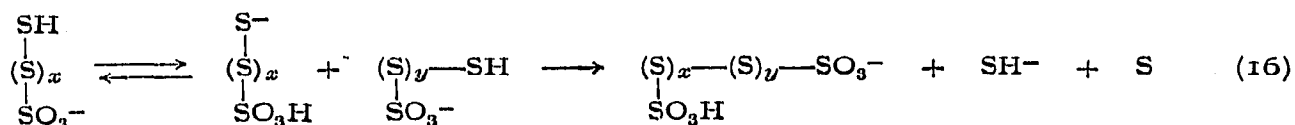
followed by:



thus the sulphane-monosulphonic acids¹⁰ are built up to:

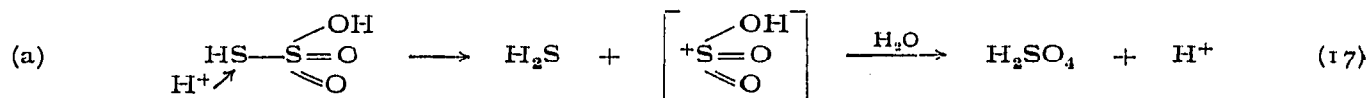


Polythionates are formed by:

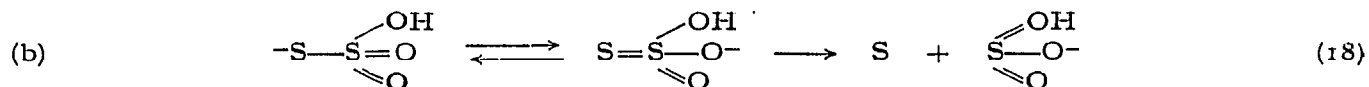


On this theory, polythionates from $\text{H}_2\text{S}_3\text{O}_6$ to $\text{H}_2\text{S}_{17}\text{O}_6$ should be formed, while the sulphur is depositing. DAVIS⁹ based his postulates and kinetics on the results of LA MER and co-workers¹¹⁻¹⁴ who studied the system spectrophotometrically in dilute aqueous solution at constant ionic strength. Chemical differentiation of the species formed was not made.

POLLARD AND JONES¹⁵ suggest a further possibility, and consider that thio-sulphate can degrade in two ways depending on the acidity of the solution:



which occurs in strongly acid solution only, and:



This breakdown yields sulphur and bisulphite which occur in weakly acid solutions. Now considering three conditions of acidity.

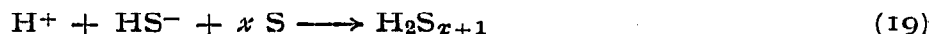
(i) *Weakly acid solution.* The reaction is entirely represented by (18).

(ii) *Strong acid solution.* Reaction (17) is the major breakdown but (18) also contributes $\text{H}_2\text{S}_2\text{O}_3$.

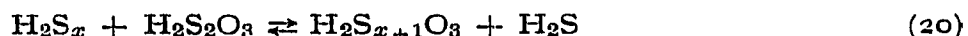
This is followed by reaction (10) and then by reaction of thiosulphate and sulphite with the formed thiosulphurous acid, polythionates up to 6 sulphur atoms are produced.

(iii) *Medium acidity.* In a strict range of acidities, sulphur hydrides (sulphanes) of high molecular weight are formed as oils^{16,17}. Their formation may be explained by assuming reaction (19) to occur to a slight extent, while (18) is the major reaction.

The formation of oils occurs by:



The absence of these oils at low acidities is explained by non-occurrence of reaction (17), whilst at high acidities it is postulated they occur only transiently, but react with thiosulphuric acid to produce sulphane-monosulphonic acids which have increased stability in concentrated acid solution:

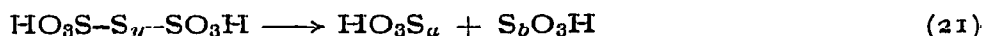


Polythionate formation is accounted for by the reaction, which shows



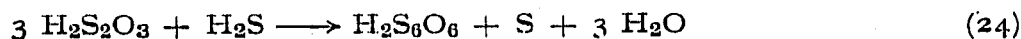
the formation of higher thionates than $\text{S}_6\text{O}_6^{2-}$ since x cannot be less than 1.

Breakdown of the higher polythionates into free radicals follows, with recombination to smaller units:

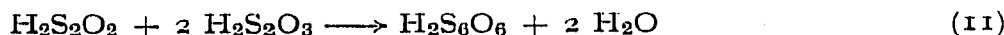
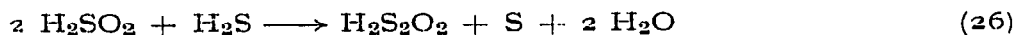


Thus a detailed chromatographic study of the acid decomposition of thiosulphate, to determine the order of formation of the thionates and the stability of these species in such acid solutions might well assist to elucidate the mechanisms involved.

According to YANITSKII AND VALANCHUNAS^{18,19} when sulphide was present with the ratio of $S_2O_3^{2-} \cdot S^{2-} \geq 3.1$, no free hydrogen sulphide remained, and 87–92 % of the original sulphur was in the form of polythionates. The stoichiometric equation is:



When hypophosphorous acid was substituted for H_2S , 95 % of total sulphur was obtained as pure hexathionate. The equations to represent the formation of this acid were given as:



Fractionation of the benzidine salts showed the presence of octathionate. These workers further report that when the available sulphur was increased by the addition of sulphite, the major product was octathionate with some hexathionate, and when a ratio of thiosulphate:sulphide:sulphite of 6:7:5 was used, 98 % of the thiosulphate sulphur occurred as octathionate.

In this case too, it seems that a qualitative investigation by paper chromatographic techniques would yield interesting confirmation of the presence of octathionate, since the Russian workers analysed their products by fractional precipitation of the benzidine salts.

EXPERIMENTAL

*Rear-phase chromatography*²⁰

Solvent: Tertiary butanol, 15 ml; acetone 65 ml; water 25 ml; potassium acetate 0.5 g; pH value of solution 9.6 (glass electrode).

When a paper chromatogram is eluted with this solvent, two phases are formed on the paper by frontal analysis. The leading phase contains free acetic acid, whilst the rear phase contains a high concentration of potassium ions. If the thionates are adsorbed on to the chromatogram whilst dry, and then eluted, the leading phase reaches the thionates and hydrolysis occurs by means of the unadsorbed hydrogen ions in the solvent, giving free polythionic acids. This process stops when all the free hydrogen ions in the area covered by the original spot are used up, and thus the thionates are present both as potassium and free acid salts. The acid salts travel faster than the salts, separation occurs, and on developing the chromatograms, two spots are obtained from a single thionate.

The "rear-phase" technique essentially consists of ensuring that the thionates remain as single spots by eluting them as potassium salts only. This is achieved by allowing the phase boundary to pass the starting line before the solution of the thionates is applied to the paper.

Even if the thionate is applied in concentrated hydrochloric acid, only one spot is obtained, the thionate being converted to the potassium salt by the buffering action of the high concentration of the potassium ions in the rear phase. The only effect noticed with such acid is slight distortion of the trithionate and tetrathionate spots due to displacement by the chloride ion interposed between them.

Apparatus

The chromatograms were run in a large glass tank (46 cm × 30 cm × 41 cm) having a ground glass edge, and plate glass lids ground against each other, rendering the tank vapour-tight. The tank contained four solvent troughs, 2.5 cm wide, 25 cm long, supported 1 cm from the top of the tank by a glass frame. At either end of each trough was a supporting glass bar, and at either side a glass bar to prevent the trough sliding along. A further 4 cm away was another horizontal bar which acted as a support for the filter paper, and provided the horizontal portion of the chromatogram for *in situ* adsorption of the solutes. The lids were arranged so that a hole, 0.6 cm diameter, was directly over the centre of each trough, and a long slit over the starting line of the chromatogram (situated approximately half-way between the trough and filter paper supporting bar). The slits, covered by a thin plate glass strip during the equilibration and elution, were only uncovered to admit the samples of solute. The circular holes were likewise plugged with rubber bungs except during the admission of the solvent.

Procedure

Whatman No. 1 paper was used for all "rear-phase" chromatography. The strips were cut out so that the solvent flowed parallel to the machine direction of the paper, with the starting line 6.5 cm from one end. Thus when this end of the paper was folded, and placed in the solvent trough, the solvent feed was 2.5 cm from the starting line and located directly beneath a slit in the tank lid. The bottom of the chromatogram was folded, forming a pad, and secured with paper clips. The length of the paper from the top to the pad was 46 cm. In this manner two objects were achieved:

(a) the paper did not trail on the bottom of the tank, and (b) there was less decrease in velocity of the solvent due to it being allowed to run off the end of the paper.

Equilibration was carried out by placing four Petri dishes in the bottom of the tank, each containing about 20 ml of solvent. The chromatogram strips were in place, and the tank sealed during this period.

After a 12 h period, the solvent was poured into the troughs and allowed to elute the paper, this process being known as pre-elution. Normally the solvent contained 1% w/v Phenol Red to indicate the position of the phase boundary. This was omitted in certain cases where it would interfere with the detecting spray used after eluting the solutes. When the phase boundary was marked in this way, it was used as an indication of the length of pre-elution needed, *i.e.* the samples were admitted when the distance between the phase boundary and the starting line was sufficient to ensure that no double spotting occurred. The samples were taken into thin drawn-out glass tubes by capillary action and these were held in contact with the paper for about 3 sec. Thus the sample was transferred to the paper. The slit was closed again and elution allowed to take place. After about 10 h, the chromatograms were removed and sprayed with developing agent, washed and dried.

The actual length of the equilibration, pre-elution and elution periods depended on the temperature at which these processes were carried out, and it was best to elute chromatograms at lower temperatures, *ca.* 10°.

Detection of thionates

The chromatograms were sprayed with 0.5 N silver nitrate solution, and warmed in

front of an electric fire to decompose the unstable silver thionates to silver sulphide and sulphur. Unless the chromatograms were washed free of the excess silver nitrate, they darkened on exposure to the light. The only reliable method was to wash them in distilled water, then in a 10% w/v solution of sodium thiosulphate, and finally in clean distilled water. The chromatograms were then dried. The sensitivity of the method is increased by viewing the dried chromatograms under ultra violet light when $7 \cdot 10^{-6}$ g of thionate over 0.5 cm^2 of developed zone is clearly visible.

Detection of other species

(i) *Dithionate*. 1% Benzidine in absolute alcohol + 0.001 M potassium permanganate gives a blue spot on a pale brown background.

(ii) *Sulphite*. 5% w/v zinc sulphate solution plus 5% sodium nitroprusside solution (freshly prepared) gives a red colour.

(iii) *Rongalite* (sodium formaldehyde sulphoxylate). 0.1 N silver nitrate solution gives silver sulphide and metallic silver.

(iv) *Sulphide*. 0.1 N silver nitrate solution gives brown-black silver sulphide.

(v) *Sulphate*. 0.1 M barium chloride solution plus sodium rhodizonate solution produces a white spot on a pink background.

R_F values

The R_F values given in Table I were calculated taking $\text{S}_4\text{O}_6^{2-} = 1.0$ as the standard, this was because of the difficulty of calculating true R_F values due to the spots being applied to the chromatograms after the solvent front had passed the starting line.

TABLE I
 R_F VALUES OF SULPHUR COMPOUNDS

Anion	R_F	Anion	R_F
SO_4^{2-}	0.02	SO_3^{2-}	0.77
S^{2-}	0.04	$\text{S}_2\text{O}_8^{2-}$	0.89
$\text{S}_2\text{O}_3^{2-}$	0.11	$\text{S}_4\text{O}_6^{2-}$	1.00
$\text{S}_2\text{O}_6^{2-}$	0.38	$\text{S}_5\text{O}_6^{2-}$	1.25
$\text{S}_3\text{O}_6^{2-}$	0.67	$\text{S}_6\text{O}_6^{2-}$	1.43
Rongalite	0.71		

Thus by combining a knowledge of R_F values and sprays, the species may be identified.

RESULTS

A preliminary study of the stability of polythionates and thiosulphate in hydrochloric acid

The aims of this investigation were to determine:

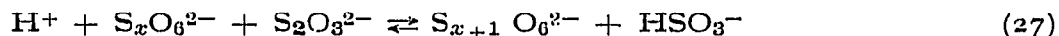
(a) The strength of hydrochloric acid in which the three lower polythionates were stable.

(b) The effects of thiosulphate on these stabilities.

(c) The effect of formaldehyde solution in these stabilities.

(d) The products from the decomposition of thiosulphate.

Many workers²¹⁻²⁵ have suggested that in reaction mixtures, higher polythionates are built up from lower polythionates by the reaction with thiosulphate:



If this is so, addition of thiosulphate to the solution should increase the higher polythionates present. Formaldehyde should remove the bisulphite ion from the equilibrium, and also assist the formation of the higher polythionates.

In this series of experiments, the thionate solution was placed in the reaction vessel, followed by hydrochloric acid. To the mixture so formed, thiosulphate and then 30 % formaldehyde solution were added where indicated, and left for 12 h at room temperature.

Stability of trithionate in hydrochloric acid

In experiments Nos. 1-8, 0.110 *M* potassium trithionate solution, and in experiments Nos. 9-13, 0.283 *M* potassium trithionate were used. In each reaction the HCl required was added to 1 ml of thionate solution. Each acidity was duplicated, and 1 ml of water was added to the first sample, whilst 1 ml of 30 % formaldehyde solution was added where indicated. This procedure was used in order that both the solution with the formaldehyde and that in which it was absent, would have the same total acidity. Results are given in Table II.

TABLE II
STABILITY OF POTASSIUM TRITHIONATE IN HCl

Expt. No.	Molarity of trithionate	Molarity of HCl	Analyses after 12 h*	
			Formalin absent	Formalin present
1	0.055	—	$\text{S}_3\text{O}_6^{2-}$	$\text{S}_3\text{O}_6^{2-}$
2	0.037	0.33	$\text{S}_3\text{O}_6^{2-}$	$\text{S}_2\text{O}_3^{2-}$
3	0.028	1.5	$\text{S}_3\text{O}_6^{2-}$	—
4	0.037	2	$\text{S}_3\text{O}_6^{2-}$ + slight S	—
5	0.028	3	$\text{S}_3\text{O}_6^{2-}$ + slight S	—
6	0.028	4.5	$\text{S}_3\text{O}_6^{2-}$ + slight S	—
7	0.0185	6	$\text{S}_3\text{O}_6^{2-}$ + slight S	—
8	0.0185	7	$\text{S}_3\text{O}_6^{2-}$ + slight S	—
9	0.047	6	$\text{S}_3\text{O}_6^{2-}$ + slight S	—
10	0.031	7	$\text{S}_3\text{O}_6^{2-}$ + slight S	—
11	0.031	8	$\text{S}_3\text{O}_6^{2-}$ + slight S	—
12	0.031	9	$\text{S}_3\text{O}_6^{2-}$ + $\text{S}_4\text{O}_6^{2-}$ + S	—
13	0.013	10	$\text{S}_3\text{O}_6^{2-}$ + $\text{S}_4\text{O}_6^{2-}$ + S + t $\text{S}_6\text{O}_6^{2-}$	—

* t = trace.

Trithionate is quite stable for up to 12 h in the range 0-1.5 *M* hydrochloric acid, above this acidity decomposition occurs to precipitate sulphur, while in strong acid conditions (> 8 *M* HCl) some tetra- and hexathionates are formed.

Formalin catalyses the decomposition of trithionate so quickly that no thionates are present in acidities greater than about 0.3 *M* acid after 12 h.

Stability of tetrathionate in hydrochloric acid

In experiments Nos. 14-21, 0.085 *M* potassium tetrathionate solution was used, while in experiments Nos. 22-26, a solution of 0.292 *M* potassium tetrathionate was employed. The reaction conditions were obtained as described for trithionate, and the results are given in Table III.

TABLE III
STABILITY OF POTASSIUM TETRATHIONATE IN HCl

Expt. No.	Molarity of tetrathionate	Molarity of HCl	Analysis after 12 h*	
			Formalin absent	Formalin present
14	0.047	Nil	S ₄ O ₆ ²⁻	S ₄ O ₆ ²⁻ , S ₃ O ₆ ²⁻ , S ₅ O ₆ ²⁻ + S
15	0.032	0.33	S ₄ O ₆ ²⁻	S ₄ O ₆ ²⁻ , t S ₂ O ₆ ²⁻ , S ₅ O ₆ ²⁻ + S
16	0.024	1.5	S ₄ O ₆ ²⁻	S ₄ O ₆ ²⁻ + S
17	0.032	2	S ₄ O ₆ ²⁻	S
18	0.024	3	S ₄ O ₆ ²⁻	S
19	0.024	4.5	S ₄ O ₆ ²⁻	S
20	0.016	6	S ₄ O ₆ ²⁻	S
21	0.016	7	S ₄ O ₆ ²⁻	S
22	0.049	6	S ₄ O ₆ ²⁻	S
23	0.033	7	S ₄ O ₆ ²⁻	S
24	0.033	8	S ₄ O ₆ ²⁻	S
25	0.036	7.9	S ₄ O ₆ ²⁻	S
26	0.013	10.0	S ₄ O ₆ ²⁻ + S	S

* t = trace.

Tetrathionate is stable for up to 12 h even in 8 *M* hydrochloric acid. Only in the strongest acid media, *ca.* 10 *M*, did the degradation of S₄O₆²⁻ occur, to deposit sulphur.

Formaldehyde assists the decomposition of tetrathionate, and at low acidities up to 1.5 *M* HCl, tri- and penta-thionates are formed. At greater acidities, degradation is complete, and only S is observed.

Stability of pentathionate in hydrochloric acid

In experiments Nos. 27-34, 1 ml of 0.106 *M* potassium pentathionate, and in experiments Nos. 35-39, 1 ml of 0.302 *M* potassium pentathionate were employed. Other conditions were analogous to those for trithionate. The results given in Table IV.

Pentathionate is unstable in hydrochloric acid solutions of low acidity, 0-2 *M*, but is stable for up to 12 h in the range 3.0-6.9 *M*. At greater acidities tetrathionate, hexathionate and sulphur appear due to disproportionation of pentathionate.



The results obtained in the presence of formalin are interesting as evidence for the production of higher thionates than hexathionate was obtained. Thus hepta- and octa-thionates are observed in the range 4.5 to 6.9 *M* hydrochloric acid. Above this range the only product found was sulphur. This phenomenon is worthy of detailed re-examination, especially in a quantitative manner.

The influence of sodium thiosulphate

Trithionate. The experimental details were as before, except for the addition of 1 ml

TABLE IV
 STABILITY OF PENTATHIONATE IN HCl

Expt. No.	Molarity of pentathionate	Molarity of HCl	Analyses after 12 h*	
			Formalin absent	Formalin present
27	0.053	—	$S_5O_6^{2-}$, t $S_4O_6^{2-}$	$S_5O_6^{2-}$, t $S_4O_6^{2-}$
28	0.035	0.33	$S_5O_6^{2-}$, t $S_4O_6^{2-}$	$S_5O_6^{2-}$, t $S_4O_6^{2-}$
29	0.0265	1.5	$S_5O_6^{2-}$, t $S_4O_6^{2-}$	$S_5O_6^{2-}$, t $S_4O_6^{2-}$
30	0.035	2.0	$S_5O_6^{2-}$, t $S_4O_6^{2-}$	$S_5O_6^{2-}$, t $S_4O_6^{2-}$
31	0.265	3.0	$S_5O_6^{2-}$	$S_5O_6^{2-}$, $S_6O_6^{2-}$
32	0.265	4.5	$S_5O_6^{2-}$	$S_5O_6^{2-}$ + S
33	0.0176	6.0	$S_5O_6^{2-}$	$S_5O_6^{2-}$, $S_7O_6^{2-}$ + S
34	0.0176	6.9	$S_5O_6^{2-}$	$S_5O_6^{2-}$, $S_7O_6^{2-}$ + S
35	0.05	6	$S_5O_6^{2-}$	S
36	0.034	7	$S_5O_6^{2-}$, t $S_4O_6^{2-}$, t $S_6O_6^{2-}$	S
37	0.036	8	$S_5O_6^{2-}$ + t S	S
38	0.038	7.9	$S_5O_6^{2-}$ + t S	S
39	0.014	10	$S_5O_6^{2-}$ + t S	S

* t = trace.

of 0.01 M sodium thiosulphate to each solution. Experiments Nos. 40–47 contained 1 ml of 0.1021 M potassium trithionate. Experiments Nos. 48–52 contained 1 ml of 0.2829 M potassium trithionate. The results are given in Table V.

Trithionate is stable in the presence of thiosulphate in the range 0 to 1.2 M HCl, at greater acidities sulphur is formed. As the acidity rises above 7 M tetra-, penta- and hexathionate are observed to be present.

Formaldehyde again assists the degradation of trithionate so that no thionates were present in acidities greater than 2.4 M HCl. Comparing these results with those obtained in Table II, it is seen that the occurrence of tetra-, penta- and hexa-thionate is increased at the high acidities, and the decomposition in formalin is retarded. Table V must also be compared with Table IX in the next section, since much of these effects will come from the degradation of thiosulphate with acid.

 TABLE V
 STABILITY OF TRITHIONATE IN THE PRESENCE OF THIOSULPHATE

Expt. No.	Molarity of trithionate	Molarity of HCl	Analyses after 12 h*	
			Formalin absent	Formalin present
40	0.034	—	$S_2O_3^{2-}$, $S_3O_6^{2-}$	$S_2O_3^{2-}$, $S_3O_6^{2-}$
41	0.0256	0.25	$S_3O_6^{2-}$	$S_2O_3^{2-}$, $S_3O_6^{2-}$
42	0.02	1.2	$S_3O_6^{2-}$	$S_2O_3^{2-}$, $S_3O_6^{2-}$
43	0.0256	1.33	$S_3O_6^{2-}$ + S	$S_2O_3^{2-}$, $S_3O_6^{2-}$
44	0.02	2.4	$S_3O_6^{2-}$ + S	$S_2O_3^{2-}$
45	0.02	3.6	$S_3O_6^{2-}$ + S	—
46	0.015	5.0	$S_3O_6^{2-}$ + S	—
47	0.015	6.0	$S_3O_6^{2-}$ + S	—
48	0.0314	6.7	$S_3O_6^{2-}$ + S	—
49	0.021	7.38	$S_3O_6^{2-}$, t $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$ + S	—
50	0.022	8.47	$S_3O_6^{2-}$, t $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$ + S	—
51	0.022	8.53	$S_3O_6^{2-}$, t $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$ + S	—
52	0.010	9.37	S	—

* t = trace.

TABLE VI

STABILITY OF TETRATHIONATE IN THE PRESENCE OF THIOSULPHATE

Expt. No.	Molarity of tetrathionate	Molarity of HCl	Analyses after 12 h*	
			Formalin absent	Formalin present
53	0.032	—	$S_2O_3^{2-}, S_4O_6^{2-}$	$S_2O_3^{2-}, S_4O_6^{2-}$
54	0.024	0.25	$S_4O_6^{2-}$	$S_2O_3^{2-}, S_4O_6^{2-}$
55	0.019	1.2	$S_4O_6^{2-}$	$S_2O_3^{2-}, S_4O_6^{2-}$
56	0.024	1.33	$S_4O_6^{2-}$	$S_2O_3^{2-}, S_4O_6^{2-}$
57	0.019	2.4	$S_4O_6^{2-}$	$S_2O_3^{2-}, S_4O_6^{2-}$
58	0.019	3.6	$S_4O_6^{2-}$	$S_2O_3^{2-}, S_4O_6^{2-}$
59	0.0135	5.0	$S_4O_6^{2-}$	$S_4O_6^{2-} + S$
60	0.0135	6.0	$S_4O_6^{2-}$	S
61	0.036	6.74	$S_4O_6^{2-}$	S
62	0.022	7.38	$S_4O_6^{2-}$	S
63	0.023	8.47	$S_4O_6^{2-}, t S$	S
64	0.023	8.53	$S_4O_6^{2-}, t S_5O_6^{2-}, S_6O_6^{2-} + S$	S
65	0.010	9.37	$S_4O_6^{2-}, t S_5O_6^{2-}, S_6O_6^{2-} + S$	S

* t = trace.

Tetrathionate. The conditions were as for trithionate (under this heading). In experiments Nos. 53–60 0.0948 *M* potassium tetrathionate, in experiments Nos. 61–65 0.2923 *M* potassium tetrathionate was used. The results are given in Table VI.

Tetrathionate is stable in the presence of thiosulphate in the range 0 to 7.4 *M* HCl. At greater acidities penta- and hexa-thionates are formed while S is deposited. Formalin again assists the breakdown of $S_4O_6^{2-}$, so that no thionates are present at acidities greater than 5 *M* hydrochloric acid.

Comparing the results of Table VI with those of Tables III and IX, it is seen that penta- and hexa-thionates occur at high acidities in the presence of thiosulphate, but not when it is absent. Thiosulphate once again retards the decomposition of formalin.

Pentathionate. The conditions were as for the experiments with trithionate

TABLE VII

STABILITY OF PENTATHIONATE IN THE PRESENCE OF THIOSULPHATE

Expt. No.	Molarity of pentathionate	Molarity of HCl	Analyses after 12 h*	
			Formalin absent	Formalin present
66	0.038	—	$S_4O_6^{2-}, S_5O_6^{2-} + S$	$S_4O_6^{2-}, S_5O_6^{2-} + S$
67	0.028	0.25	$S_4O_6^{2-}, S_5O_6^{2-}, S_6O_6^{2-}$	$S_4O_6^{2-}, S_5O_6^{2-}, S_6O_6^{2-}$
68	0.023	1.20	$S_5O_6^{2-}, S_6O_6^{2-}$	$S_5O_6^{2-}, S_6O_6^{2-}$
69	0.028	1.33	$S_5O_6^{2-}, S_6O_6^{2-}$	$S_5O_6^{2-}, S_6O_6^{2-}$
70	0.023	2.4	$S_5O_6^{2-}, S_6O_6^{2-}$	$S_5O_6^{2-}, S_6O_6^{2-}$
71	0.023	3.6	$S_5O_6^{2-}, S_6O_6^{2-}$	$S_8O_6^{2-} + S$
72	0.016	5.0	$S_5O_6^{2-}, S_6O_6^{2-}$	$S_8O_6^{2-} + S$
73	0.016	6.0	$S_5O_6^{2-}, S_6O_6^{2-}$	S
74	0.036	6.74	$S_5O_6^{2-}, S_6O_6^{2-}$	S
75	0.0235	7.38	$S_5O_6^{2-}, S_6O_6^{2-} + t S$	S
76	0.025	8.47	$S_5O_6^{2-}, S_6O_6^{2-} + t S$	S
77	0.025	8.53	$S_5O_6^{2-}, S_6O_6^{2-} + t S$	S
78	0.011	9.37	$S_5O_6^{2-}, S_6O_6^{2-} + t S$	S

* t = trace.

solution. In experiments Nos. 66-73 0.126 *M* potassium pentathionate was used. In experiments Nos. 74-78 0.3025 *M* potassium pentathionate was used. The results are given in Table VII.

Pentathionate is unstable in the presence of thiosulphate in neutral solution, and at low acidities (0-2.5 *M* HCl), $S_4O_6^{2-}$ is formed, whilst at any acidity greater than this $S_6O_6^{2-}$ also occurs. Formalin again assists the production of octathionate in the range 3.6 to 6 *M* HCl, while at higher acidities there is complete degradation to sulphur. Comparing these results with those of Table IV, it is seen that hexathionate occurs at much lower acidities when the thiosulphate ion is present, both in the presence and absence of formalin.

GENERAL CONCLUSION AND DISCUSSION

The region of stability of the thionates under investigation in hydrochloric acid, have been tabulated in Table VIII.

TABLE VIII
STABILITY OF THIONATES

Anion	Range of stability			
	Without thiosulphate		With thiosulphate	
	Formalin absent	Formalin present	Formalin absent	Formalin present
Trithionate	Neutral to 1.5 <i>M</i>	Neutral	Neutral to 1.2 <i>M</i>	Neutral to 1.3 <i>M</i>
Tetrathionate	Neutral to 5 <i>M</i>	—	Neutral to 7.4 <i>M</i>	Neutral to 3.6 <i>M</i>
Pentathionate	3-6 <i>M</i>	1.5 <i>M</i>	—	—

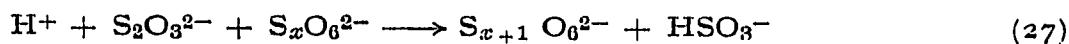
Whilst these results are only qualitative, and a further detailed quantitative investigation is needed, experiments being repeated at intermediate acidities, and also at different time intervals, some general principles are shown.

(i) As the number of sulphur atoms in the polythionic acids increases, the region of stability is formed at higher acidities.

(ii) Thiosulphate undergoes exchange reactions with the thionates, the products depending on the acidities of the media, but also prolongs the existence of tri- and tetrathionate in formalin.

(iii) Formalin also accelerates reaction, probably by the removal of any sulphite ions from the solutions as formaldehyde bisulphite.

The absence of higher thionates in solutions of trithionate may be explained by the instability of these substances at low acidities, while at higher acidities trithionate itself is unstable. Each time the SO_3^{2-} fraction is hydrolysed off, it is complexed by the formalin, and thus the total thionate sulphur content of the solution is diminished. Eventually all the sulphur is converted into the formaldehyde bisulphite form and free sulphur, which is formed by complete degradation of a high polythionate:



When $x = 6$ or 7 , it appears such thionates have very limited stability ranges of acidity; outside these ranges complete degradation rapidly occurs.

Since this work was undertaken, Blasius and co-workers^{25,26} have extended these studies to alkaline pH's, and the results are confirmatory. All the reactions are slow, which allows a correct analysis of the polythionates present by the paper-chromatographic method.

Decomposition of sodium thiosulphate

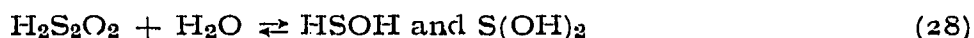
30.0 mmol of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 25 ml of water was added to 40 mmol of hydrochloric acid (20 ml of 2 *M* acid). The solution was analysed for thionate at time intervals. Sulphur precipitated immediately. The results are given in Table IX.

TABLE IX
DECOMPOSITION OF THIOSULPHATE

Time (min)	Thionates present
0	$\text{S}_2\text{O}_3^{2-}$
0.5	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$
1.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$
2.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$
4.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$
8.5	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$
11.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$
13.5	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$
20.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$
26.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$
32.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$
39.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$
43.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$
67.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$, t $\text{S}_5\text{O}_6^{2-}$
80.0	$\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{S}_5\text{O}_6^{2-}$

These results confirm BLASIUS AND BURMEISTER's results²⁸ and show that the first polythionate formed in the decomposition of thiosulphate in 1 *M* hydrochloric acid is trithionate. The remaining species are built up from this as the decomposition continues. This supports SCHMIDT's¹⁰ mechanism which regards the primary reaction as the decomposition of thiosulphuric acid as depicted by eqn. (2), followed by eqn. (4), and reactions with excess thiosulphate to yield higher thionates.

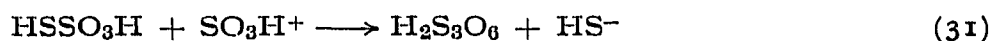
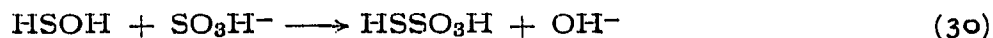
Another possible mechanism is the formation of thiosulphurous acid¹⁵ which is hydrolysed to monosulphurhydrate^{27,28} and sulphylic acid:



The sulphylic acid reacts with sulphite to give trithionate:



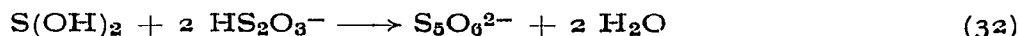
or more probably:



As the concentration of trithionate increases, so formation of higher thionates proceeds.

Because $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$ are not found in the early stages of the reaction, it must be assumed that:

- the hydrolysis according to eqn. (28) lies to the right hand side,
- that reaction (29) is fast compared to the reaction:



cf. ref. 29 and 30.

A comparison of the rates of reaction of sulphite, and thiosulphate with sulphur dichloride in aqueous solution, is being undertaken to help to substantiate the above mechanism.

Investigations on the effect of the addition of sulphide, hypophosphite and sulphite on the acid decomposition of sodium thiosulphate^{18,19}

50 mmol of sodium thiosulphate and 12 mmol of sodium sulphide or hypophosphite were dissolved separately in 35 ml of water. This was added to 35 ml of concentrated hydrochloric acid at -5° . Sulphur deposited immediately in the sulphide experiment and in 45 min with the hypophosphite. The mixture was analysed chromatographically and the results are given in Table X.

TABLE X
REACTION OF THIOSULPHATE WITH SULPHIDE OR HYPOPHOSPHITE

Time (min)	Polythionates present (F) $S_nO_6^{2-}$	
	Sulphide	Hypophosphite*
1	<u>4</u> , <u>5</u> , <u>6</u> , 7, 8	<u>8</u>
5	<u>4</u> , <u>5</u> , <u>6</u> , 7, 8	<u>8</u>
10	<u>4</u> , <u>5</u> , <u>6</u> , 7, 8	t 4, 5, 6, <u>8</u>
15	4, 5, <u>6</u> , 7, 8	4, 5, 6, <u>8</u>
20	4, 5, <u>6</u> , 7, 8	4, 5, 6, 7, <u>8</u>
30	4, 5, <u>6</u> , 7, 8	4, 5, 6, 7, <u>8</u>
40	4, 5, <u>6</u> , 7, 8	4, 5, 6, 7, <u>8</u>
50	4, 5, <u>6</u> , 7, 8	4, 5, <u>6</u> , 7, <u>8</u>
120	t 4, 5, <u>6</u> , 7, 8	4, <u>5</u> , <u>6</u> , 8
210	t 4, t 5, <u>6</u> , 7, 8	

* Underlined species denotes the predominant species; t = trace.

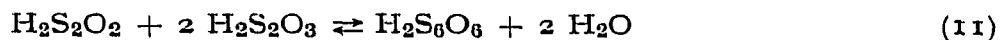
Hexathionate is the predominant species, which is in agreement with YANITSKII AND VALANCHUNAS's^{18,19} results, for the sulphide addition, whilst octathionate is formed initially in the hypophosphite case which breaks down to lower thionates, the main product after 100 min being pentathionate. In this latter case, the Russian workers^{18,19} found 95 % pure hexathionate, which they precipitated by the addition of benzidine hydrochloride after removal of the sulphur. Benzidine octathionate was obtained first, then the hexathionate salt, and finally the mother liquor contained pentathionate.

Thus in general outline the two series of experiments agree.

The reactions involved in the sulphide addition seem to be pretty clear, in that it involves a large concentration of H_2S being present to drive the reaction:



to completion, then follow two reactions:



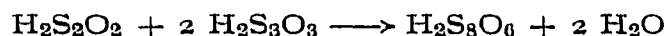
and



followed by build-up and degradation of these two species to give S_5 , S_7 and S_8 species.

However, the hypophosphite case is not so clear, because only one product was initially found, *i.e.* octathionate, and we feel the only explanation somehow involves the reducing power of hypophosphorous acid.

If this could force an extra-sulphur atom into $\text{H}_2\text{S}_2\text{O}_3$ to form the disulphane-monosulphonic acid $\text{H}_2\text{S}_3\text{O}_3$, then with thiosulphurous acid:



but even under such circumstances, the initial appearance of other thionates would be expected.

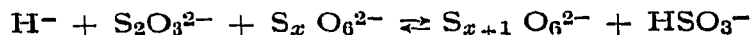
When studies of the decomposition of thiosulphate in the presence of both sulphide and sulphite are carried out, a complex series of thionates are produced from traces of $\text{S}_4\text{O}_6^{2-}$ to $\text{S}_7\text{O}_6^{2-}$, whilst hexathionate is the predominant species. This is in contrast to the results found by YANITSKII AND VALANCHUNAS¹⁹, who found pentathionate the predominant species; however, it must be remembered that the precipitation by benzidine as means of analysis was not complete until after 3-4 days. Thus it is possible that hexathionate was their primary product, but pentathionate being more stable in the acidity range studied, was formed, but one would have thought that indications of other thionates besides pentathionate would have been observed.

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SUMMARY

Since many of the reactions involving thionic acids occur in acid media, it was felt that a qualitative study of the stability of these substances in various concentrations of hydrochloric acid was desirable. One of the main reactions in acid media is said to be:



The effect of thiosulphate and formaldehyde (which removes bisulphite) was therefore observed.

Results obtained agreed with the above equation and also showed that as the number of sulphur atoms in the thionates increases, the concentration of acid in which the thionate is stable increases. Experiments conducted to ascertain the primary thionate produced in the decomposition of acidified thiosulphate solution are described, this being trithionate; a possible mechanism is suggested for this reaction.

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