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HYDROLYTIC REACTIONS OF TETRASULPHUR TETRANITRIDE IN A HOMOGENEOUS MEDIUM

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Abstract—The hydrolytic reactions of tetrasulphur tetranitride are studied in a homogeneous medium. Alkaline hydrolysis gives sulphite, thiosulphate, sulphate and sulphide whereas the products in acid hydrolysis are mainly sulphur dioxide, elemental sulphur and hydrogen sulphide, with traces of polythionates. Under optimum conditions, tetrasulphur tetranitride reacts with sulphite consuming 2 moles of sulphite per mole of sulphur nitride to give 2 moles of trithionate. The reaction of sulphur nitride with thiosulphuric acid gives pentathionate and tetrathionate.

THE constitution of tetrasulphur tetranitride has been the subject of much discussion and the hydrolytic reactions of the compound are of special interest since they furnish the main chemical evidence for its constitution. The hydrolysis of sulphur nitride has been investigated by GOEHRING(1), who carried out two-phase hydrolytic studies by shaking solid sulphur nitride with benzene and an aqueous solution of the appropriate reagent. The reactions under these conditions are slow and require mechanical shaking for several hours. Sulphite, thiosulphate and trithionate were found to be the products of alkaline hydrolysis; trithionate was observed only in weakly alkaline solutions. Trithionate was found to be the major product of the reaction of sulphur nitride and sulphite; a small quantity of thiosulphate was also observed in this reaction. During all these reactions, Goehring observed that the entire quantity of nitrogen was converted into ammonia.

The difficulties of the two-phase studies can be obviated and the experimental technique can be simplified by working in a homogeneous medium. Such a homogeneous medium can be obtained by using suitable solvents. For instance, the two-phase system (benzene–water) adopted by GOEHRING can be easily homogenized by the addition of a sufficient quantity of alcohol. The hydrolytic reactions under these conditions have been found to be quite rapid and quantitative. Similar experimental results were obtained when sulphur nitride was dissolved in dioxan and shaken with aqueous reagents. As dioxan is completely miscible with water the system would be homogeneous; it may be pointed out that dioxan is also a better solvent for sulphur nitride than benzene.

The hydrolytic reactions of sulphur nitride in alkaline and acid media as well as in the presence of sodium sulphite and thiosulphate are described in the present communication.

EXPERIMENTAL

Tetrasulphur tetranitride was prepared by the reaction of ammonia with disulphur dichloride, as described by GOEHRING.[2] The product was twice recrystallized from extra-pure benzene. The melting point of the pure sample was found to be 177° (reported(2) 178°). Analysis for nitrogen and sulphur

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(1) M. GOEHRING, *Ber. Dtsch. Chem. Ges.* **80**, 110 (1947).

(2) M. BECKE-GOEHRING, *Inorganic Synthesis*, Vol. 6, p. 124. Interscience, New York (1960).

showed: 69·31 per cent sulphur and 30·26 per cent nitrogen; theoretical: 69·61% S and 30·40% N.

The solvents benzene, dioxan and alcohol were purified by standard methods.⁽³⁾ Other reagents used were all of the analytical reagent grade.

General procedure

A known weight of the sulphur nitride was dissolved in 10 ml of benzene and 40–50 ml of an aqueous solution of carbonate-free sodium hydroxide (or hydrochloric acid, sodium sulphite or sodium thiosulphate—depending upon the particular reaction under study) were added. The immiscible liquid system was then homogenized by the addition of 65–75 ml of alcohol and the contents were shaken well. It was found convenient to use dioxan instead of benzene as solvent; in this case the addition of alcohol was not necessary for the sake of homogenization; yet, alcohol was added in some experiments so as to serve as an inhibitor of the atmospheric oxidation of sulphite.⁽⁴⁾ All the experiments were conducted at room temperature, (28 ± 2°C).

After the completion of the reaction, the products were analysed, following the analytical procedures, of KURTENACKER and co-workers⁽⁵⁾ for a mixture of sulphide, sulphite, thiosulphate and polythionates, and of Geohring, Feldmann and Helbing[6] for a mixture of polythionates. The total sulphur in solution was estimated as barium sulphate after oxidation with either sodium peroxide or bromine and nitric acid.

Preliminary experiments showed that hydrogen sulphide and sulphur dioxide were among the products in acid hydrolysis. To prevent the escape of these gaseous products, the experiments were carried out in an all-glass apparatus fitted with suitable ground-glass joints and leads and the gaseous products were swept off by a stream of pure nitrogen and absorbed in an alkaline suspension of cadmium hydroxide. The cadmium hydroxide helped to fix the hydrogen sulphide as cadmium sulphide immediately on absorption; the sulphur dioxide was fixed as alkali sulphite which remained in solution. No thiosulphate is produced when the mixed gases are absorbed in alkali containing cadmium hydroxide. The sulphide and sulphite were then iodometrically determined.⁽⁵⁾

The analytical results of alkaline and acid hydrolyses are presented in Tables 1 and 2 respectively while Tables 3 and 4 give the results of hydrolytic reactions in presence of sodium sulphite and thiosulphuric acid, respectively. Blank experiments were conducted in each case. There was no need for

TABLE 1.—ALKALINE HYDROLYSIS OF TETRASULPHUR TETRANITRIDE
(Over-all alkali strength 0·50 N)

Expt. no.*	Amount of sulphur nitride taken†	Sulphide† (%)	Sulphite† (%)	Thiosulphate† (%)	Sulphate† (%)	Total sulphur found (%)
1	24·95	2·36	62·63	24·42	10·59	100·0
2	36·83	1·95	58·29	23·57	16·19	100·0
3	42·40	2·73	59·24	24·98	14·50	101·5
4	25·22	1·67	57·98	27·83	11·90	99·4
5	28·38	3·11	64·63	14·38	17·30	99·4
6	25·38	4·12	69·53	12·06	13·79	99·5
7	31·24	4·04	67·33	13·74	14·89	100·0

* Experiments 1–4 were carried out using benzene as solvent for sulphur nitride, whereas dioxan was used as solvent for experiments 5–7.

† Quantities of sulphur and sulphur compounds are all expressed in terms of gramme atoms of sulphur $\times 10^4$.

⁽³⁾ A. WEISSBERGER, *Organic Solvents*. Interscience, New York (1955).

⁽⁴⁾ I. M. KOLTHOFF and V. A. STENGER, *Volumetric Analysis*, Vol. 1, p. 161. Interscience, New York (1942).

⁽⁵⁾ A. KURTENACKER *Analytische Chemie der Sauerstoffsauren des Schwefels*. Stuttgart (1938).

⁽⁶⁾ M. GOEHRING, U. FELDMANN and W. HELBING, *Z. Analyt. Chem.* **129**, 346 (1939).

any blank correction in the case of alkaline and acid hydrolyses and the reaction with sodium sulphite. In the case of the reaction with sodium thiosulphate in acid medium, it was found that blank corrections were necessary; this could be attributed to the probable decomposition of thiosulphuric acid during the reaction time.

TABLE 2.—ACID HYDROLYSIS OF TETRASULPHUR TETRANITRIDE
(Over-all acidity 4·0 N)

Expt. no.*	Amount of sulphur nitride taken†	Hydrogen sulphide† (%)	Sulphur dioxide† (%)	Thiosulphate† (%)	Tetra-thionate† (%)	Elemental sulphur† (%)
1	30·96	3·67	77·50	1·65	3·29	13·89
2	45·44	7·79	71·48	—	—	20·73
3	38·27	4·95	69·31	—	—	25·74

* Benzene was used as solvent for sulphur nitride in expt. No. 1. and dioxan in expts. no. 2 and 3.
† Quantities of sulphur and sulphur compounds are all expressed in terms of gramme atoms of sulphur $\times 10^4$.

TABLE 3.—REACTION OF TETRASULPHUR TETRANITRIDE WITH SODIUM SULPHITE IN NEUTRAL MEDIUM

Expt. no.*	Sulphur nitride taken ($M \times 10^4$)	Sodium sulphite taken ($M \times 10^4$)	Sulphite unconsumed ($M \times 10^4$)	Sulphite used up ($M \times 10^4$)	Sulphite expected to be used up ($M \times 10^4$)	Trithionate formed ($M \times 10^4$)	Trithionate expected to be formed ($M \times 10^4$)
1	7·50	15·00	5·07	9·93	15·00	10·11	15·00
2	8·31	33·24	19·33	13·91	16·62	13·57	16·63
3	6·77	54·16	40·73	13·43	13·54	13·44	13·54
4	7·50	75·00	59·40	15·60	15·00	14·91	15·00
5	7·79	77·90	61·78	16·12	15·58	15·44	15·58

* Dioxan was used as solvent for sulphur nitride in expts. 1–4 whereas benzene was used in expt. 5.

TABLE 4.—REACTION OF TETRASULPHUR TETRANITRIDE WITH SODIUM THIOSULPHATE IN ACETIC ACID MEDIUM
(Over-all acidity 0·60 N)

Expt. no.*	Sulphur nitride taken ($M \times 10^4$)	Thiosulphate taken ($M \times 10^4$)	Thiosulphate left over ($M \times 10^4$)	Sulphite formed ($M \times 10^4$)	Pentathionate formed ($M \times 10^4$)	Tetra-thionate formed ($M \times 10^4$)
1	5·31	42·48	1·06	2·64	11·45	10·38
2	6·51	52·08	—	3·60	13·30	15·97
3	4·09	52·08	7·72	—	13·84	8·91
4	nil	52·08	35·66	10·37	2·13	0·27

* Benzene was used as solvent for sulphur nitride in expt. 1 and dioxan in expts. 2 and 3. The blank expt. 4 was carried out in a solvent mixture of the same composition as expts. 2 and 3.

RESULTS

Alkaline hydrolysis

Tetrasulphur tetranitride is quantitatively hydrolysed by alkali in a homogeneous medium. The products of hydrolysis are sulphite, thiosulphate, sulphate and a small quantity of sulphite. Using an over-all alkali strength of 0·50 N and benzene as solvent for sulphur nitride, it was found that nearly 60 per cent of the sulphur nitride was converted into sulphite (Table I). About 23–28 per cent thiosulphate, 10–16 per cent sulphate and 2–3 per cent of sulphide were also obtained. When dioxan was used as solvent, the thiosulphate yield decreased to 12–14 per cent while sulphite yield increased to 65–70 per cent; about 15 per cent sulphate and 3–4 per cent sulphide were also obtained. Alkaline hydrolysis was complete in 2 hr; this was indicated by the gradual disappearance of the yellow colour of the sulphur nitride. The solution remained clear throughout and became colourless at the end.

Acid hydrolysis

Acid hydrolysis of sulphur nitride was found to be slower than alkali hydrolysis. The hydrolysis was sluggish with dilute acid; but the reaction could be hastened by using an acidity of 4 N. It may be seen from Table 2 that the main product of acid hydrolysis of sulphur nitride is sulphur dioxide. Using benzene as solvent, about 78 per cent of sulphur dioxide, 14 per cent of elemental sulphur, 4 per cent of hydrogen sulphide and small quantities of thiosulphate and tetrathionate were obtained. No thiosulphate or tetrathionate was obtained when dioxan was used as solvent; the sulphur dioxide yield was 70 per cent, elemental sulphur 20–25 per cent and hydrogen sulphide 5–8 per cent. The absence of polythionates when dioxan was used as solvent could be attributed to the decomposition of polythionates to give elemental sulphur as shown by the increased yield of elemental sulphur in a dioxan solution.

Reaction of sulphur nitride with sodium sulphite

It may be seen from Table 3 that sulphur nitride reacts with sodium sulphite in a neutral medium to give trithionate quantitatively. A neutral medium was employed throughout this study since an acid medium would render the estimation of the unconsumed sulphite inaccurate and an alkine medium might cause the decomposition of the polythionates expected to be formed. A known amount of a standard solution of sodium sulphite (stabilized by alcohol, 15 per cent by volume) was added and after about 30 min, the sulphite left unconsumed as well as the trithionate formed were estimated. It was observed that a high concentration of sulphite was necessary for the reaction to be quantitative. With a twofold or fourfold molar concentration of sulphite, trithionate yields were not quantitative; but when an eightfold or higher concentration of sulphite was employed, it was found that two moles of sulphite were consumed per mole of sulphur nitride to give two moles of trithionate. The yellow colour of the sulphur nitride solution deepened to a transient red on the addition of sulphite and homogenization; the solution became colourless in less than 5 min when a large excess of sulphite was present. No thiosulphate or higher polythionates were observed among the products.

Reaction of sulphur nitride with thiosulphuric acid

The reaction of sulphur nitride with thiosulphate could be studied only in acid conditions since the higher polythionates expected to be formed would be decomposed in an alkaline solution. The acid hydrolysis of sulphur nitride is, however, slow; also the acidity had to be kept low to minimize the decomposition of thiosulphate. Acetic acid (0·60 N) was therefore employed.

Sulphur nitride was completely consumed in about 1½–2 hr time using an eight to twelvefold molar concentration of thiosulphate. The products are mainly pentathionate and tetrathionate. (It may be seen from expt. 4, Table 4, however, that thiosulphate itself, when left in a similar acid medium for 2 hrs, undergoes some conversion to pentathionate, sulphite and elemental sulphur.)

The yellow colour of the sulphur nitride solution deepened to a red colour on the addition of thiosulphate and gradually faded and the solution became colourless after 1½–2 hrs.

DISCUSSION

The constitution of sulphur nitride is discussed at length by GOEHRING(7), who suggests resonance between 8 canonical forms leading to the equivalence of all the N—S bonds. The N—S bond length(8) in sulphur nitride is 1·60 Å, compared with the value of 1·74 Å for a N—S single bond and 1·54 Å for a N═S double bond; this indicates a partial double bond character for the N—S bond in sulphur nitride. The interatomic distance between two sulphur atoms connected through a nitrogen atom is 2·71 Å and that between two sulphur atoms not connected through nitrogen is 2·58 Å. This latter interatomic distance is much smaller than the Van Der Waals' distance of 3·7 Å although larger than the S—S single bond length of 2·1 Å. While this short distance is explained as due to contributions from cross-bonded structures in resonance, it is clear that no S—S chemical bond in the conventional sense exists in sulphur nitride. The absence of N—N bonds, established by X-ray analysis,(8) is supported by hydrolytic results where all the nitrogen is converted into ammonia.(1) When sulphur nitride is allowed to react with anhydrous hydrogen iodide in non-aqueous solvents like carbon tetrachloride,(9) all the sulphur is reduced to hydrogen sulphide and the entire nitrogen is converted into ammonia as per the equation

$$S_4N_4 + 20HI \rightarrow 4H_2S + 4NH_3 + 10I_2 \qquad (1)$$

The oxidation state of sulphur in hydrogen sulphide is -2; in order to bring all the four sulphur atoms present in sulphur nitride to this state, twenty equivalents of reductant are consumed. Therefore the average oxidation number of sulphur in sulphur nitride may be taken as $+3$. Further evidence for the $+3$ oxidation state of sulphur in sulphur nitride has been adduced by the present authors from oxidation studies using chloramine-T.(10) In this reaction, all the sulphur is oxidized to sulphuric acid and all the nitrogen is converted to ammonia.

$$S_4N_4 + 6(O) + 10H_2O \rightarrow 4H_2SO_4 + 4NH_3 \qquad (2)$$

The oxidation state of sulphur in sulphuric acid is $+6$; since twelve equivalents of oxidant are consumed to bring all the four sulphur atoms in sulphur nitride to this state, the average oxidation number of sulphur in sulphur nitride may be seen to be $+3$. This implies an oxidation state of -3 for nitrogen in sulphur nitride. The fact that all the nitrogen is converted into ammonia in all these hydrolytic, reductive and oxidative reactions proves that the oxidation state of nitrogen is unaltered in these reactions. The electropositive nature of sulphur in sulphur nitride is in agreement with Pauling's electro-negativity scale. (N 3·0, S 2·5).

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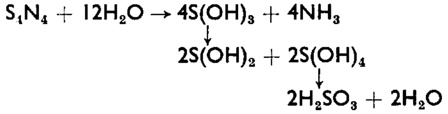
(7) M. BECKE GOEHRING, *Progress in Inorganic Chemistry*, Vol. 1, p. 208. Interscience, New York (1959).

(8) D. CLARK, *J. Chem. Soc.* 1615 (1952).

(9) A. R. VASUDEVA MURTHY, *Proc. Indian Acad. Sci.* **37**, 25 (1953).

(10) C. G. R. NAIR and A. R. V. MURTHY, *Chem. and Industr.* (In press).

These observations are compatible with the results of hydrolytic reactions if we assume the formation of a derivative of S^{3+}, viz., "sulphur trihydroxide" $S(OH)_3$ as the primary product of hydrolysis. Such a product will be extremely unstable and will have only a transient existence, being transformed into sulphoxylic acid (in which sulphur is in the +2 oxidation state) and sulphurous acid (where sulphur is in the +4 oxidation state)



$$\begin{array}{l} S_4N_4 + 12H_2O \rightarrow 4S(OH)_3 + 4NH_3 \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad 2S(OH)_2 + 2S(OH)_4 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad 2H_2SO_3 + 2H_2O \end{array} \qquad (3)$$

Sulphoxylic acid itself, while not isolated in the pure state or in solution, is known to be a highly reactive species as seen from studies on its derivatives.(11) The secondary reactions undergone by sulphoxylic acid explain the formation of the various products in the hydrolysis of sulphur nitride.

Alkaline and acid hydrolyses

On the basis of reaction (3), one might expect 50 per cent of the sulphur in sulphur nitride to be converted into sulphurous acid, whereas the actual percentage of sulphurous acid (or sulphite) obtained in acid or alkaline hydrolyses is much higher. (60–75 per cent). This can be attributed to the decomposition reactions of sulphoxylic acid leading to the formation, among other products, of extra sulphite. Sulphoxylic acid is known to undergo the following reactions in an alkaline medium.(1,12)

$$2H_2SO_2 \rightarrow H_2S_2O_3 + H_2O \qquad (4)$$

$$2H_2SO_2 \rightarrow H_2S + H_2SO_4 \qquad (5)$$

$$3H_2SO_2 \rightarrow H_2S + 2H_2SO_3 \qquad (6)$$

Besides, sulphoxylic acid reacts with sulphurous acid to form trithionate.(11)

$$H_2SO_2 + 2H_2SO_3 \rightarrow H_2S_3O_6 + 2H_2O \qquad (7)$$

Trithionate is known to be hydrolysed in presence of alkali in two ways depending upon the alkali strength.(13)

$$S_3O_6^{2-} + OH^- \rightarrow HSO_4^- + S_2O_3^{2-} \qquad (8)$$

$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \qquad (9)$$

The absence of trithionate and the presence of sulphate among the products are explained by these hydrolytic reactions of trithionate. All the products of alkaline hydrolysis are thus accounted for qualitatively in terms of reactions (4) to (9); these analytical results are not amenable to exact quantitative evaluation due to the large number of complicating secondary reactions involved. It may be mentioned that GOEHRING(1) did not observe sulphide among hydrolytic products, although MEUWSEN,(14) who heated sulphur nitride with aqueous alkali, had noticed a small quantity of sulphide.

While acid hydrolysis is much more complicated than alkaline hydrolysis, the

(11) M. GOEHRING, *Z. Anorg. Chem.* **253**, 304 (1947).

(12) A. R. V. MURTHY, *Proc. Indian Acad. Sci.* **36**, 396 (1952).

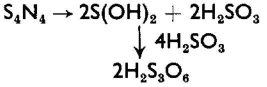
(13) O. FOSS, Kjl. *Norsk. Viden. Selsk. Skrift.* No. 2 p. 5 (1945).

(14) A. MEUWSEN, *Ber. Dtsch. Chem. Ges.* **62**, 1968 (1929).

primary reaction (3) may be supposed to take place. It may be further supposed that sulphoxylic acid disproportionates according to Equation (6) which explains the formation of some hydrogen sulphide. A part of the hydrogen sulphide and sulphur dioxide react with each other giving elemental sulphur and polythionates.

Reaction with sulphite and thiosulphate

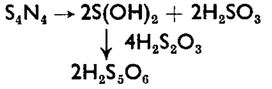
The sulphite ion ranks high in "thiophilicity"(15) and is known to be very active in nucleophilic attacks on elemental sulphur(16,17) and several sulphur compounds. The sulphoxylic acid produced in reaction (3) is quantitatively converted into trithionate by the sulphite present in excess, as per reaction (7). This reaction is known to take place rapidly in a neutral medium.(11) The net result of reactions (3) and (7) would be that one mole of sulphur nitride consumes two moles of sulphite to give two moles of trithionate.



$$\begin{array}{l} S_4N_4 \rightarrow 2S(OH)_2 + 2H_2SO_3 \\ \qquad\quad \downarrow 4H_2SO_3 \\ \qquad 2H_2S_3O_6 \end{array} \qquad (10)$$

It may be seen from Table 3 that these predictions are verified by the experimental results when an excess of sulphite is employed. An excess of sulphite is necessary in order to suppress the competitive side reactions, viz., decomposition reactions of sulphoxylic acid. The present analytical results confirm the observations of GOEHRING.(1)

The following reaction may be expected to occur between thiosulphate and sulphur nitride.



$$\begin{array}{l} S_4N_4 \rightarrow 2S(OH)_2 + 2H_2SO_3 \\ \qquad\quad \downarrow 4H_2S_2O_3 \\ \qquad 2H_2S_5O_6 \end{array} \qquad (11)$$

Pentathionate is thus expected to be the main product. However, due to the sulphite degradation of pentathionate, which takes place to some extent in the weakly acid medium, tetrathionate is also to be expected.

$$S_5O_6^{2-} + SO_3^{2-} \rightarrow S_4O_6^{2-} + S_2O_3^{2-} \qquad (12)$$

The source for this sulphite is reaction (3) itself. The situation is further complicated due to the fact that thiosulphate itself, left in the acid medium for 1½–2 hr, leads to the formation of some pentathionate. While quantitative correlations could not be made due to these complicating factors, it may be noted that pentathionate and tetrathionate are the main products, as expected.

The ring system in sulphur nitride is opened up in all these hydrolytic reactions. Also, the fact that polythionates and other sulphur chain compounds are present among the hydrolytic products although there there is no S—S bond in sulphur nitride testifies to the marked tendency for the sulphur atoms to link with one another forming straight sulphur chain compounds, this tendency being especially strong in the presence of thiophilic reagents like sulphite and thiosulphate.

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(15) W. A. PRYOR *Mechanisms of sulphur reactions*, p. 60. McGraw-Hill, New York (1962).

(16) M. SCHMIDT and G. TALSKY. *Ber. Chem. Dtsch. Ges.* **90**, 1673 (1957).

(17) A. R. V. MURTHY and V. R. S. RAO, *J. Sci. and Industr. Res.* **18 B**, 40 (1959).