SULPHUR NITRIDE AND ITS DERIVATIVES

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THE chemistry of the sulphur nitrides began a long time ago. As early as 1835 Gregory[1] discovered a sulphur nitride formed by reaction of sulphur monochloride (S_2Cl_2) and ammonia. Today many sulphur–nitrogen compounds are known which are derived from this nitride, and their chemistry has been thoroughly investigated. It shows hardly any analogy with that of the nitrogen–oxygen compounds. It is governed by the great stability of the linkage between nitrogen and sulphur, by a tendency to formation of negatively charged ions, and by the ease of polymerisation which can lead to large molecules containing long-chain or six-membered or eight-membered ring systems.

Tetrasulphur Tetranitride, S_4N_4.—In 1835 it was found that reaction between sulphur monochloride and ammonia gave, besides other substances, a compound which contained only sulphur and nitrogen;[1, 2] but it was not until 1850 that the exact composition of this compound was worked out, and not until 1896 that a determination of the molecular weight gave the formula S_4N_4.[3, 4, 5] Tetrasulphur tetranitride, S_4N_4, is solid at room temperature. It forms orange-yellow crystals of the class C_{2h} and space group $P2_1/n$.[6] It is diamagnetic and strongly endothermic. The melting point is 178°.

There are two convenient methods for the preparation of tetrasulphur tetranitride. First, one can obtain it from sulphur chlorides and ammonia: it is particularly advantageous to use a sulphur chloride in which sulphur and chlorine are in the atomic ratio 1 : 3 or 1 : 4.[7] This method affords tetrasulphur tetranitride in good yield; but the reaction is complicated in its detail, and it is not known what the intermediate stages are. A second method for the preparation of tetrasulphur tetranitride, which however is hardly feasible for preparative purposes, uses the disproportionation of sulphur occurring when elementary sulphur is dissolved in liquid ammonia with gentle warming and the blue solution is then set aside at room temperature:[8]

$$10S + 4NH_3 \rightleftharpoons 6H_2S + S_4N_4 \quad . \quad . \quad . \quad (1)$$

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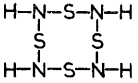
[1] M. Gregory, *J. Pharm.*, 1835, **21**, 315; **22**, 301.
[2] E. Soubeiran, *Ann. Chim. Phys.*, 1838, **67**, 71.
[3] J. M. Fordos and A. Gélis, *Compt. rend.*, 1850, **31**, 702.
[4] A. Andreocci, *Z. anorg. Chem.*, 1896, **14**, 246.
[5] R. Schenck, *Annalen*, 1896, **290**, 171.
[6] D. Clark, *J.*, 1952, 1615; cf. M. Buerger, *Amer. Mineral.*, 1936, **21**, 575.
[7] H. Jonas and W. Knauff, "Naturforschung und Medizin in Deutschland", 1939—46, Dietrichsche Verlagsges., Wiesbaden, Vol. 23, p. 195.
[8] O. Ruff and E. Geisel, *Ber.*, 1905, **38**, 2659.

The constitution of tetrasulphur tetranitride has been investigated by many authors. Chemical investigation[9, 10, 11] has shown that the oxidation number of the sulphur in this compound is $+ 3$. Further, it has been shown that hydrolysis of tetrasulphur tetranitride always gives ammonia or ammonium ions as well as sulphur oxy-acids, which is in good agreement with the fact that the electronegativity of nitrogen is greater than that of sulphur.[12] In weakly alkaline solution the hydrolysis occurs according to equation (2), but in strongly alkaline solution according to equation (3):

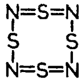
$$2S_4N_4 + 6OH^- + 9H_2O \longrightarrow 2S_3O_6{}^{2-} + S_2O_3{}^{2-} + 8NH_3 \quad . \quad (2)^{10}$$

$$S_4N_4 + 6OH^- + 3H_2O \longrightarrow 2SO_3{}^{2-} + S_2O_3{}^{2-} + 4NH_3 \quad . \quad (3)^{13}$$

The result of the hydrolysis is typical for a substance in which sulphur has the oxidation number $+ 3$ as this can then easily undergo dismutation half into S^{2+} and half into S^{4+}. It cannot be reconciled with an assumption that in tetrasulphur tetranitride one is dealing with a nitrile of dithionous acid, $H_2S_2O_4$; for it is impossible that reaction (2) could occur by way of $S_2O_4{}^{2-}$ as intermediate.[10] On reduction of tetrasulphur tetranitride with tin(II) chloride,[13, 14] or with dithionite, $S_2O_4{}^{2-}$,[15] the sulphur with oxidation number $+ 3$ is reduced to sulphur with oxidation number $+ 2$, and tetrasulphur tetraimide, $S_4(NH)_4$, results. It has been shown by chemical[16] as well as by physical[17] methods that this reduction product of tetrasulphur tetranitride, which is a white solid, has formula (I). Since this tetraimide is easily oxidised back to tetrasulphur tetranitride—for example, by chlorine[15]—it is reasonable to assume that tetrasulphur tetranitride has formula (II),[18, 10] which is nicely in line with the results of reduction and of hydrolysis.



(I)



(II)

Nevertheless, it became evident that formula (II) which contains sulphur bound in two different ways does not correctly reproduce the valency states of tetrasulphur tetranitride. It was shown that the sulphur atoms in the tetranitride molecule cannot be differentiated either chemically or physically. Attempts to effect this differentiation were undertaken[19] by labelling with

[9] O. Ruff and E. Geisel, *Ber.*, 1904, **37**, 1573.

[10] M. Goehring, *Chem. Ber.*, 1947, **80**, 110.

[11] V. Murthy, *Proc. Judien Acad. Sci.*, 1953, **37**, *A*, 23.

[12] L. Pauling, " The Nature of the Chemical Bond ", Cornell Univ. Press, New York, 1940.

[13] A. Meuwsen, *Ber.*, 1929, **62**, 1959.

[14] H. Wölbling, *Z. anorg. Chem.*, 1908, **57**, 281.

[15] E. Fluck, Diplomarbeit, Heidelberg, 1956.

[16] M. H. M. Arnold, *J.*, 1938, 1596.

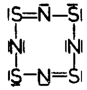
[17] E. R. Lippincott and M. C. Tobin, *J. Amer. Chem. Soc.*, 1951, **73**, 4990.

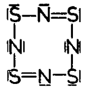
[18] M. H. M. Arnold, J. A. C. Hugill, and J. M. Mutson, *J.*, 1936, 1645.

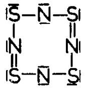
[19] M. Goehring and J. Ebert, *Z. Naturforsch.*, 1955, **10**b, 241.

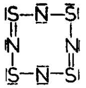
^{35}S. Tetrasulphur tetranitride was prepared by reaction of compounds which contained only S^{4+} with compounds which contained only S^{2+}. The S^{4+} was labelled with ^{35}S. Then the tetrasulphur tetranitride molecule was cleaved into compounds which contained only either S^{4+} or S^{2+}. If formula (II) were strictly correct then the radioactivity should be found only in the compounds with S^{4+}. In fact, however, the activity was found to be equally divided between the S^{4+} and the S^{2+} compounds which were formed on the fission of the tetrasulphur tetranitride. This experiment shows then that in tetrasulphur tetranitride the sulphur atoms cannot be differentiated as S^{4+} and S^{2+} atoms, as formula (II) would demand, but that an equalisation of valency must take place in the molecule. This result is supported by investigation of the $K\alpha$ X-ray emission spectrum of the sulphur in tetrasulphur tetranitride. The position of the $K\alpha$ doublet of sulphur depends on the oxidation number of the sulphur in the compound under investigation and on its electron demand.[21] If a single compound contains sulphur atoms with differing electron demands, then $K\alpha$ doublets are observed in more than one position. Such duplication can be observed for instance for $S_2O_3^{2-}$ or $S_3O_6^{2-}$.[22, 20] For tetrasulphur tetranitride only a single sulphur $K\alpha$ doublet appears, and its position corresponds to that which one would expect for a substance containing sulphur with the oxidation number + 3.[20] Thus it is clear that in the tetrasulphur tetranitride molecule all the sulphur atoms present must be in the same valency state.

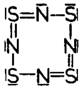
These results require that tetrasulphur tetranitride shall have the electronic formulæ (IIa—f). Resonance between the limiting formulæ would account for the impossibility of differentiating the sulphur atoms. Other formulæ such as (IIg—i) could be brought into the resonance system, although (IIk) appears less likely as a result of the $K\alpha$ spectrum.

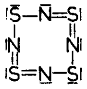

(IIa)

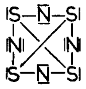

(IIb)

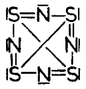

(IIc)

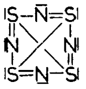

(IId)

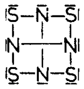

(IIe)


(IIf)


(IIg)


(IIh)


(IIi)


(IIk)

The view that one is dealing with a resonance system in tetrasulphur tetranitride, which had been concluded from chemical data,[10, 18] has been verified by determinations of structure. Chia-Si Lu and Donohue [23] were

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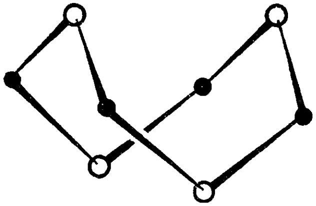
[20] A. Faessler and M. Goehring, *Naturwiss.*, 1952, **39**, 169.

[21] *Idem*, *ibid.*, 1943, **31**, 567.

[22] A. Faessler, *Z. Physik*, 1931, **72**, 734.

[23] Chia-Si Lu and J. Donohue, *J. Amer. Chem. Soc.*, 1944, **66**, 818.

also led to formulæ (IIa—i) by the results of a study of electron diffraction in tetrasulphur tetranitride vapour. Since the molecule was shown to be far from planar, resonance formulæ such as (IIe) and (IIf), in which *d*-levels participate, are essential for interpretation of the complete system. *X*-Ray investigations by D. Clark[6] have underlined this result; for Clark found in tetrasulphur tetranitride a S–N distance of 1·62 Å and this corresponds to a single link with considerable double-bond character (theoretical for S–N 1·74 Å and for S═N 1·54 Å). Since in tetrasulphur tetranitride the distance between any two non-adjacent sulphur atoms, *i.e.*, sulphur atoms which are not connected only to nitrogen, was found to be only 2·58 Å, whilst the van der Waals radius and a single S–S bond require 3·7 and 2·08 Å respectively, it appears likely that forms such as (IIg—i) have a certain weight. This structure determination leads to the molecule shown in the Figure, in which the nitrogen atoms lie in one plane while the sulphur atoms form a slightly distorted tetrahedron. The angle at the sulphur is 102°, that at nitrogen 115°. A different structure has been proposed by von Hassel and Viervoll[24] in which the sulphur atoms lie in a plane and the nitrogen atoms form a tetrahedron: this would bring in formula (IIk), which has been discussed also as a consequence of infrared and Raman spectra.[25] It has been demonstrated with certainty, at any rate, that tetrasulphur tetranitride contains a wavy 8-ring with N–S links; linkages are perhaps possible between sulphur atoms which are bound not only to nitrogen, or between nitrogen atoms which are bound not only to sulphur.



Disulphur Dinitride, S_2N_2, **and Polysulphur Nitride,** $(SN)_x$.—The ring system of tetrasulphur tetranitride can be cleaved easily. If one heats tetrasulphur tetranitride vapour at 300°/0·01 mm. and cools the issuing gases strongly, one obtains an easily volatile white solid, soluble in organic solvents, with the formula S_2N_2, the molecular weight of which has been established cryoscopically.[26] This disulphur dinitride is stable only at low temperature. Even at room temperature it polymerises to a substance, $(SN)_x$, which is brass-coloured in mass, dark blue in thin layers, insoluble in organic solvents, and obviously of high molecular weight. If atmospheric moisture is present then dimerisation to S_4N_4 accompanies the polymerisation. The dimerisation is quantitative if one treats solutions of disulphur dinitride in inert organic solvents with traces of alkali metals, sodium hydroxide,

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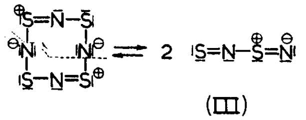
[24] O. Hassel and H. Viervoll, *Tidskr. Kemi Bergvesen Met.*, 1943, **3**, 7.

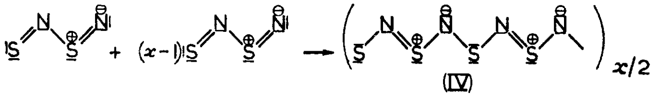
[25] E. R. Lippincott and M. C. Tobin, *J. Chem. Phys.*, 1953, **21**, 1559.

[26] M. Goehring and D. Voigt, *Naturwiss.*, 1953, **40**, 482; *Z. anorg. Chem.*, 1956, **285**, 181.

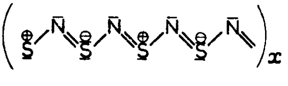
potassium cyanide, or sodium carbonate. Reaction (4) is thus reversed, and in addition disulphur dinitride can undergo reaction (5).*

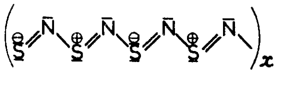

(III)

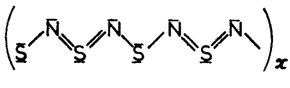
(4)


(IV)

(5)


(Va)


(Vb)


(Vc)

The polysulphur nitride which is formed by reaction (5) is diamagnetic and forms fibre-like crystals with a metallic sheen, and shows the remarkable property that it is a semiconductor. At 25° the specific resistance of the pressed powder, extrapolated to infinite pressure, is $0{\cdot}01_3$ ohm cm. The resistance of the powder decreases with rising temperature. This phenomenon can be explained if one assumes that in polysulphur nitride the bonds are not fixed, as shown in formula (IV) or (V), but that the electrons of the double bonds can move at will through the whole macromolecule.

If one considers the compounds $(SN)_2$, $(SN)_4$, and $(SN)_x$, one sees that with increasing molecular weight an increasing number of limiting formulæ is required for complete description of the electronic state of the compound. Increase in the possibilities for resonance deepens the colour. It also stabilises the compound : disulphur dinitride is very sensitive to shock and decomposes into its elements explosively above 30° ; tetrasulphur tetranitride is sensitive to shock and decomposes explosively also when heated rapidly to above 130° ; polysulphur nitride apparently decomposes explosively neither on shock nor when heated.

Reactions of Tetrasulphur Tetranitride with Ammonia and with Alcohols.—Cleavage of the tetrasulphur tetranitride ring system into two molecules of disulphur dinitride can be effected not merely by heat but apparently also by many chemical reactions. This occurs, for instance, on treatment with ammonia or with alcohols. Ruff and Geisel [9] showed that tetrasulphur tetranitride and ammonia give an ammoniate of the composition $S_4N_4,2NH_3$. In a similar reaction disulphur dinitride gives an ammoniate S_2N_2,NH_3.[27] However, according to the *X*-ray patterns and the absorption spectra it now appears that these two ammoniates are identical. The volatile disulphur dinitride can be sublimed from these ammoniates even at room temperatures,

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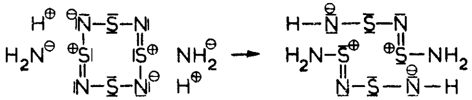
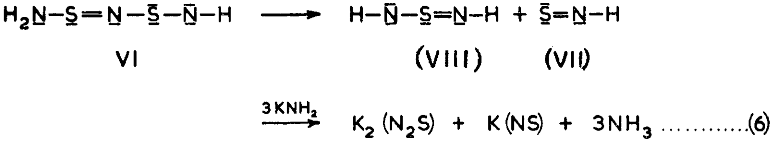
[27] W. Gesierich, Diplomarbeit, Heidelberg, 1954.

* This reaction explains an old experiment by F. P. Burt (*J.*, 1910, **97**, 1171) who found a blue film in the reaction vessel after heating tetrasulphur tetranitride on a silver gauze.

so it must be assumed that tetrasulphur tetranitride is cleaved during its reaction with ammonia :



In liquid ammonia this ammoniate behaves as a proton-donor, like a normal inorganic acid amide. Accordingly solutions of the ammoniate (VI) in liquid ammonia conduct an electric current. With potassium amide, which in consequence of the reaction $NH_2^- + H^+ = NH_3$ is a base in liquid ammonia, a reaction analogous to neutralisation occurs ; in accordance with reaction (6) one obtains a mixture of yellow, solid, pyrophoric, and extremely reactive potassium salts K(NS) and $K_2(N_2S)$.[28] This interpretation of the reaction assumes fission of the ammoniate (VI) into an imide (VII) of sulphoxylic and an imide (VIII) of orthosulphurous acid.



$$\underset{\text{VI}}{H_2N{-}S{=}N{-}S{-}N{-}H} \longrightarrow \underset{\text{(VIII)}}{H{-}N{-}S{=}N{-}H} + \underset{\text{(VII)}}{S{=}N{-}H}$$

$$\xrightarrow{3KNH_2} K_2(N_2S) + K(NS) + 3NH_3 \ldots\ldots\ldots\ldots(6)$$

The reactions of disulphur dinitride and of tetrasulphur tetranitride with alcohols are analogous to those with ammonia. Formation of a product $S_2N_2,CH_3{\cdot}OH$ analogous to the compound (VI) can be demonstrated by means of the absorption spectra of the solutions.[27]

Metal Thionitrosylates from Tetrasulphur Tetranitride.—Metal thionitrosylates can be prepared from the ammoniate of tetrasulphur tetranitride by way of the imide (VII). Thus reaction with lead iodide gives the red $Pb(NS)_2$,[9, 29] with thallium nitrate the red-brown $Tl(NS)_3$ or the ochre-coloured $Tl(NS),5Tl(NS)_3$, with silver nitrate the red-brown $Ag(NS)_2$, and with cuprous chloride the brown $Cu(NS)_2$.[29] For preparation of these thionitrosylates one can use solutions of the imide (VI) in liquid ammonia or in alcohol. In these reactions with metals of a low oxidation number, thionitrosylates of metals having a higher oxidation number can be formed—as, for example, in the case of the thallium compound, where $Tl^{III}(NS)_3$ is formed from $Tl^{I}(NO_3)$: this is due to the strong oxidising properties of the compound (VIII) which is formed from the ammoniate (VI) and can oxidise the metal ions whilst being itself reduced to the compound (VII).

Metal Thionitrosylates from Tetrasulphur Tetraimide.—Tetrasulphur tetraimide (I), $S_4(NH)_4$, the reduction product of tetrasulphur tetranitride, also readily gives metal thionitrosylates. In these reactions in contrast to those with tetrasulphur tetranitride the metal does not change its oxidation number. Mixing tetrasulphur tetraimide with cuprous chloride in solution

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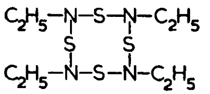
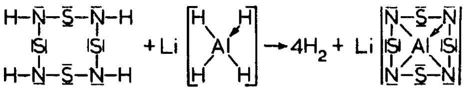
[28] W. Berg and M. Goehring, *Z. anorg. Chem.*, 1954, **275**, 273.

[29] M. Goehring, J. Weiss, and G. Zirker, *Z. anorg. Chem.*, 1955, **278**, 1.

in pyridine gives a precipitate of the brown-black $[Cu(NS)]_x$, and with silver nitrate the red-brown $[Ag(NS)]_x$.[29] A mercurous compound $[Hg_2(NS)_2]_x$ [30] can also be obtained. From mercury of oxidation number + 2 one can prepare the compounds $[Hg(NS)_2]_x$ and $Hg_5(NS)_8$.[31] However, it is not certain whether the ring system of tetrasulphur tetraimide (I) is still retained in these compounds. It is also questionable whether the metal is bound to the nitrogen or to the sulphur of the NS group. The fact that silver iodide and $[C_2H_5{\cdot}NS]_4$ (IX) are formed on reaction between $[Ag(NS)]_x$ and ethyl iodide makes it perhaps probable that the metal is bound to nitrogen in these strongly polarised substances.


(IX)[32]



(I) (X)

A more definite statement can be made about the structure of another complex compound which can be obtained from tetrasulphur tetraimide. On reaction of lithium aluminium hydride with tetrasulphur tetraimide the white, solid, very explosive $Li[Al(NS)_4]$ is formed.[33] Since gentle hydrolysis of this compound regenerates tetrasulphur tetraimide it is reasonable to assume that the product retains the ring system of the tetraimide (I).

Thionitrosyl Complex Compounds with Metals of the Eighth Transition Group.—It has been found that very stable complex compounds can be obtained from tetrasulphur tetranitride and metals of the eighth transition group. These complex compounds have the composition $[M(NS)_4]$. So far, nickel, palladium, platinum, cobalt, and iron have been incorporated as central atom in compounds of this type.[34, 35]

Three methods have been used for preparation of these complex compounds. First, an anhydrous halide of a metal of oxidation number + 2 can be treated in alcoholic solution with tetrasulphur tetranitride: the yield is particularly good if dithionite is added as reducing agent. Secondly, metal carbonyls can be treated with tetrasulphur nitride in an inert solvent; and thirdly finely divided metals can be shaken with a solution of disulphur dinitride. The first process is particularly suitable for the preparation of the nickel, palladium, and cobalt compounds; the second particularly for the preparation of the nickel, cobalt, and iron compounds; but the third process gives only small yields. The platinum compound can be obtained by treatment of chloroplatinic acid with tetrasulphur tetranitride in hot dimethylformamide.[35]

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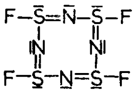
[30] M. Goehring and G. Zirker, *ibid.*, 1956, **285**, 70.
[31] A. Meuwsen and M. Lösel, *ibid.*, 1953, **271**, 221.
[32] F. Lengfeld and J. Stieglitz, *Ber.*, 1895, **28**, 2742.
[33] M. Goehring and G. Zirker, *Z. Naturforsch.*, 1955, **10**b, 58.
[34] M. Goehring, K.-W. Daum, and J. Weiss, *ibid.*, p. 298.
[35] E. Fluck, M. Goehring, and J. Weiss, *Z. anorg. Chem.*, 1956, **287**, 51.

These metal thionitrosyls are crystalline and very stable. The iron compound appears almost black, the nickel and the cobalt compound are deep violet, the palladium compound is red, and the platinum compound is dark blue. All are soluble in organic compounds and insoluble in water.

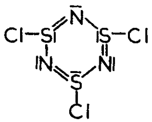
Nickel tetrathionitrosyl [36] is diamagnetic, cobalt tetrathionitrosyl [37] has a magnetic moment of 1·90 Bohr magnetons, and iron tetrathionitrosyl [38] has a moment of 2·94 magnetons. In this compound cobalt thus apparently has one unpaired *d*-electron ; and iron has two unpaired *d*-electrons. *X*-Ray investigations by Lindqvist and Weiss [38a] have shown that there are S_2N_2 groups (III) in the compounds, acting as ligands.

These complex compounds have no known analogues in the chemistry of the metals of the eighth transition group. The peculiarities, particularly the resonance system, of the $(NS)_2$ group are apparently able to stabilise otherwise unusual valency states of these metals.

Halogenation of Tetrasulphur Tetranitride.—Treatment of tetrasulphur tetranitride with halogens affords " thiazyl halides ". The ring system of tetrasulphur tetranitride remains intact on cautious fluorination with silver fluoride, which yields the compound (XI).[39] This compound $S_4N_4F_4$ is colourless and solid. Besides this product there have also been obtained the volatile SN_2F_2 and SNF. Chlorination of tetrasulphur tetranitride yields the chloride (XII) which is a yellow solid ; its molecular weight corresponds to the trimeric formula (XII).[40] Finally bromination gives a bronze-coloured solid bromide (XIII), whose molecular weight is not yet known.[41]



(XI)



(XII)

$[\mathrm{Br{-}S{\equiv}N}]_x$

(XIII)

These compounds contain sulphur with oxidation number + 4. Accordingly, treatment of the trimeric chloride with concentrated hydrochloric acid gives all the sulphur as sulphur dioxide.[42]

Of these halides the chloride has been most investigated. It has been shown that this compound undergoes reactions in which the original six-membered ring system remains intact as well as reactions in which it is destroyed. Thus, for instance, the chloride is converted into a pale-yellow SO_3 adduct (XIV) if it is cautiously treated with sulphur trioxide. If this

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[36] M. Goehring and A. Debo, *Z. anorg. Chem.*, 1953, **273,** 319.

[37] K.-W. Daum, M. Goehring, and J. Weiss, *ibid.*, 1955, **278,** 260.

[38] M. Goehring and K.-W. Daum, *ibid.*, 1955, **282,** 83.

[38a] J. Lindqvist and J. Weiss, *Angew. Chem.*, 1956, in the press.

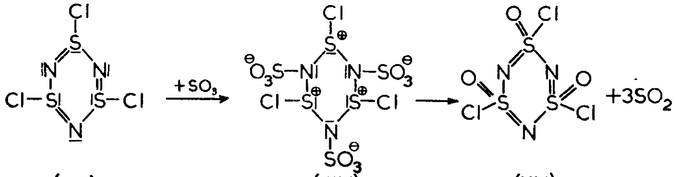
[39] O. Glemser, R. Schröder, and H. Haeseler, *ibid.*, 1955, **279,** 28.

[40] A. Meuwsen, *Ber.*, 1931, **64,** 2311.

[41] A. Clever and W. Muthmann, *Ber.*, 1896, **29,** 340.

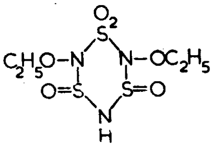
[42] A. Meuwsen, Colloquium of the Inorg. Chem. Section, Int. Union Pure Appl. Chem., Münster (Westphalia), Sept. 2—6, 1954, p. 130.

adduct is heated sulphur dioxide is given off and the ring system of the chloride is oxidised to that of sulphanuric chloride (XV).[43]



(XII) (XIV) (XV)

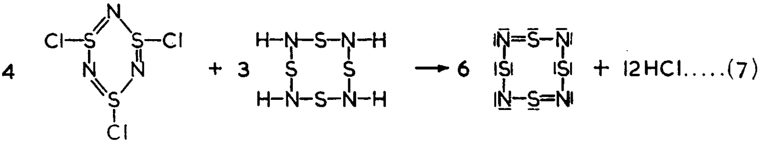
The ring system is also retained on oxidation with ethyl hypochlorite, and the substance (XVI) is obtained by an obscure reaction.[42]



(XVI)

However, other oxidants lead to complete destruction of the original ring system. For instance, nitrogen dioxide affords a compound $[NO]_2S_2O_7$,[42] as it does in an analogous reaction with tetrasulphur tetranitride,[44] but nitric oxide gives the dark green compound S_3N_2Cl, whose constitution is still unknown.

Tetrasulphur tetranitride can be re-formed from the thiazyl chloride : the reaction (7) can be made to occur quantitatively.[43]



Ammonolysis apparently also destroys the ring system (XII). A red substance is formed which with mercuric iodide in solution with liquid ammonia gives the olive-green compound $Hg(N_2S)$ which can also be obtained from the ammonia of tetrasulphur tetranitride, being then produced from the intermediate product (VIII).[45]

$$\begin{aligned}[ClSN]_3 + 3NH_3 &\rightarrow 3HCl + [H_2N{\cdot}SN]_3\\ &\rightarrow 3HCl + 3HN{:}S{:}NH\\ S(NH)_2 + Hg^{2+} &\rightarrow Hg(H_2S) + 2H^+\end{aligned}$$

It is thus shown that a thiazyl halide can serve as starting material for the preparation of derivatives of the imide of orthosulphurous acid. This

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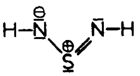
[43] M. Goehring and H. Malz, *Z. Naturforsch.*, 1954, **9b**, 567.

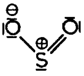
[44] A. Meuwsen and S. Krüger, *Z. anorg. Chem.*, 1938, **236,** 221.

[45] W. Berg, M. Goehring, and H. Malz, *ibid.*, 1956, **283,** 13.

imide (VIII), which is derived from sulphur dioxide (XVII) by replacement of oxygen by the isosteric NH group, has not yet been itself obtained pure ;



(VIII)

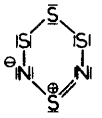


(XVII)

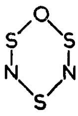
but its potassium salt can be prepared.[45] This salt K_2N_2S is obtained on treatment of $[BrSN]_x$ with ammonia and potassium amide. Further an *n*-butyl derivative of this amide, $S(NC_4H_9)_2$, can be prepared.[46]

Thiotrithiazyl Compounds.—The most stable compounds which are derived from tetrasulphur tetranitride belong to a peculiar group with the composition $[S_4N_3]X$, where X may be halogen, HSO_4, or NO_3. This class of compound was discovered [47] as early as 1880. The most accessible is thiotrithiazyl chloride, S_4N_3Cl, which is obtained as a yellow solid on reaction, for example, of tetrasulphur tetranitride with hydrogen chloride [48] or with sulphur monochloride,[49] or from $[NSCl]_3$ with sulphur monochloride.[50] Reaction of tetrasulphur tetranitride with sulphur monochloride or other acid halides proceeds by way of a green intermediate product S_3N_2Cl. Thiotrithiazyl chloride is soluble only in concentrated acids. Attempts have been made to determine the structure of the thiotrithiazyl compounds from chemical and physical data,[51] but no proposal has yet been fully confirmed.

Tetrasulphur Dinitride.—Tetrasulphur tetranitride reacts, when heated with sulphur, best in carbon disulphide solution in an autoclave, forming a further sulphur nitride.[52] After purification by distillation in a high vacuum, this product corresponds in analysis and molecular weight with the formula S_4N_2.[53] It is a dark-red substance which has an obnoxious smell and melts at 23°. Its diamagnetism shows beyond doubt that tetrasulphur dinitride does not dissociate at room temperature into smaller



(XVIII)



(XIX)

fragments $\cdot S_2N\cdot$ of radical character, like the formally analogous dinitrogen tetroxide.[54] Detailed discussion [54] of the results of hydrolysis of tetra-

[46] G. Weis, Diplomarbeit, Heidelberg, 1955.

[47] E. Demarçay, *Compt. rend.*, 1880, **91,** 1066.

[48] A. G. MacDiarmid, *Nature*, 1949, **164,** 1131.

[49] W. Muthmann and E. Seitter, *Ber.*, 1897, **30,** 627.

[50] A. Meuwsen, *Ber.*, 1932, **65,** 1724.

[51] Cf., *e.g.*, ref. 50 and M. Goehring and D. Schuster, *Z. anorg. Chem.*, 1953, **271,** 281.

[52] W. Muthmann and E. Clever, *ibid.*, 1897, **13,** 200 ; F. L. Usher, *J.*, 1925, **127,** 730.

[53] A. Meuwsen, *Z. anorg. Chem.*, 1951, **266,** 250.

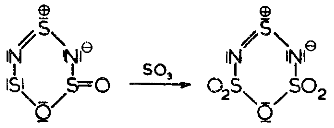
[54] M. Goehring, H. Herb, and W. Wissemeier, *ibid.*, 1952, **267,** 238.

sulphur dinitride and of its absorption spectrum has led to proposal of the formula (XVIII). This structure appears the more likely since sulphur–nitrogen chemistry includes a whole series of compounds containing the skeleton (XIX). Tetrasulphur dinitride of formula (XVIII) takes its place in this group by replacement of oxygen with sulphur.

Sulphur–Nitrogen Compounds with a Cyclic Skeleton containing Sulphur, Nitrogen, and Oxygen.—From tetrasulphur tetranitride one can obtain trisulphur dinitrogen dioxide on reaction with thionyl chloride, particularly in presence of sulphur dioxide.[55] This product $S_3N_2O_2$ forms yellow crystals which are easily soluble in organic solvents and are not wetted by water. It is readily hydrolysed to ammonium trithionate ; in presence of a little water it decomposes according to the equation (8) :

$$2S_3N_2O_2 \longrightarrow 2SO_2 + S_4N_4 \quad . \quad . \quad . \quad . \qquad (8)$$

Trisulphur dinitrogen dioxide, which very probably has the formula (XX), contains, as can be shown [56] by labelling with ^{35}S, two sulphur atoms derived from tetrasulphur tetranitride and one sulphur atom derived from thionyl chloride. According to reaction (8), the sulphur atom which is derived from the thionyl chloride is given up as sulphur dioxide and accordingly is that which is bound to the two oxygen atoms. Trisulphur dinitrogen dioxide is smoothly oxidised by sulphur trioxide to a white solid substance, $S_3N_2O_5$, which is soluble in organic solvents and can readily be sublimed ; it has the formula (XXI).[57]



(XX) (XXI)

It is now interesting to ask why the single quadrivalent sulphur atom in trisulphur dinitrogen dioxide is not oxidised while the two other sulphur atoms are oxidised. Comparison with (XVII) shows that this single sulphur atom is in the same valency state as in sulphur dioxide (XVII). But, as is shown by experiments with ^{35}S, sulphur dioxide is not oxidised by sulphur trioxide, whereas the ion SO_3^{2-} is so oxidised.[58] Sulphur trioxide appears to be an almost specific oxidising agent for trebly bound sulphur of oxidation number + 4. A reaction of this type was noted earlier in the formation of the compound (XV) from the chloride (XII).

The compound $S_3N_2O_5$, which is a substituted cyclic amide of pyrosulphuric acid, is also accessible directly from tetrasulphur tetranitride.[57] The nitrogen atom of tetrasulphur tetranitride, acting as donor, can add on sulphur trioxide so that the compounds $S_4N_4,2SO_3$ and $S_4N_4,4SO_3$ are

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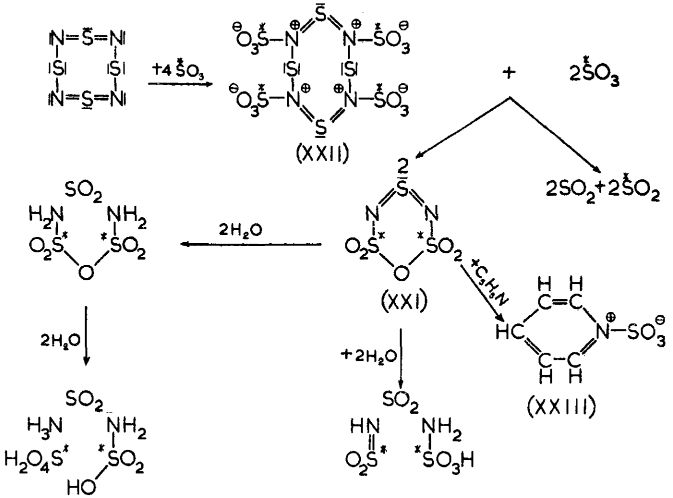
[55] M. Goehring and J. Heinke, *Z. anorg. Chem.*, 1953, **272**, 297.

[56] *Idem*, *ibid.*, 1955, **278**, 53.

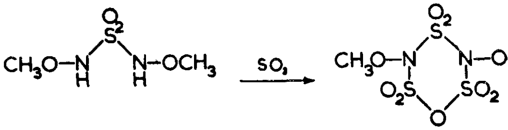
[57] M. Goehring, H. Hohenschutz, and J. Ebert, *ibid.*, 1954, **276**, 47.

[58] J. L. Huston, *J. Amer. Chem. Soc.*, 1951, **72**, 3049.

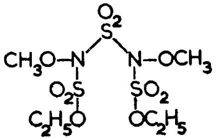
formed.[59] The adduct (XXII) can then react further with sulphur trioxide. The resulting $S_3N_2O_5$ is able to react with pyridine as a true derivative of pyrosulphuric acid, forming the adduct (XXIII). On treatment with water it undergoes hydrolysis as shown in the annexed scheme. If throughout the whole reaction one uses sulphur trioxide labelled with ^{35}S, the activity is divided as shown in the scheme, and this at the same time constitutes the proof of formula (XXI).



The cyclic skeleton of compounds (XX) and (XXI) appears to be favoured energetically in the chemistry of sulphur-nitrogen compounds. It is also possible to build in a six-membered ring of this kind if nitrogen with oxidation number − 1 is present.[60] *NN'*-Dimethoxysulphamide (XXIV), which is

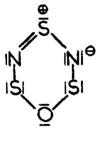


(XXIV) (XXV)



(XXVI)

obtained from sulphuryl chloride and hydroxylamine methyl ether, reacts with sulphur trioxide to give a compound (XXV) which contains this ring system. This product also is a colourless solid soluble in organic solvents, and readily sublimable. Naturally the compound (XXV), like other compounds with the same skeleton, is sensitive to hydrolysis. Solvolysis yields an ester (XXVI).



(XXVII)

Treating $Hg_5(NS)_8$ with thionyl chloride affords a compound S_3N_2O,[61] but it is an open question whether this belongs to the

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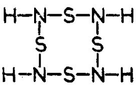
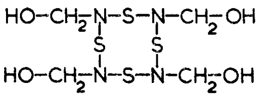
[59] M. Goehring, H. Hohenschutz, and R. Appel, *Z. Naturforsch.*, 1954, **9**b, 678.
[60] M. Goehring and H. K. A. Zahn, *Chem. Ber.*, 1956, **89,** 179.
[61] A. Meuwsen and M. Lösel, *Z. anorg. Chem.*, 1953, **271,** 221.

present series of compounds. It is a mobile orange-red oil and it is possible that it has formula (XXVII), being then an oxygen analogue of tetrasulphur dinitride.

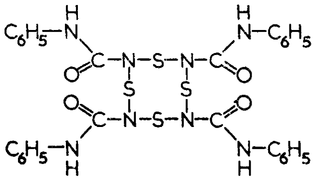
Sulphur Imides.—As mentioned earlier, tetrasulphur tetranitride is readily reduced to tetrasulphur tetraimide $S_4(NH)_4$. This compound crystallises as colourless needles of the class C_{2h} ; the melting point is 152°. The oxidation number of the sulphur in this compound is + 2, as is shown by the reaction with hydrogen iodide.[10] Since the infrared spectrum clearly shows NH frequencies but no SH frequencies,[17] formula (I) is firmly established. However, this formula also follows from chemical reactions, for instance, that with formaldehyde which gives the substance (XXVIII), and that with phenyl *iso*cyanate which gives the substance (XXIX) whence hydrochloric acid affords phenylurea.[16]



(I)



(XXVIII)



(XXIX)

Thus this sulphur imide is formally derived from elementary sulphur, S_8 : four of the sulphur atoms in the S_8 molecule are replaced by NH groups.

It has been further found that a second sulphur imide can be obtained which is also derived from S_8, namely, a heptasulphur imide in which one sulphur atom of the S_8 molecule is replaced by one NH group. Heptasulphur imide (XXX) is formed on reaction of sulphur monochloride with ammonia. This compound was early discovered but it was first given the formula S_6NH_2,[62] or $S_{18}N_3H_5$,[18] and it was not until 1942 that it was shown [63] to be S_7NH. The compound forms colourless crystals of the class D_{2h}[16] and the space group Pbnm, and melts at 113·5° ; it has been thoroughly investigated physically and chemically.[64] The infrared spectrum [30] shows NH bands. This at once indicates formula (XXX), which is confirmed by the result of hydrolysis. Heptasulphur imide forms stable mercuric compounds, $Hg(NS_7)_2$ with mercuric mercury,[65] and $Hg_2(NS_7)_2$ with mercurous mercury.[30] Like tetrasulphur tetraimide, heptasulphur monoimide forms a stable hydroxymethyl derivative (XXXI) with formaldehyde ; further it is readily acetylated and benzoylated, giving compounds (XXXII).[66] The nitrogen acts as donor atom towards sulphur trioxide ; so an *N*-sulphonic acid can be obtained from heptasulphur imide by means of sulphur trioxide.[67]

[62] A. K. Macbeth and H. Graham, *Proc. Roy. Irish Acad.*, 1923, **36,** 31.

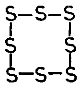
[63] M. H. M. Arnold, B.P. 544,577/1942 ; M. H. M. Arnold and W. E. Perry, U.S.P. 2,364,414/1944 ; 2,372,046/1945 ; 2,382,845/1945.

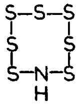
[64] M. Goehring, H. Herb, and W. Koch, *Z. anorg. Chem.*, 1951, **264,** 137.

[65] A. Meuwsen and F. Schlossnagel, *ibid.*, 1953, **271,** 226.

[66] M. Goehring and W. Koch, *Z. Naturforsch.*, 1952, **7b**, 634.

[67] M. Goehring and H. Hohenschutz, *Naturwiss.*, 1953, **40,** 291.





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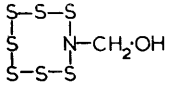
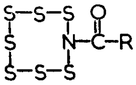
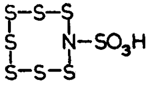


(XXXI)

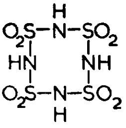


(XXXII)



(XXXIII)

Thus, as in other sulphur–nitrogen compounds one finds in these sulphur imides an eight-membered ring system as the skeleton. Here we shall only mention that such eight-membered rings occur also with higher valency stages of sulphur provided that it is linked to nitrogen. Thus in the chemistry of sulphur with the oxidation number + 6, a tetrameric sulphimide (XXIV) has been found in the form of derivatives—a silver salt and an *N*-methyl derivative—that is to be considered formally as a direct oxidation product of tetrasulphur tetraimide.[68] However, there is no genetical relation between these compounds (XXIV) and (I).



(XXIV)

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[68] R. Appel and M. Goehring, *Z. anorg. Chem.*, 1953, **271**, 171.