AMIDES AND IMIDES OF THE OXYACIDS OF SULFUR

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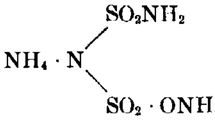
I. Introduction

Acid amides are derived from the oxyacids of nonmetallic elements by replacement of the OH group of the acid by NH_2, the amide group. Similarly, nonmetallic oxides yield their amino analogs when the oxygen of the oxide is replaced wholly or in part by the NH group, which is isosteric with oxygen. In general, this substitution is not effected by direct reaction of the oxide or acid with ammonia. Other methods for preparing the amides and imides have frequently to be devised. The products are often more stable than the corresponding oxides and oxyacids.

TABLE I

OXIDES AND OXYACIDS OF SULFUR WITH THE NITROGEN ANALOGS

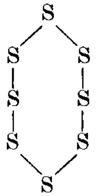
Sulfur oxides		Nitrogen analogs	
Formula	Stability	Formula	Stability
S_xO	Low	S_7NH	+
		S_7NR	+
		S_7NMe	Low
S_2O	Very low	$S_4(NR)_2$	+
SO	Very low	$S_4(NH)_4$	+
		$S_4(NR)_4$	+
		$S_4(NMe)_4$	+
S_2O_3	Low	$H_3N_3S_2$	Low
		$Na_3N_3S_2$	Low
SO_2	+	$S(NMe)_2$	+
		$OSNH$	Low
		$(OSNH)_n$	+
		$(OSNH)_4$	+
		$HOSN$	Low
		$Na(OSN)$	+
SO_3	+		
$(SO_3)_3$	+	$(O_2SNMe)_3$	+
		$(O_2SNR)_3$	+
$(SO_3)_n$	+	$(O_2SNMe)_4$	+
		$(O_2SNR)_4$	+
H_2SO	– Only RSOH and R_2SO	$[S(NH_3)_3]_2$	Low
		$[S(NH_3)_6]_2$	Low
		$R_2S{=}NH$	Low
H_2SO_2	– Only esters and organo derivatives	$S(NR_2)_2$	+
		$R_2S(O)NH$	+
H_2SO_3	– Only esters and other organo derivatives, salts	$NH_4(OSN)$	Low
		$OS(NR_2)_2$	+
		$SO_2 \cdot NH_3$ (?)	Low
H_2SO_4	+	$O_2S(NH_2)_2$	+
		Salts and organo derivatives	+
		$O_2S(OH)NH_2$	+
		Salts and organo derivatives	+
$H_2S_2O_2$	– Only esters	$S_2(NR_2)_2$	+
$H_2S_2O_3$	+	–	
$H_2S_4O_4$	– Only salts	–	
$H_2S_2O_5$	– Only salts	$HN[(S(O)NH_2)]_2$	+
		Ag-salt	+
$H_2S_2O_6$	– Only salts	–	
$H_2S_nO_6$	+	–	
$H_2S_2O_7$	+	$HN(SO_2NH_2)_2$	+
		 $NH_4 \cdot N(SO_2NH_2)(SO_2 \cdot ONH_4)$	+
$H_2S_nO_{3n+1}$	+	$HO_3S{-}(NH{-}SO_2)_nOH$	+
		$H_2NSO_2{-}(NH{-}SO_2)_nNH_2$	+

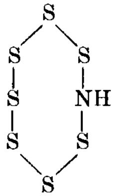
The numerous oxides and oxyacids of sulfur which are known are listed in the accompanying table I together with the nitrogen analogs which have been found up to the present: R denotes an organic radical and Me a metal atom.

II. Sulfur Imides Derived from Oxides of Sulfur in Oxidation States between (0) and (III)

A. HEPTASULFUR IMIDE

In the normal stable forms of elementary sulfur, that is, in the rhombic and monoclinic modifications as well as in the melt up to 160° (*36*), it is known that molecules are present which contain eight atoms. These molecules form puckered eight-membered rings which may be represented by Formula (I). It has been found that either one or four sulfur atoms in these eight-membered rings may be replaced by the NH group. When one sulfur atom is replaced one obtains heptasulfur imide [Formula (II)].


(I)

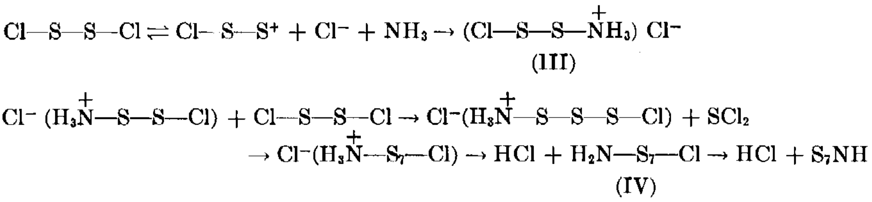

(II)

This substance was first discovered by Macbeth and Graham (*85*) among the products of the reaction between disulfur dichloride and ammonia. In addition to the main reaction products, namely, tetrasulfur tetranitride, S_4N_4, sulfur and ammonium chloride, these authors found white laminae, melting at 105°, which resembled sulfur and gave a transitory blue color with alcoholic alkali. Macbeth and Graham thought that the compound had the formula S_6NH_2. Later Arnold *et al.* (*11*) thought it to be $S_{18}N_3H_5$, and finally Arnold and his co-workers discovered the correct formula, S_7NH. The compound was then studied further by Goehring *et al.* (*45*), and the constitution was elucidated as that shown by Formula (II).

Heptasulfur imide is formed from elementary sulfur or from the product of the reaction of sulfur with sulfur trioxide by treatment with liquid ammonia at room temperature. A disproportionation reaction takes place in which, in addition to H_2S and S_4N_4, S_7NH is produced from the elementary sulfur or S_2O_3 (*1, 39*).

In the preparation of S_7NH it is better to use the reaction of sulfur chlorides with ammonia. This can occur both in organic solvents (*9, 15, 45*) and in water (*23*). Dimethylformamide is a very convenient solvent for the reaction. Becke-Goehring *et al.* (*15*) assume in this case that the reaction occurs in the manner described in the following paragraph.

In the polar solvent there is first a dissociation of the S_2Cl_2. Ammonia, as a nucleophilic reagent, attaches itself to the cation S_2Cl^+. The unstable intermediate (III) will then have a considerable tendency to split off positive groups and is able to react with further S_2Cl_2 and so lengthen the sulfur chain. The stepwise reaction which lengthens the chain leads finally to compound (IV), which can stabilize itself by splitting off HCl and closing the ring to form S_7NH.



$$Cl—S—S—Cl \rightleftharpoons Cl–S—S^+ + Cl^- + NH_3 \rightarrow \underset{(III)}{(Cl—S—S—\overset{+}{N}H_3)\ Cl^-}$$

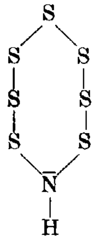
$$Cl^-\ (H_3\overset{+}{N}—S—S—Cl) + Cl—S—S—Cl \rightarrow Cl^-(H_3\overset{+}{N}—S—S—S—Cl) + SCl_2$$
$$\rightarrow Cl^-(H_3\overset{+}{N}—S_7—Cl) \rightarrow HCl + \underset{(IV)}{H_2N—S_7—Cl} \rightarrow HCl + S_7NH$$

Heptasulfur imide melts at 113.5° without decomposition, but the melting point is strongly depressed by small admixtures with sulfur. A eutectic between S_7NH and S_8 is observed at 91.5° with 46% of sulfur (*15*). Otherwise the physical behavior of S_7NH strongly resembles that of elementary sulfur. Thus, for example, it is not wetted by water but dissolves in many organic solvents—indeed more readily than sulfur itself.

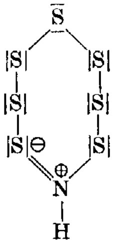
On rapidly heating S_7NH in vacuum above the melting point the following reaction occurs:

$$7S_7NH \rightarrow 2H_2S + NH_3 + 47S + 3N_2 - 450.1 \text{ kcal.}$$

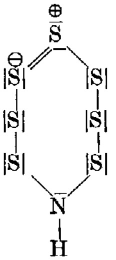
From the heat of this reaction the enthalpy of formation of S_7NH from its elements may be calculated as −67.4 kcal/mole. It is seen that S_7NH is unexpectedly stable—more so than would be anticipated from a knowledge of the electronegativities of the partners forming the bond. This stability can be traced back to resonance energy if the limiting forms



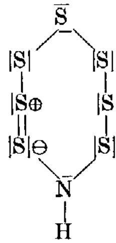
(Va)



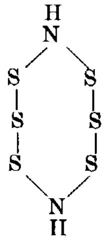
(Vb)



(Vc)

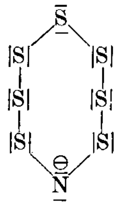


(Vd)



(Vc)

(Va–d) are taken into consideration. If this view is correct, there should be a considerable decrease in the stability of the eight-membered ring system in the transition from the hydrogen compound to the ion (VI).

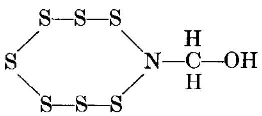


(VI)

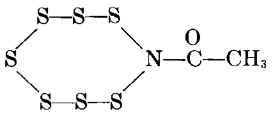
By decomposition of ethereal solutions of heptasulfur imide with triphenylmethyl sodium, an olive green sodium salt $Na(NS_7)$ may be prepared (*17*) which probably contains the ion (VI) and which, as expected, is much more reactive than S_7NH itself. For example, $NaNS_7$ undergoes hydrolysis even in contact with moist air.

The hydrogen atom which, as the infrared spectrum shows (*39*), is linked with the nitrogen atom of the S_7NH molecule, can be replaced readily by mercury, as would be expected. By decomposing S_7NH with mercury(II) acetate yellow-white $Hg(NS_7)_2$ is obtained (*93*) and bright yellow $Hg_2(NS_7)_2$ may be precipitated from a solution of S_7NH in dimethylformamide by mercury(I) nitrate (*56*). The mercury compounds are rapidly decolorized at room temperature with decomposition.

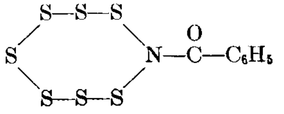
Compounds in which the hydrogen is replaced by an organic group are more stable than the more or less salt-like metallic derivatives of S_7NH. As examples, mention may be made of the reaction product with formaldehyde (*49,93*) Formula (VII), in which both the whole OH group or its hydrogen atom may be replaced by other organic groups; the reaction product with acetyl chloride (VIII); and the corresponding product with benzoyl chloride (IX) (*49*).



(VII)

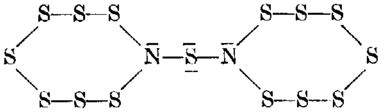


(VIII)

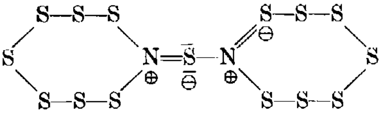


(IX)

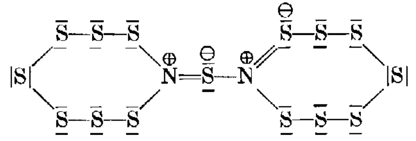
Reaction of S_7NH with other inorganic acid halides is also vigorous. Thus, interaction with SCl_2, with the addition of pyridine as an acceptor for HCl, gives good yields of crystalline yellow $S_{15}N_2$ (Xa–c), which melts without decomposition at 137°; whereas with S_2Cl_2 the compound $S_{16}N_2$ (XI)(*16*) is obtained (mp, 95–100°). Particularly $S_{15}N_2$ appears to be stabilized by resonance, as is indicated by Formulas (Xa–c).



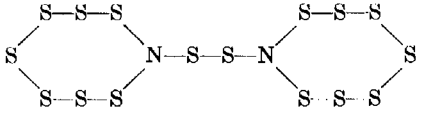
(Xa)



(Xb)

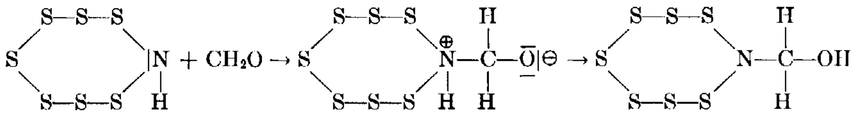


(Xc)

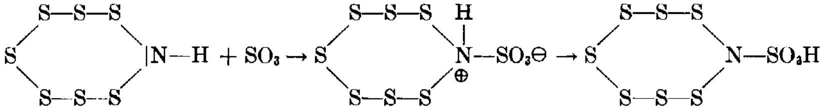


(XI)

The reaction of S_7NH with formaldehyde indicates that S_7NH is able to function as a Lewis base, that is, as a nucleophilic reagent. This mode of



reaction is even more apparent in the interaction of S_7NH with the strong Lewis acid, sulfur trioxide. A carmine red SO_3 adduct, S_7NHSO_3, is formed, which very probably has the formula (XII)(*46*).



(XII)

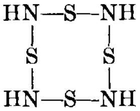
B. HEXASULFURDIIMIDE

It has been shown recently (*115a*) that the reaction between S_2Cl_2 and ammonia results not only in ammonium chloride, sulfur, heptasulfurimide, and S_4N_4, but also in the compound $S_6(NH)_2$. The compounds S_7NH and $S_6(NH)_2$ can be separated by adsorption chromatography on aluminum oxide. The hydrogen atoms in the compound are acidic like those in S_7NH

and can be estimated quantitatively by the method of Zerewitinoff. The colorless, crystallized compound is soluble in many organic solvents and insoluble in water. The crystals change color to yellow by heating up to 120° and melt at 140° with decomposition, forming a red liquid. The compound has the formula (Ve).

C. TETRASULFUR TETRAIMIDE

As has already been mentioned, it is possible formally to replace not only one or two sulfur atoms in its eight-membered ring [Formula (I)] by NH, but also four such atoms. In this way one obtains tetrasulfur tetraimide (XIII).



(XIII)

This compound was discovered by Wölbling (*118*), who reduced tetrasulfur tetranitride, S_4N_4, with tin(II) chloride. Formula (XIII) was first proposed by Arnold (*10*), although Meuwsen (*89*) had already suggested a ring structure on the basis of a molecular weight determination, though he placed the hydrogen atoms on sulfur. After evidence for NH groups in the molecule and a sulfur oxidation number of +2 had been adduced from the chemical properties (*10*) and from the Kα X-ray emission spectrum of the sulfur (*32*), the presence of N—H bonds was established from the infrared spectrum (*83*).

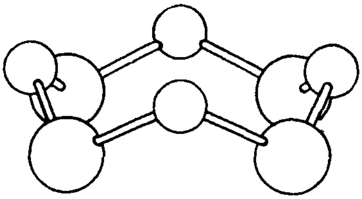
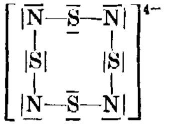


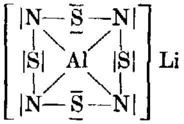
FIG. 1. Molecular structure of $S_4(NH)_4$ (*84*, *105*).

The structure of $S_4(NH)_4$ is completely elucidated (*84*, *105*). The colorless substance crystallizes in the orthorhombohedral system. There are four molecules in the unit cell and the molecule has the configuration shown in Fig. 1. Both the sulfur and the nitrogen atoms have a square planar arrangement. According to Sass and Donohue the S-N-S angle is 122° and the N-S-N angle 103.4°. The N-S distance is 1.67 Å. The molecule of $H_4N_4S_4$ is seen to be extraordinarily similar to that of elementary sulfur.

As in the case of S_7NH, hydrogen in $S_4(NH)_4$ may be replaced by metals. Attempts to prepare an alkali salt of tetrasulfur tetraimide go back to Meuwsen (*90*), who allowed KNH_2 to react with $S_4(NH)_4$ and showed $KNS \cdot KNH_2$ was probably formed. Becke-Goehring and Schwarz (*17*) studied the reaction of $S_4(NH)_4$ with triphenylmethyl sodium and obtained orange-red solid $Na_4(N_4S_4)$. It is likely that citron yellow $Na_2(H_2N_4S_4)$ is also formed. These sodium salts are extremely unstable. They react with water with inflammation, but even in moist air a reaction may occur which is accompanied by detonation.

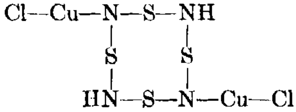
These experiments already indicate that the ion (XIV) is of low stability, and this conclusion is supported by attempts to prepare complex salts with this ion as a ligand. It is found that $S_4(NH)_4$ reacts rapidly and quantitatively with lithium aluminum hydride, $Li(AlH_4)$. Hydrogen and a solid white compound $Li(Al(N_4S_4))$ [Formula (XV)] result. This compound is very unstable:


(XIV)


(XV)

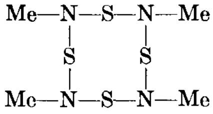
When well dried it detonates on touch. On careful hydrolysis (XV) may be reconverted to the hydrogen compound (XIII) (*55*).

Compounds of heavy metals with the $(NS)_4$ group are more stable than those substances which contain the ion (XIV), in which the bonding must be supposed to be largely heteropolar. From copper(I) chloride and $S_4(NH)_4$ in pyridine solution one obtains brown-black solid $(CuNS)_4$ (*54*), and red-brown $(AgNS)_4$ may be prepared similarly. Copper(II) chloride likewise yields the solid yellow compound (XVI), while copper(II) nitrate reacts


(XVI)

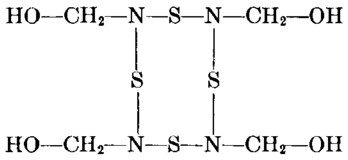
only partially to yield $(CuNO_3)_2H_2N_4S_4$, which is the analog (XVI). Mainly $Cu(NO_3)_2$ tends to oxidize $S_4(NH)_4$ and to convert it to S_4N_4. The mercury compounds are quite stable, yellow $Hg_4(N_4S_4)$ resulting from the reaction of $Hg_2(NO_3)_2$ with $S_4(NH)_4$ in dimethylformamide (*56*), while yellow $Hg_2(NS)_4$ and yellow $Hg_5(NS)_8$ is obtained by the reaction of $S_4(NH)_4$ with mercury(II) acetate (*92*).

For all of these heavy metal compounds the molecular weight is not yet established and it is only a matter of conjecture that the ring system remains intact, as in formulas (XVI) and (XVII). It is highly probable, however, that the metal in the compound is linked to nitrogen. To check this point the silver compound was reacted with ethyl iodide (*54*), and the product was then reduced and hydrolyzed. Formation of ethylamine showed that the ethyl group replacing the silver atom was bonded to nitrogen.

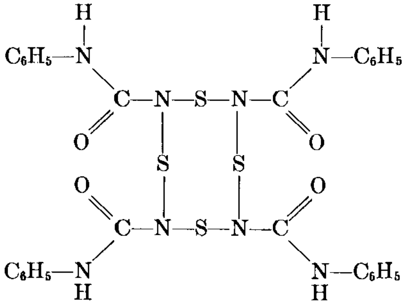


(XVII)

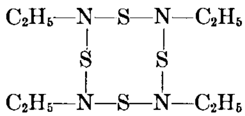
Just as in the case of S_7NH, organic derivatives of $S_4(NH)_4$ may be prepared. The methylol compound (XVIII) (*10*, *89*) has been known for a long time, and from it, further derivatives may be prepared (*10*). Arnold (*10*) prepared (XIX) from $S_4(NH)_4$ and phenylisocyanate. Lengfeld and Stieglitz (*79*) obtained $S_4(NH)_4$ derivatives by an entirely different route involving the interaction of ethylamine with SCl_2. In this way a yellow oil is obtained to which the author ascribed formula (XX). Whether this oil is really the pure product (XX) or a mixture of it with other polymeric compounds of the formula $(C_2H_5NS)_x$ remains uncertain. It seems the more questionable since Stone and Nielsen (*109*) obtained from methylamine and SCl_2 a mixture of polymers $(CH_3NS)_x$, in which higher polymeric substances (with a molecular weight of 600 and more) were present to a considerable extent. Jenne (*67*) obtained a crystalline derivative (mp, 163°),



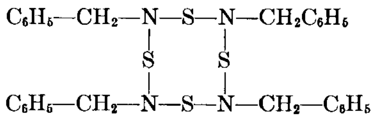
(XVIII)



(XIX)



(XX)

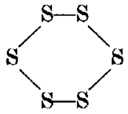


(XXI)

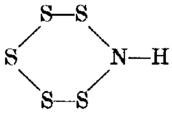
which probably has the Formula (XXI) from benzylamine and SCl_2 at high dilution. This product is almost certainly a monomer, but the molecular weight has not yet been definitely established. Stone and Nielsen prepared recently the analog methyl compound (*109a*).

D. OTHER SULFUR IMIDES

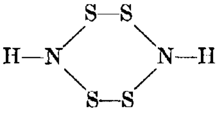
In addition to S_8 molecules which constitute the stable modifications of sulfur, S_6 molecules may be obtained, the structure of which has been elucidated (*28*) and which form a puckered six-membered ring, Formula (XXII). The question then arises as to whether one or more sulfur atoms in this ring system can be replaced by the NH group, that is, whether there are compounds such as (XXIII) or (XXIV).



(XXII)

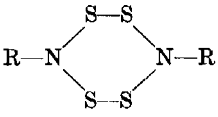


(XXIII)

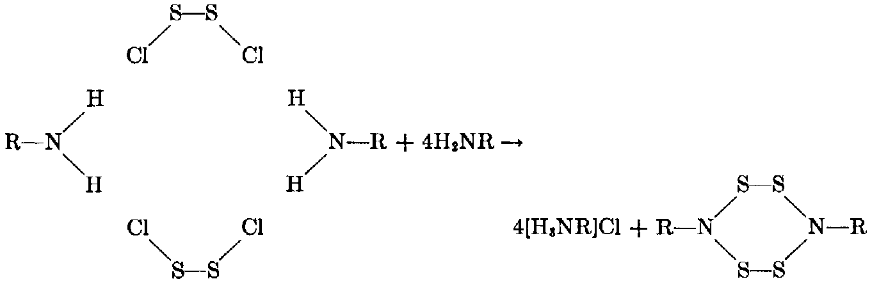


(XXIV)

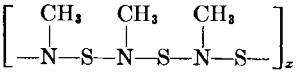
It has not yet proved possible to prepare these sulfur imides, but derivatives of at least (XXIV) have been found in which the hydrogen of the imide group is replaced by an organic radical (XXV). The first representative of these *N,N'*-dialkyl tetrasulfur dinitrides was found by Levi (*81*) in very small yield when he allowed S_2Cl_2 to react with ethylamine and distilled the product with steam. This group of compounds becomes readily accessible if S_2Cl_2 is allowed to react with alkylamines in ether solution using the Ruggli-Ziegler dilution principle (*14*).



(XXV)

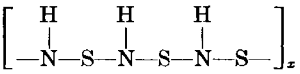


R = C_2H_5, $C_{12}H_{25}$, C_6H_{11}, $C_6H_5{\cdot}CH_2$, $C_6H_5{\cdot}CH_2{\cdot}CH_2$, Sulfur imides in which the NH groups are incorporated in sulfur chains and chain-like sulfur imides in general, have not yet been prepared. There are also no organic derivatives of these compounds unless the polymeric substances of Stone and Nielsen (XXVI) (*109*), which are derived from the hypothetical imide (XXVII) are counted as such.



$$\left[-\overset{\overset{CH_3}{|}}{N}-S-\overset{\overset{CH_3}{|}}{N}-S-\overset{\overset{CH_3}{|}}{N}-S-\right]_x$$

(XXVI)

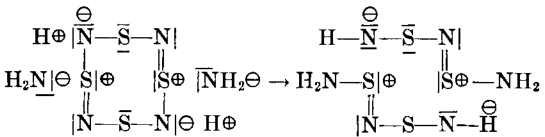


$$\left[-\overset{\overset{H}{|}}{N}-S-\overset{\overset{H}{|}}{N}-S-\overset{\overset{H}{|}}{N}-S-\right]_x$$

(XXVII)

E. The Compound $H_3N_3S_2$

If the nitrides of sulfur, S_4N_4 and S_2N_2 (*38*), are dissolved in liquid ammonia, then a reaction occurs at about $-70°$ for S_2N_2 and at about $-40°$ for S_4N_4. A dark red solution is produced as the reaction proceeds, and after driving off ammonia, a red mass of the composition S_4N_4, $2NH_3$ (*104*) or S_2N_2,NH_3 (*39*) is obtained. The solution spectra of these ammoniates in the visible and ultraviolet regions are identical, as are the X-ray powder photographs of the two solids. Accordingly the two substances are almost certainly the same. Since volatile S_2N_2 is readily formed from the ammoniate, it is probable that the S_4N_4 molecule is decomposed during the reaction with ammonia into S_2N_2 fragments. The process can then be formulated as follows:



(XXVIII)

If this view is correct, the ammoniate should behave as an acid in liquid ammonia (*12*), that is, the solution should conduct and the hydrogen should be replaced by metal in a neutralization reaction. Actually the conductivity of liquid ammonia is increased considerably when S_4N_4 dissolves in it and the solution is warmed to $-47°$ (*17*). Thus with a $S_2N_2 \cdot NH_3$ molarity of 1.67×10^{-4} mole/liter, the specific conductivity is 0.104×10^{-3}; at 21.01×10^{-4} mole/liter it is 0.62×10^{-3}; and at 13.24×10^{-3} mole/liter, 2.84×10^{-3} ohm^{-1} cm^{-1}.

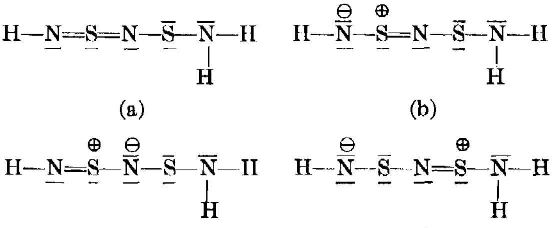
The metal amides are the outstanding bases in the ammonia system with which acid (XXVIII) can be neutralized. In order to convert this acid (XXVIII) into a salt, Berg and Goehring (*19*) reacted its solutions in ammonia with KNH_2. A yellow solid with the composition $K_3N_3S_2$ was produced. This potassium compound proved to be unusually sensitive to dry, and, especially, to moist air, and reacted with inflammation.

The yellow solid $K_3N_3S_2$ may be a salt of the ammoniate (XXIX), or, as was at first assumed, an equimolecular mixture of the salts (XXX) and (XXXI). Since no difference was observed in the reactivity of the H atoms of the ammoniate during the reaction with potassium amide, the theory favored initially was that there was first a dissociation of $H_3N_3S_2$ to HNS and $S(NH_2)_2$, followed by salt formation. Later, however, it proved possible, by using a much milder neutralization reaction, to establish a difference between reactivity of the separate hydrogen atoms of (XXXII), as would be expected for an imide-amide. The $S_2N_2 \cdot NH_3$ was titrated in ethereal solution with triphenylmethyl sodium solution (*17*), and two color changes were observed. At the first the red solution became citron yellow. When twice the volume of the triphenylmethyl solution required to produce this color is then added there is a further color change to red. After the first color change, there was a deposit which was brown when dry and had the composition $Na(-N{=}S{=}N-S-NH_2)$. After the second color change, a yellow solid phase is obtained, which has the formula $Na_3(-N{=}S{=}N-S-N{=})$. The latter is very unstable and detonates on touch.

$$K_3[-\overline{\underline{N}}-\overline{\underline{S}}-N{=}\underline{S}-\overline{\underline{N}}-] \qquad K[-\overline{N}{=}\overline{S}|] \qquad K_2[|\overline{N}{=}\overline{S}-\overline{\underline{N}}-]$$

(XXIX) (XXX) (XXXI)

It is seen from all these experiments that $H_3N_3S_2$ is a substance with acid properties. The limiting structures (XXXIIa–d) must probably be considered. The imide hydrogen should be replaced readily by metal atoms, but the amide hydrogen is also replacable in this way.



$$H-\underline{N}{=}\underline{S}{=}\underline{N}-\overline{\underline{S}}-\underset{\substack{|\\ H}}{\overline{N}}-H \qquad H-\overset{\ominus}{\underline{\overline{N}}}-\overset{\oplus}{\underline{S}}{=}\underline{N}-\overline{\underline{S}}-\underset{\substack{|\\ H}}{\overline{N}}-H$$

(a) (b)

$$H-\underline{N}{=}\overset{\oplus}{\underline{S}}-\overset{\ominus}{\underline{\overline{N}}}-\overline{\underline{S}}-\underset{\substack{|\\ H}}{\overline{N}}-H \qquad H-\overset{\ominus}{\underline{\overline{N}}}-\underline{S}-\underline{N}{=}\overset{\oplus}{\underline{S}}-\underset{\substack{|\\ H}}{\overline{N}}-H$$

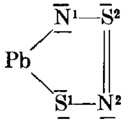
(c) (d)

(XXXII)

In the reaction with triphenylmethyl sodium the molecule of $H_3N_3S_2$ certainly remains intact, since the isolation of the monosodium salt would otherwise be difficult to understand. It is still uncertain whether, in the reaction with potassium amide, the molecule is decomposed or remains intact; that is, whether the potassium salt has the formula (XXIX) or (XXX) and (XXXI).

Cleavage of the molecule (XXXII) into two fragments with sulfur in different oxidation states, which cannot be established with certainty in the reaction with KNH_2, is however observed if the compound is decomposed with PbI_2 or $Pb(NO_3)_2$ or with HgI_2 in liquid ammonia as solvent (*104*). In the reaction with lead salts, green $Pb(NS)_2 \cdot NH_3$ which is sparingly soluble in ammonia, is precipitated. After filtering this substance, yellow-green $Hg(N_2S)NH_3$ may be precipitated by adding HgI_2. The metallic salts may also be added in the reverse order.

The structure of $Pb(NS)_2NH_3$ has now been elucidated (*117*). It crystallizes in the monoclinic system and there are four molecules in the unit cell. The molecule, which is not planar, has the formula (XXXIII), with the N^1-Pb-S^1 bond angle 78°; N-S-N, 114°; Pb-N^1-S, 115°, and S-N^2-S, 103°.



(XXXIII)

The following interatomic distances have been found: Pb-S, 2.75 Å; Pb-N^1, 2.27 Å; S^1-N^2, 1.72 Å; S^2-N^1, 1.70 Å; S^2-N^2, 1.60 Å. Since the distance between N^2 and the lead atom of the neighboring molecule is relatively small (2.83 Å), one can perhaps assume the existence of a secondary valency from this nitrogen atom to the next molecule. The position of ammonia has not yet been determined with certainty.

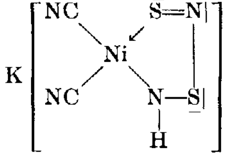
The structure of $Pb(NS)_2$ shows that $H_3N_3S_2$ undergoes intermolecular disproportionation under the influence of heavy metal salts such as PbI_2.

$$2H_3N_3S_2 \rightarrow H_2N_2S_2 + 2H_2N_2S.$$

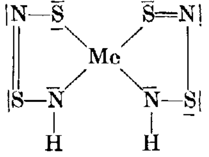
The products of the disproportionation reaction react with heavy metal salts forming compounds of low solubility. A similar disproportionation of sulfur nitride ammoniate was proposed earlier by Meuwsen (*90*), but he assumed the formation of $H_4N_4S_4$, whereas, in fact, as follows from Formula (XXXIII), the acid from which the lead salt is derived has only half the molecular weight.

Thallous nitrate reacts with (XXXII) in the same way as lead iodide and nitrate. Red-brown $2Tl(NS)_3 \cdot NH_3$ may be precipitated from ammonia solution and may be converted to red-brown $Tl(NS)_3$ (*54*). Ochre colored $Tl_3(NS)_8$ is precipitated from alcoholic solution. With copper(I) chloride, brown $Cu(NS)_2$ is precipitated, while with silver nitrate red-brown $Ag(NS)_2$ is obtained (*54*). The structures of these metallic derivatives are not yet established.

A series of inner complex salts of metals of the eighth subgroup is derived from the hydrogen compound $H_2N_2S_2$, on which the lead compound (XXXIII) is based. The possibility of forming such complexes was first recognized by Goehring and Debo (*42*) from the intense red color which results from the interaction of Belluci's salt, $K_4[Ni(CN)_3]_2$, and S_4N_4 in alcoholic solution. Weiss (*115*) later succeeded in isolating the compound $K(Ni(CN)_2(HN_2S_2))$ as one of the products of this reaction. Since this compound is diamagnetic and the presence of hydrogen has been established unambiguously by the Zerewitinoff-Tschugaeff method (*116*), formula (XXXIV) is very probably correct, with nickel in the bivalent state. It is found that other complex compounds with the same sulfur imide as a ligand are also very readily made. The nickel and cobalt carbonyl compounds, $(Ni(CO)_4)$ and $Co_2(CO)_8$ or $HCo(CO)_4$ are allowed to react with S_4N_4 in an indifferent organic solvent. Alternatively, $NiCl_2$, $CoCl_2$, $PdCl_2$, or $H_2(PtCl_6)$ may be used in alcoholic or dimethylformamide solution (*25*, *35*). Heavy metal compounds of the formula (XXXVa–e) may be isolated from the reaction products, in some cases in very good yield. On prolonged boiling of $NiCl_2$ with S_4N_4 in alcohol, compounds other than (XXXVa–e) are formed in small amounts (*102*). Compounds of the type (XXXVa–e) are well crystallized and deeply colored. The nickel and cobalt compounds are deep violet, the palladium compound is red-brown and the platinum compound blue-black. These substances are freely soluble in many organic solvents. They were originally formulated as $Me(NS)_4$ without hydrogen, largely on account of their formation from carbonyls and S_4N_4, since it was not apparent how the formation of $(HS_2N_2)^-$ could arise. Piper has, however, proved that the compounds actually contain hydrogen (*101*), and subsequently Weiss and Becke-Goehring have established the presence of hydrogen by the Zerewitinoff-Tschugaeff method (*116*). An iron compound $Fe(NS)_4$, which is formed in the reaction of $Fe(CO)_5$ with S_4N_4, also belongs to this series (*40*). Whether it has the formula (XXXVa–e) or is hydrogen free is still unknown. It is striking that the iron compound does not dissolve in nonpolar organic solvents.



(XXXIV)



(XXXVa)

(Me = Ni, Co, Pd, Pt and probably Fe also)

The constitution of the platinum complex has been elucidated by crystal structure investigation (*82*), and the molecule (XXXVa–e) has been found to be completely planar. The interatomic distances and bond angles are given in Fig. 2. As would be expected, the nickel compound is diamagnetic, and the cobalt and iron compounds show paramagnetism, corresponding with one and two unpaired *d*-electrons, respectively (*41*). These

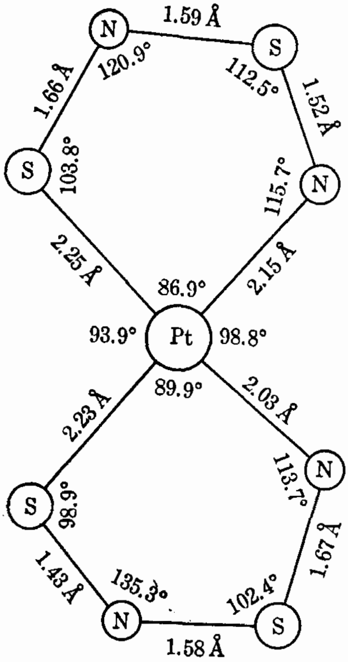
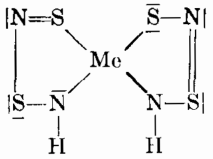
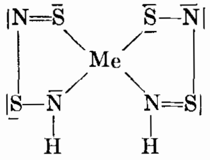


Fig. 2. Interatomic distances and bond angles in $Pt(HN_2S_2)_2$ (Lindqvist and Weiss, *82*).

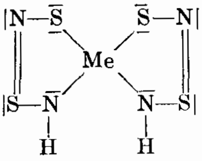
properties are quite unexpected, at least as far as cobalt and iron compounds are concerned, and they indicate that an abnormal electronic state of the metal is stabilized by an unusual ligand field. The planar structure, the high stability, and the special physical properties, lead one to suppose that the compounds possess special possibilities of resonance. In fact, numerous mesomeric resonance structures may be formulated, some of which are given by Formulas (XXXVa–e).



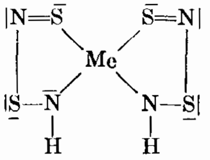
(XXXVb)



(XXXVc)

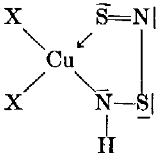


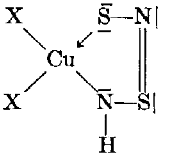
(XXXVd)

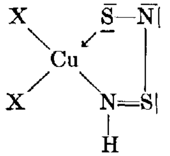


(XXXVe)

The copper compounds which are obtained by the reaction of $CuCl_2{\cdot}2H_2O$ or $CuBr_2$ with S_4N_4 in dimethylformamide are clearly similarly constituted (*34*). If Formula (XXXVIa–c) is assumed in accordance with the analytical results, which fit the formula $CuX_2N_2S_2$, copper will have an oxidation number of +3. As the deep violet solid chloro compound is diamagnetic, the physical properties of the compound appear to support this theory. Resonance stabilization of the complex is also possible here.


(XXXVIa)


(XXXVIb)


(XXXVIc)

(X = Cl, Br)

F. Amides of the Lowest Sulfur Oxyacids

The compound $H_3N_3S_2$ is an imide-amide of sulfur. Amides of sulfur with a simpler structure, such as the compounds (XXXVII–XL) have not yet

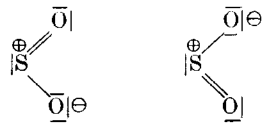
$H_2N{-}S{-}NH_2$	$H_2N{-}S{-}S{-}NH_2$	$H_2N{-}S{-}S{-}S{-}NH_2$	$H_2N{-}S{-}S{-}S{-}S{-}NH_2$
(XXXVII)	(XXXVIII)	(XXXIX)	(XL)

been prepared, though organic derivatives of these compounds, in which hydrogen is replaced by alkyl radicals, are well known and quite stable. Derivatives of (XXXVII) and (XXXVIII) were prepared quite early (*78*, *94*, *95*). Levi (*80*) has made derivatives of (XXXIX) by the reaction of dialkylamines with sulfur and lead oxide. Derivatives of (XL) are available by several routes; for example, by reaction of sulfur with secondary amines and HgO or PbO, by reaction of S_7NH with amines, by reaction of S_2Cl_2 with NH_3 and dimethylformamide, and, finally, from secondary amines with S_2Cl_2, a method which also gives compounds with 1, 2, and 3 sulfur atoms in the chain (*68*).

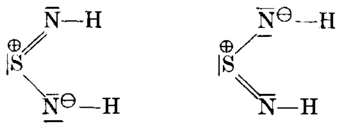
III. Sulfur Imides Derived from Sulfur Dioxide

A. Sulfur Diimide

If both oxygen atoms in sulfur dioxide (XLI) are replaced by isosteric imide groups, sulfur diimide (XLII) is obtained. As in the dioxide, sulfur in this compound should have an oxidation number of +4. Derivatives of this diimide were obtained in the reaction of S_4N_4 with NH_3 and HgI_2 (*104*). The compound HgN_2S, which results in this reaction through the



(XLI)



(XLII)

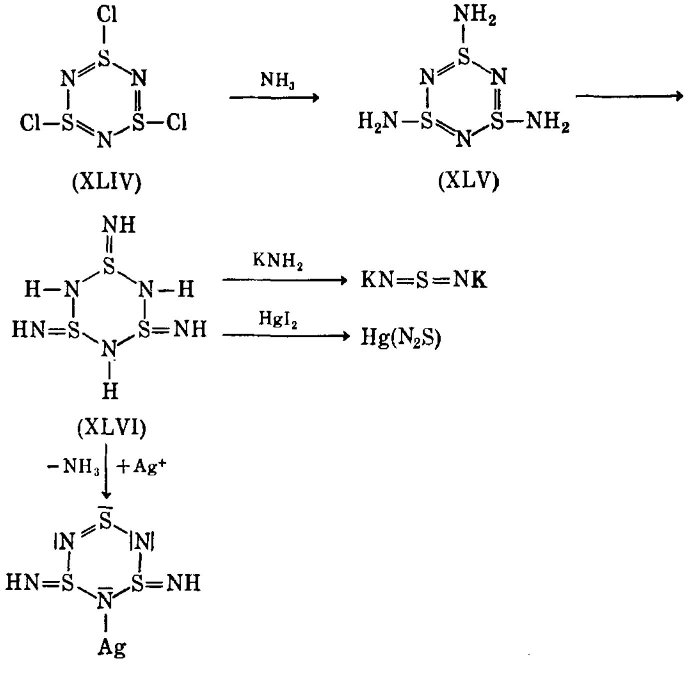
intermediate $H_3N_3S_2$, should be regarded as a mercury derivative of (XLII).

Sulfur diimide should be obtained most simply by ammonolysis of a halide of tetravalent sulfur. Sulfur tetrachloride or trithiazylchloride (XLIV) are available as acid halides for such a reaction. The former is very readily decomposed by ammonia, but $S(NH)_2$ cannot be identified among the reaction products which consist chiefly of S_4N_4, NH_4Cl, and chlorine (*43*). Only an organic derivative of (XLII) could be prepared in a solvolytic reaction of this sort with SCl_4, in which butylamine gave the *n*-butylimide (XLIII) (*53*).

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}N{=}S{=}N{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

(XLIII)

Thiazyl halides, such as thiazyl chloride (XLIV) or thiazyl bromide, the molecular weight of which is unknown, are rapidly solvolyzed by ammonia, in which they dissolve to give a red color. Analysis shows the prod-



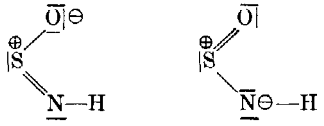
(XLVII)

uct to be a mixture of ammonium halide and $[S(NH_2)_2]_x$. Compounds in which sulfur has an oxidation number of +4, however, disproportionate readily to sulfur nitrides (tervalent S) and compounds of sexvalent sulfur. The derived hydrogen compound may, however, be isolated as a metallic derivative when the structure is stabilized (*20*). Thus the product for which the Formula (XLVI) is proposed interacts with potassium amide in liquid ammonia to give solid yellow $K_2(N_2S)$, while with HgI_2, one obtains from liquid ammonia yellow-green solid $Hg(N_2S)NH_3$, which is transformed to yellow $Hg(N_2S)$ in high vacuum at 90°.

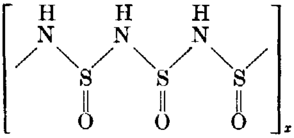
When the reaction product of (XLIV) is taken up with ammonia and precipitated with silver nitrate, red-brown silver salts of variable composition are obtained. When part of the ammonia is removed carefully from the filtrate one obtains a yellow crystalline silver salt which analysis shows to have the composition AgN_6S_3 and which can very probably be represented by formula (XLVII). This silver compound is light sensitive but otherwise stable at room temperature. It detonates with extreme violence on impact (*86*).

B. Thionyl Imide and Its Isomers

Reaction between thionyl chloride and ammonia should in principle lead to a further sulfur imide (XLVIII), derived from sulfur dioxide by replacing one oxygen atom by the isoteric NH group.



(XLVIII)



(XLIX)

P. W. Schenk (*106*) studied the reaction between $OSCl_2$ and NH_3 in the gas phase at low temperature. He obtained a product which was colorless and solid below −85° and melted at about −85° to a colorless liquid with an appreciable vapor pressure at −70°. Analysis and vapor density determinations indicated the formula OSNH, and one can assume with some certainty that this volatile substance is a true analog of sulfur dioxide with the structure (XLVIII).

Monomeric thionyl imide polymerizes very rapidly. Even at above −60° a yellow solid separates from the liquid which, with further warming becomes glass-clear yellow-brown, red, and finally brown. The brown polymer, which does not dissolve in organic solvents, is found from the infrared spectrum to contain NH groups (*18*), so that Formula (XLIX) proposed by Schenk appears to be established.

Reaction between thionyl chloride and ammonia takes a different course at room temperature in an organic solvent such as chloroform. The solution becomes deep red, and, particularly if lime is added to fix the HCl, the following decomposition occurs almost quantitatively:

$$OSCl_2 + NH_3 + CaO \rightarrow HOSN + CaCl_2 + H_2O.$$

The red solid compound HOSN may be isolated after evaporating the solvent. It is not, however, very stable and readily goes over into the brown polymer (XLIX). The red compound, which is monomeric in organic solvents, is an isomer of Schenk's thionyl imide. It polymerizes so readily that only chemical methods have hitherto been applied successfully in establishing the structure as (La) (*18*).

$$H-\overline{\underline{O}}-\overset{\oplus}{\underline{S}}=\overset{\ominus}{\overline{\underline{N}}} \qquad H-\overset{\oplus}{\underline{O}}=\overset{\oplus}{\underline{S}}-\overline{\underline{N}}|\ominus\ominus \qquad H-\overset{\oplus}{\underline{O}}=\underline{S}=\overline{\underline{N}}\ominus$$

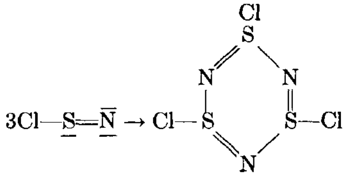
(La) (Lb) (Lc)

$$\ominus|\overline{\underline{O}}-\overset{\oplus}{S}=\overline{\underline{N}}\ominus \qquad \overline{\underline{O}}=\overset{\oplus}{\underline{S}}-\overline{N}|\ominus\ominus \qquad \overline{\underline{O}}=\overline{S}=\overline{\underline{N}}\ominus$$

(LIa) (LIb) (LIc)

This is transformed readily by excess of thionyl chloride into the acid chloride, which goes over to the stable trimer (XLIV).

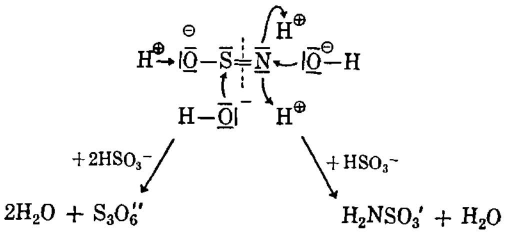
$$H-\overline{\underline{O}}-\underline{S}=\overline{\underline{N}} + OSCl_2 \rightarrow Cl-\underline{S}=\overline{N}| + SO_2 = + HCl$$



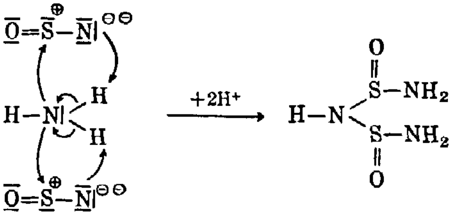
(XLIV)

In solvents which are not proton acceptors (L) may be shown by cryoscopic measurements to be present in the undissociated state. If the solvent is itself a proton acceptor it follows that the ions (LIa–c) must result.

In an aqueous medium the ion undergoes rapid hydrolysis, the results of which are especially apparent if the bisulfite ion HSO_3^- is added to the reaction medium. The changes taking place may then be represented by the following scheme:



When ammonia is used as solvent a deep red solution is formed which contains the ammonium salt $(NH_4)(OSN)$. At elevated temperatures the ammonia also exerts a solvolytic action.



The ion $(NSO)^-$ is more stable than the hydrogen compound. This is at once apparent if one considers the limiting formulas (LIa–c) which describe the ion. The incidence of mesomerism becomes much smaller in passing from the ion to the hydrogen compound. In fact, the latter can also be represented by several limiting formulas (La–c), but (Lb) is improbable because neighboring atoms have formal charges of the same sign, while (Lc) also has only a small effect as the charge distribution does not correspond with the electronegativities of the elements. The resonance-stabilized ion is present in the lattice of the sodium salt which may readily be prepared by treating an ethereal solution of HOSN with triphenylmethyl sodium (*18*). The solid brown-violet salt Na(OSN) is, in contrast to the hydrogen compound HOSN, stable for some days when air and moisture are excluded, and the tendency to polymerization shown by (La) is no longer observed. A red-silver salt Ag(NSO) can also be prepared (*51*). As might be expected, this is much less stable than the sodium salt, since the ability of the ion (LI) to show resonance is much restricted by polarization.

Starting from imidosulfinamide (LII), the ammonolysis product of red HOSN, it is possible to obtain a further isomer of thionyl imide. Thus, when hydrogen chloride is condensed on to (LII) a yellow solution results

$$H_2N—SO—NH—SO—NH_2$$

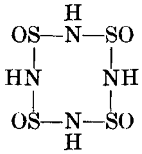
(LII)

from which, on distilling off the HCl, yellow crystals separate. The yellow substance passes over into the brown polymer (XLIX) with great ease. The absorption spectrum of the yellow substance is very similar to that of C_2H_5NSO (LIII) (*69*). Probably, therefore, it has the same arrangement of atoms as in (LIII) or (XLVIII). The isomer must differ from monomeric thionyl imide in its degree of polymerization, but the great instability of the substance does not allow this to be determined. It is striking that the yellow isomer is able not only to go over rapidly to brown polymeric thionyl imide at low temperatures (above −60°) but can also yield the red isomer when it is rapidly warmed to about +60° (*51*),

$$C_2H_5-\overset{\ominus}{N}-\overset{\oplus}{S}=O \qquad C_2H_5-N-\overset{\oplus}{S}-\overset{\ominus}{O}$$

(LIII)

Finally, yet a fifth isomer of thionyl imide may be obtained in quite another way. Fluck and Becke-Goehring (*33*) started with tetrasulfur tetraimide (XIII) and oxidized it by heating with air at 110–120°. Among the products was the solid red tetramer of thionyl imide (LIV) which was soluble in organic solvents such as methanol. The tetramer could not be transformed into the other isomers. The following scheme shows the transformations of these various isomers.



(LIV)

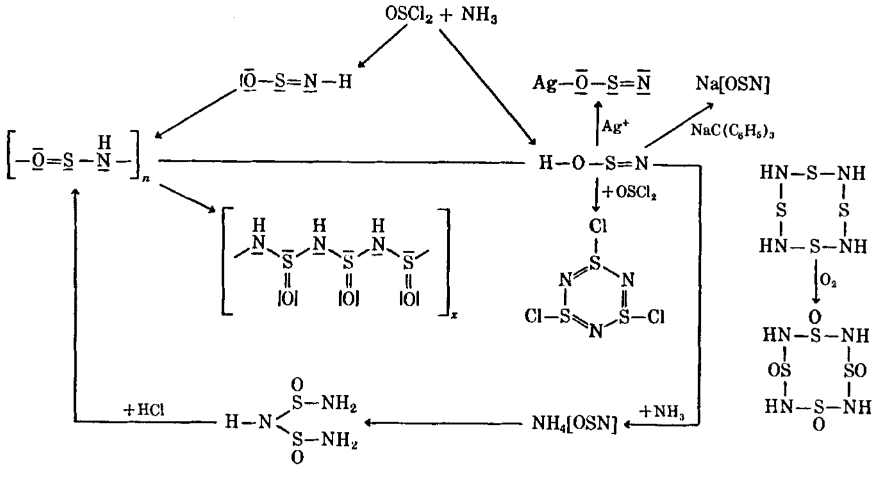


FIG. 3. The interrelationship of the isomers of thionyl imide.

IV. Amides of Oxyacids of Sulfur (IV)

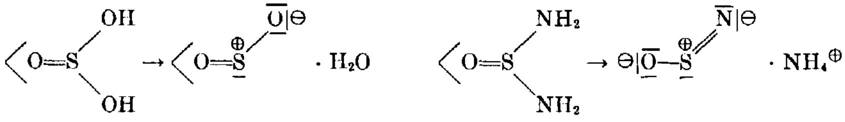
A. THIONYL AMIDE

Schiff first suggested that the diamide of sulfurous acid was formed in the reaction of thionyl chloride with ammonia (*107*). Later Meslans (*87, 88*) thought it likely that the same substance was formed from thionyl fluoride and ammonia;

$$OSX_2 + 4NH_3 \rightarrow OS(NH_2)_2 + 2NH_4X.$$

These speculations have not so far been confirmed. In the reaction between thionyl chloride and ammonia, using liquid ammonia and cooling carefully, a compound with sulfur and nitrogen in the atomic ratio of 1:2 does indeed result (*37*); but it shows the same absorption spectrum in solution as salts of HOSN, so that its structure is probably not that of an amide of sulfurous acid, but of the isomeric ammonium salt $NH_4(OSN)$. This salt goes over very readily to (LII). Meslans' experiments could not be confirmed either by Moissan and Lebeau (*97*, *98*, *99*) or in later work, although it was thought possible that thionyl amide is formed from OSF_2 and NH_3 (*96*).

It is not surprising that thionyl amide (LV) has hitherto not been obtained. Its analog, sulfurous acid, has also not been made in the pure state and readily decomposes to SO_2, so that one can expect $OS(NH_2)_2$ to react in an analogous way.



(LV)

In contrast with the hydrogen compound (LV), its organic derivatives, in which H is replaced by alkyl, are well known.

B. IMIDOSULFINAMIDE

The ammonium salt of thionyl imide, $NH_4(OSN)$, is transformed in a few hours at room temperature into imidosulfinamide (LII), with evolution of ammonia;

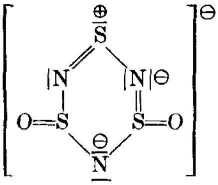
$$2NH_4(OSN) \rightarrow NH_3 + H_2N{-}SO{-}NH{-}SO{-}NH_2.$$

(LII)

Imidosulfinamide can also be obtained directly from $OSCl_2$ and NH_3, without first making $NH_4(OSN)$ (*48*). Finally, it can be made from SO_2 and NH_3 by allowing one molecular proportion of NH_3 to react with two of SO_2 at −10° to −20° to form orange-red $SO_2 \cdot 2NH_3$. The latter decomposes with loss of NH_3 and SO_2 and (LII) can be isolated from the decomposition products (*48*).

The diamide of imidosulfinic acid is a yellow solid which is relatively stable. A silver salt $AgN(SONHAg)_2 3H_2O$ may be prepared from it. When one attempts to recrystallize the substance, which comes down in the amorphous state, from water, HOSN, which can be recognized by the transitory red color, and also a well-crystallized compound with the composition $S_3N_4O_2H_{4-6}$ (*110*) are formed. Molecular weight determination in water shows this to be an ammonium salt for which the Formula (LVI) is proposed.

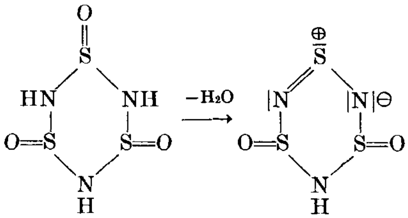
$$2HN(SONH_2)_2 \rightarrow H_2O + HOSN + NH_4^{\oplus}$$



(LVI)

The imide from which the salt (LVI) is derived is the oxygen analog of the imide corresponding to the silver salt (XLVII). Its probable mode of formation entails initially the loss of ammonia and HOSN from two molecules of $HN(SONH_2)_2$. The resulting trimeric thionyl imide then tends to form its anhydride

$$2HN(SONH_2)_2 \rightarrow NH_3 + HOSN +$$

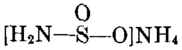


(LVII) (LVIII)

Loss of water from (LVII) corresponds to the loss of ammonia from the corresponding imide (XLVI) (cf. p. 175).

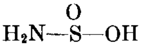
C. Amidosulfuric Acid and Imidosulfuric Acid

When sulfur dioxide reacts with excess of ammonia at low temperature in an indifferent solvent, one obtains, according to Divers and Ogawa (*27*), the colorless ammonium salt of imidosulfinic acid (LIX). Schumann (*108*) thought that he had isolated the corresponding free acid (LX) from the product of the reaction of ammonia with excess of sulfur dioxide. The constitution of the yellow reaction product SO_2NH_3 has, however, not yet been elucidated, especially since its molecular weight cannot be determined.



$$[H_2N{-}\overset{O}{S}{-}O]NH_4$$

(LIX)

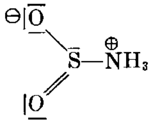


$$H_2N{-}\overset{O}{S}{-}OH$$

(LX)

$$[O{=}S(NH_3)_2][SO_3]$$

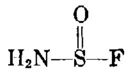
(LXI)



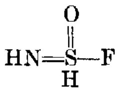
(LXII)

The compound SO_2NH_3 could be (LX) or a thionyl ammonium sulfite (*65*), but it may also be considered as a simple adduct of NH_3 and SO_2 (LXII). It shows a strong tendency to disproportionation to compounds with a sulfur oxidation number of +6 and others with sulfur in a lower oxidation state (*47*).

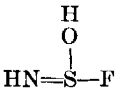
Organic derivatives of compound (LX) are again well known and are formed by addition of SO_2 to primary or secondary amines. A pure inorganic derivative of (LX) is found in compound (LXIII), which is formed from OSF_2 and ammonia as a gas and which is soluble in ether (*52*). The tautomeric forms (LXIV) and (LXV) are possible, though (LXIII) polymerizes very readily to a yellow solid (LXVI).


$H_2N{-}\overset{\overset{O}{\|}}{S}{-}F$

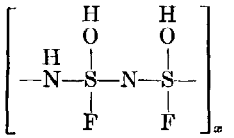
(LXIII)


$HN{=}\underset{H}{\overset{\overset{O}{\|}}{S}}{-}F$

(LXIV)

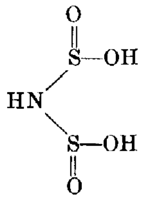

$HN{=}\overset{\overset{\overset{H}{O}}{|}}{S}{-}F$

(LXV)

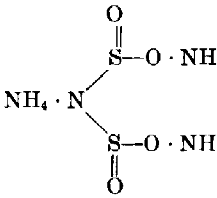

$\left[{-}\overset{H}{N}{-}\underset{\underset{F}{|}}{\overset{\overset{\overset{H}{O}}{|}}{S}}{-}N{-}\underset{\underset{F}{|}}{\overset{\overset{\overset{H}{O}}{|}}{S}}{-}\right]_x$

(LXVI)

Organic derivatives of the type $R_2NS(O)F$ have also been prepared from (LXIII). The existence of an imidosulfuric acid (LXVII) is more probable than that of an amidosulfuric acid. According to Ephraim and Piotrowski (*31*), the ammonium salt of this acid (LXVIII) is formed when SO_3 is added to excess of NH_3. It seems that there are two compounds with the composition SO_22NH_3, one of which is formed at very low temperatures in the form of glistening plates (*48*), and a compound which is obtained at room temperature. The latter is probably the triammonium salt of imidodisulfinic acid.



(LXVII)



(LXVIII)

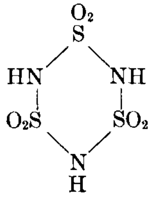
V. Sulfur Imides Derived from Sulfur Trioxide

A. SULFIMIDE

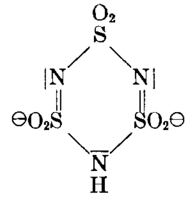
Various sulfur imides based on sulfur trioxide are possible. Thus one, two, or three oxygen atoms in the monomeric trioxide could be replaced by the isosteric NH group, and numerous imides can be formulated which are derived from the various polymers of sulfur trioxide by a similar replacement of O by NH. Hantzsch and Holl (*61*) were the first to prepare such a polymeric sulfimide. They obtained derivatives of the sulfimide (LXIX) both from the products of the decomposition of sulfuryl chloride with ammonia and also from the product of a rearrangement which sulfuryl amide undergoes when heated to 180–200°.

The exothermic reaction which occurs when sulfuryl amide is heated was discovered by Traube (*111*).

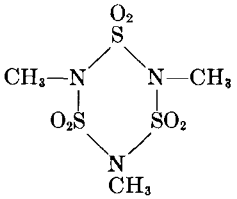
$$O_2S(NH_2)_2 \rightarrow NH_4(NSO_2)$$



(LXIX)



(LXX)



(LXXI)

The ammonium salt which results from the transformation of sulfuryl amide can be converted to a silver salt, $AgNSO_2H_2O$, by silver nitrate (*64*) and this readily gives $AgNSO_2$. The silver salt with methyl iodide yields the N-methyl derivative (LXXI) (*61*). Since molecular weight determinations show the methyl derivative to be a trimer, it may also be assumed that the salts, and particularly that of silver, are also trimeric. Attempts to isolate the hydrogen compound (LXIX) have so far failed, but Heinze and Meuwsen (*64*) have prepared many salts of (LXIX). They also were able to show that when the silver salt was decomposed with an equivalent quantity of hydrochloric acid a tribasic acid resulted which was to some extent stable in water. It readily lost two protons, but one proton was split off only with difficulty. The ion (LXX) clearly has a high stability. The dipyridinium salt of the trimeric sulfimide, which is derived from the ion (LXX), can be obtained (*1a*) in a yield of 70% by reaction of amidosulfuric acid chloride with pyridine at 20°:

$$3H_2NSO_2Cl + 5C_5H_5N \rightarrow (O_2SNH)_3 \cdot 2C_5H_5N + 3[C_5H_5NH][Cl]$$

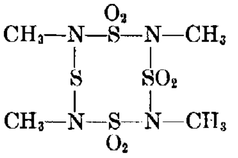
Since sulfimide is a derivative of sulfur trioxide, it was natural to attempt its synthesis by direct ammonolysis of sulfur trioxide. Appel and Goehring (*4*) reacted NH_3 with excess SO_3 in nitromethane solution. The product was $(NH_4)_2S_3O_{10}$, formation of which shows that a process yielding water occurred during the ammonolysis.

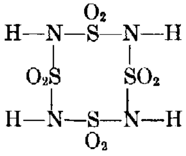
$$SO_3 + NH_3 \rightarrow HNSO_2 + H_2O$$

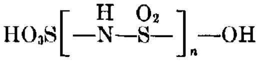
$$3SO_3 + H_2O \rightarrow H_2S_3O_{10}$$

$$H_2S_3O_{10} + 2NH_3 \rightarrow (NH_4)_2S_3O_{10}$$

Actually a substance was present in the nitromethane solution which was acid in water and for which the composition $(HNSO_2)_n \cdot H_2SO_4$ was adduced. Various silver salts could be precipitated from the aqueous solution with silver nitrate and could be separated by their solubility. In addition to the silver salt of the trimeric sulfimide, $(AgNSO_2)_3$, a further silver salt of the formula $AgNSO_2$ was obtained which was converted by methyl iodide into the tetramer of CH_3NSO_2 (LXXII), thus proving the existence of derivatives of tetrameric sulfimide (LXXIII), as well as of the trimer. A salt of LXXIII is also obtained from H_2NSO_2Cl and pyridine (*1a*).


(LXXII)


(LXXIII)


$$HO_3S\left[-\overset{H}{N}-\overset{O_2}{S}-\right]_n-OH$$
(LXXIV)

The quantity of trimeric and tetrameric sulfimide recovered from the reaction products of NH_3 with excess SO_3 in nitromethane did not in any way correspond with that expected from the equations given above and only 10% of the quantity of sulfimide expected was isolated. The residue which had the composition $(HNSO_2)_nH_2SO_4$ proved to be polysulfimide sulfonic acid (LXXIV) (*5*). This may be regarded as an imido derivative of the polysulfuric acids. Amides of these acids have already been obtained by Ephraim and Michel (*30*) by decomposing sulfuryl chloride with ammonia.

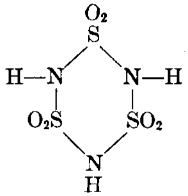
Definite sulfimide sulfonic acids are formed from SO_3 adducts and sulfamide in a melt the pyridinium salt of the sulfamide disulfonic acid, $HO(O_2SNH)_2—SO_3H$ was obtained. The analogous reaction with imidosulfamide results in the dipyridinium salt of trisulfimide sulfonic acid $HO(O_2SNH)_3—SO_3H$. Besides the pyridinium salts, several potassium, ammonium and sodium salts were prepared (*92a*).

B. Sulfanuric Acid

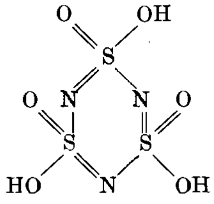
As Hantzsch and Stuer (*62*) suggested, trimeric sulfimide (LXXVa) should have an isomer (LXXVb), to which the name sulfanuric acid has been given. However, this acid, like sulfimide, cannot be isolated as the hydrogen compound itself, though the acid chloride (LXXVI) is readily accessible. It can be made by the reaction of amidosulfonic acid with PCl_5 and thermal decomposition of the product (*73*, *74*).

$$HO—SO_2NH_2 + 2PCl_5 \rightarrow 3HCl + OPCl_3 + Cl—SO_2—NPCl_3$$
$$3Cl—SO_2 \cdot NPCl_3 \rightarrow 3POCl_3 + [Cl—S(O)N]_3$$

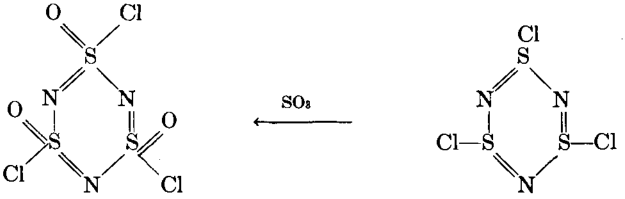
A second method is to decompose a mixture of sulfuryl chloride and thionyl chloride with ammonia (*44*). It is also possible to obtain sulfanuryl chloride by oxidizing thiazyl chloride (LXXVII) with sulfur trioxide (*50*).



(LXXVa)



(LXXVb)



(LXXVI) (LXXVII)

Sulfanuric acid (LXXVb) should be the first product of the hydrolysis of sulfanuryl chloride (LXXVI), but this substance is clearly very unstable. Even on careful acid hydrolysis, imidosulfamide (LXXVIII) and sulfuric acid are formed immediately.

$$H_2N \cdot SO_2 \cdot NH \cdot SO_2 \cdot NH_2$$

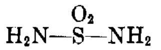
(LXXVIII)

It is striking that compound (LXXVa) is clearly much more stable than the isomer (LXXVb) and that hydrolysis leads to different products. Whereas sulfimide in an acid medium gives sulfuryl amide, amidosulfonic acid and sulfuric acid, the hydrolysis of sulfanuric acid leads to imidosulfamide (*86*).

VI. Amides of Oxyacids of Sulfur (VI)

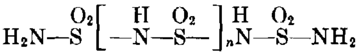
A. SULFURYL AMIDE

Sulfuryl amide (LXXIX), the diamide of sulfuric acid, has been known for a very long time. It was discovered by Traube (*111*, *112*) and isolated as a colorless solid; mp, 92–93°. It is formed in a quite normal way both in the ammonolysis of sulfuryl halides (see, for example, refs. *22*, *26*, *29*, *77*, *103*, *119*) and also in the ammonolysis of sulfur trioxide (*6*). It is common to both modes of preparation that other reactions occur besides the formation of sulfuryl amide. Thus sulfuryl fluoride reacts fairly smoothly to form sulfuryl amide (*113*), but sulfuryl chloride is able, according to the conditions and also by using excess of ammonia, to give salts of sulfimide (LXIX), imidodisulfamide (LXXVIII), or long-chain sulfuryl imido amides (LXXX) (*21*, *30*), in addition to sulfuryl amide. The situation is similar in the reaction between sulfur trioxide and ammonia, when only by working with excess of liquid ammonia is an appreciable yield (approximately 10%) of sulfuryl amide formed (*6*).



$H_2N-\overset{O_2}{S}-NH_2$

(LXXIX)



$H_2N-\overset{O_2}{S}\left[-\overset{H}{N}-\overset{O_2}{S}-\right]_n\overset{H}{N}-\overset{O_2}{S}-NH_2$

(LXXX)

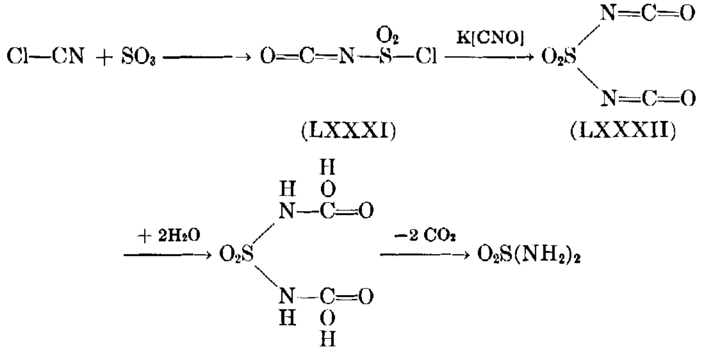
According to current views on the formation of sulfuryl amide (*6*, *44*), a condensation reaction probably leads in each case to the formation of (LXXIX).

$$O_2SCl_2 \rightleftharpoons O_2SCl^+ + Cl^-$$
$$O_2SCl^+ + HNH_2 \rightarrow (O_2SNH_2)^+ + HCl$$
$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$O_2SNH_2^+ + NH_2^- \rightarrow H_2N - SO_2 - NH_2$$

$$O_2SO + HNH_2 \rightarrow O_2SNH_2^+ + OH^-$$
$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$O_2SNH_2 + NH_2^- \rightarrow H_2N - SO_2 - NH_2$$

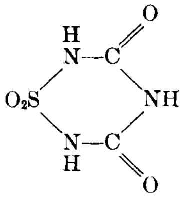
Since, however, both SO_3 and the ion O_2SCl^+, which is analogous to sulfur trioxide, are not only capable of undergoing condensation reactions but, as Lewis acids, also have a strong tendency to undergo addition reactions, the formation of sulfuryl amide cannot be the only reaction of these substances with ammonia.

An interesting and almost quantitative formation of sulfuryl amide is based on the use of sulfuryl diisocyanate (LXXXII), which can be made by the action of cyanogen bromide on sulfur trioxide (*60*), or by the reaction of chlorosulfonyl isocyanate (LXXXI), with silver cyanate (*3*).



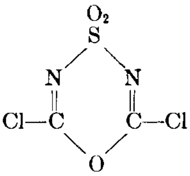
Scheme 1

Hydrolysis of this substance leads by intermediate steps to sulfamide (Scheme 1). Ammonolysis, on the other hand, yields a cyclic mixed derivative of sulfuric acid and carbonic acid (LXXXIII). Sulfuryl amide gives salts and also numerous organic derivatives. A silver salt $(AgNH)_2SO_2$ is readily obtained in an aqueous medium. Sulfuryl amide is a strong acid in liquid ammonia and both a dipotassium salt, $(KNH)_2SO_2$, and also a tetrapotassium salt, $(K_2N)_2SO_2$, are formed by reaction with KNH_2.

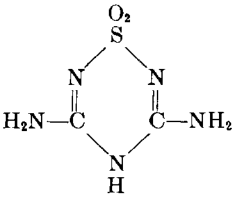


(LXXXIII)

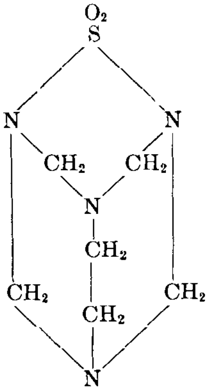
The number of organic derivatives is very large, for all four H atoms of sulfuryl amide can be replaced by alkyl, aryl, or acyl groups, either singly or together. The tendency of sulfuryl amide to stabilize itself by forming a six-membered ring, which is seen in the formation of the ring system of sulfimide on heating sulfuryl amide (compare p. 183), is also apparent in many reactions with products containing carbon; for example, in the formation of (LXXXV) from dicyanamide and amidosulfonic acid (*114*). A sulfuryl amide with an adamantine structure (LXXXVI) which is produced from sulfuryl amide, ethylene diamine, and formaldehyde as a white solid (mp, 195–196°), can be used in the analytical detection of sulfuryl amide (*100*).



(LXXXIV)



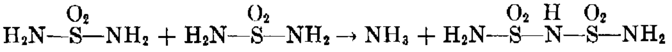
(LXXXV)



(LXXXVI)

B. IMIDODISULFAMIDE

Imidodisulfamide (LXXVIII) is formed extraordinarily readily from sulfuryl amide when it is heated for some time with dilute sodium hydroxide solution (*75*). The resulting sodium salt is decomposed with sulfuric acid and the imidodisulfamide dissolved out with acetone. Like sulfuryl amide, imidodisulfamide is also a colorless solid (mp, 169°) which dissolves in water and in some organic solvents, such as acetone or ethyl acetate.



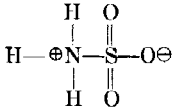
$$H_2N-\overset{O_2}{S}-NH_2 + H_2N-\overset{O_2}{S}-NH_2 \rightarrow NH_3 + H_2N-\overset{O_2}{S}-\overset{H}{N}-\overset{O_2}{S}-NH_2$$

(LXXVIII)

Imidodisulfamide is a strong acid, which when titrated with sodium hydroxide solution behaves as if it were monobasic. Particularly the hydrogen on the imide nitrogen atom is readily replaced by metals, though with silver ions also a tri-silver salt, $AgNH-SO_2-NAg-SO_2-NHAg$, is obtained (*73, 76*).

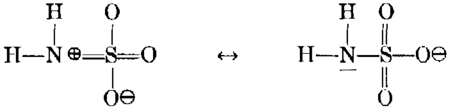
C. AMIDOSULFONIC ACID

When sulfuryl amide or imidodisulfamide is heated with strong sodium hydroxide solution, the sodium salt of amidosulfonic acid results. The free acid itself may be prepared in various ways; for example, from urea and sulfuric acid, from many adducts of sulfur trioxide and ammonia, from hydroxylammonium salts and sulfur dioxide, or from SO_2 and acetoxime. Amidosulfonic acid, which is colorless and melts at 205° with decomposition, has, as Baumgarten supposed (*13*), the structure (LXXXVII).



$$H-{}^{\oplus}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{\ominus}$$

(LXXXVII)



$$H-\overset{\overset{H}{|}}{N}{}^{\oplus}=\underset{\underset{O^{\ominus}}{|}}{\overset{\overset{O}{|}}{S}}=O \leftrightarrow H-\underset{-}{\overset{\overset{H}{|}}{N}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{\ominus}$$

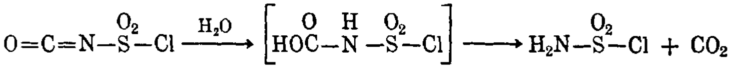
(LXXXVIII)

According to crystal structure investigations of Kanda and King (*71*), the S-N distance is 1.73 Å and the S-O distance is 1.48 Å. The amidosulfonate ion, in which the S-N distance is smaller (*66, 72*), has the formula (LXXXVIII).

Amidosulfonic acid is a strong monobasic acid in water but is dibasic in ammonia (*24*) and reacts, for example, with sodium, forming the salt $NaNH \cdot SO_3Na$. The two hydrogen atoms on nitrogen are readily substituted if one allows it to react with mercury(II) salts: one can, for example, prepare a salt $HgN-SO_3Na$ or $HgN-SO_3K$.

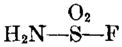
The derivatives of amidosulfonic acid are very numerous. The acid halides will be considered particularly here. Amidosulfonic acid chloride may be prepared in the following way:

Chlorosulfonyl isocyanate (LXXXI) is formed in the reaction of cyanogen chloride with sulfur trioxide in a 1:1 molar ratio (*57*, *58*), and this is saponified by water vapor (*59*) or formic acid (*2*) to amidosulfonic acid chloride (LXXXIX), H_2NSO_2Cl. It is colorless and crystalline and melts at 40–41°. The reaction with water is explosive, amidosulfonic acid and HCl being formed.



$$\underset{\text{(LXXXI)}}{O{=}C{=}N{-}\overset{O_2}{S}{-}Cl} \xrightarrow{H_2O} \left[HO\overset{O}{C}{-}\overset{H}{N}{-}\overset{O_2}{S}{-}Cl\right] \longrightarrow \underset{\text{(LXXXIX)}}{H_2N{-}\overset{O_2}{S}{-}Cl} + CO_2$$

From amidosulfonic acid chloride the corresponding acid fluoride (XC) may be made by reaction with potassium fluoride in boiling acetonitrile (*7*), or by the reaction of (LXXXVI) with NaF followed by careful hydrolysis (*70*). Amidosulfonic acid fluoride is colorless, melts at 8°, and is soluble



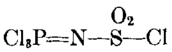
$$H_2N{-}\overset{O_2}{S}{-}F$$

(XC)

in organic solvents such as ether or chloroform. Towards water, in which it dissolves, it is astonishingly stable. The aqueous solution hydrolyzes only slowly to amidosulfonic acid and hydrogen fluoride. Amidosulfonic acid fluoride can also be obtained (*2a*) in a yield of 40% by ammonolysis of disulfurylfluoride, $S_2O_5F_2$:

$$FSO_2{-}O{-}SO_2F + 2NH_3 \rightarrow FSO_3NH_4 + NH_2SO_2F$$

Purely inorganic derivatives of amidosulfonic acid are accessible through the reaction of $H_3N{-}SO_3$ with PCl_5 (*73*, *74*) in which, as already mentioned (compare p. 184) the compound (XCI) results.



$$Cl_3P{=}N{-}\overset{O_2}{S}{-}Cl$$

(XCI)

$$OSN{-}SO_3Me \quad (Me = Na, K)$$

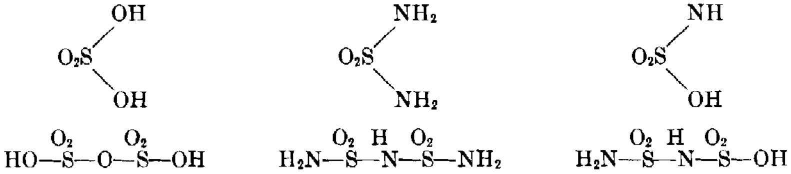
(XCII)

The compound (XCI) is naturally, as in an acid chloride, sensitive to hydrolysis. With water it yields amidosulfonic acid and phosphoric acid quantitatively; the high stability of the nitrogen-sulfur bond, which is manifestly greater than that of the phosphorus-nitrogen bond, is clear from these results.

Thionyl chloride reacts in an analogous manner to PCl_5 with mercury amidosulfonate (*91*), though not with free amidosulfonic acid. Thionyl amidosulfonates (XCII) are quite stable and are clearly polymers.

D. Imidosulfonic Acid Monoamide

Just as a diamide and a monoamide are formed from sulfuric acid, so it should be possible to prepare amides from disulfuric acid.



$$\mathrm{HO{-}\overset{O_2}{S}{-}O{-}\overset{O_2}{S}{-}OH} \qquad \mathrm{H_2N{-}\overset{O_2}{S}{-}\overset{H}{N}{-}\overset{O_2}{S}{-}NH_2} \qquad \mathrm{H_2N{-}\overset{O_2}{S}{-}\overset{H}{N}{-}\overset{O_2}{S}{-}OH}$$

(LXXVIII) (XCIII)

It would be expected that in the ammonolysis reaction the oxygen bridge would disappear and, in its place, an NH bridge would be formed. From this point of view, imidodisulfamide (LXXVIII), which has already been described, is a diamide derived from disulfuric acid. The question then arises as to whether the corresponding monoamide (XCIII) can exist.

Appel *et al.* (*8*) were able to prepare a diammonium salt of (XCIII) by the reaction of pyrosulfuryl chloride, $S_2O_5Cl_2$ or trisulfuryl fluoride, $S_3O_8F_2$, with ammonia.

$$\mathrm{H_2N{-}\overset{O_2}{S}{-}\overset{NH_4}{N}{-}{-}\overset{O_2}{S}{-}ONH_4}$$

(XCIV)

The compound (XCIV) is probably identical with the compound described earlier by Hayek *et al.* (*63*) as a diammonium salt of a pyrosulfamide. The pyridinium salt of (XCIII) can be obtained too, when $C_5H_5N{\cdot}SO_3$ is allowed to react with an excess of sulfamide (*92a*).

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