NOMENCLATURE OF THE NITROGEN COMPOUNDS OF PHOSPHORUS AND OF SULFUR[1]

L. F. AUDRIETH, R. STEINMAN, AND A. D. F. TOY

William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois

Received February 14, 1942

It was not until Franklin (2) had developed the nitrogen (ammonia) system of compounds that the classification of hundreds of nitrogen compounds became possible. While these can be called "ammono" and mixed "ammono aquo" compounds, such designations mean little to the average chemist despite the fact that the specialist in nitrogen chemistry finds the Franklin concept of tremendous value. However, the fundamental chemical relationships which characterize many of the compounds of nitrogen become apparent only when they are considered as "ammono" compounds. Consequently, the names of such compounds not only should take into account their chemical character, but should also be sufficiently explicit so that structure and composition are evident.

In many instances it would be unwise to propose entirely new names for compounds which are well characterized and known. When, however, the same substance has been given three or more different names, it would seem desirable to subject these to a critical examination and either to choose the one which best describes its composition, or to propose one which most nearly conforms to accepted rules of nomenclature. The present discussion is limited to the nitrogen compounds of phosphorus and of sulfur, in particular to the ammono and mixed ammono aquo acids of these elements.

A. NITROGEN COMPOUNDS OF PHOSPHORUS

A. The ammonophosphoric and ammonoaquophosphoric acids

The generic relationships which formally characterize the ammonophosphoric and the mixed ammonoaquophosphoric acids are represented diagrammatically in tables 1 and 2. For purposes of comparison the various aquo acids are also presented in table 1. Deammonation of (removal of ammonia from) $P(NH_2)_5$ leads to the various other ammonophosphoric acids and eventually to the phosphoric anammonide, P_3N_5, just as dehydration of orthophosphoric acid, either

---

[1] This paper has been the subject of considerable comment and correspondence, not only prior to its presentation at the St. Louis Meeting of the American Chemical Society (April 7-11, 1941), but also subsequently by a committee of referees all of whom are recognized authorities in the field of chemical nomenclature. The recommendations here proposed represent the efforts of the authors as well as those of Professor A. M. Patterson, Dr. Janet D. Scott, and Dr. Elmer Hockett, to all of whom the original manuscript was submitted for comment. The authors consider it a privilege to acknowledge their indebtedness to these referees for their helpful suggestions.

Specific comments by the referees have been included in this paper, especially in those instances where recommendations with respect to particular compounds represent opinions by the authors and are not approved by the referees.

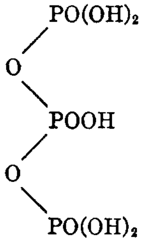
directly or indirectly, may give the polymetaphosphoric or the polyphosphoric acid. The ammonophosphoric acids are the nitrogen analogs of the aquophosphoric acids.

TABLE 1

A. Nomenclature of the aquophosphoric acids

$$P(OH)_5 \longrightarrow OP(OH)_3 \longrightarrow HOPO_2 \longrightarrow P_2O_5$$

$P(OH)_5$	$OP(OH)_3$	$HOPO_2$	P_2O_5
Holophosphoric* acid	Orthophosphoric acid	Metaphosphoric acid	
	↓	↓	
	$O[PO(OH)_2]_2$†	$(HPO_3)_x$†	
	Pyro(or di)phosphoric acid	(where $x = 2, 3$, etc., the terms "dimeric", "trimeric", or "dimer of", "trimer of", etc. are to be used)	
	↓		



Triphosphoric acid

B. Nomenclature of the ammonophosphoric acids

$$P(NH_2)_5 \longrightarrow NP(NH_2)_{2,3,4,x} \longrightarrow (NPNH)_x \longrightarrow P_3N_5$$

$P(NH_2)_5$	$NP(NH_2)_{2,3,4,x}$	$(NPNH)_x$	P_3N_5
Phosphorus pentamide* (phosphopentamide)	Phosphonitrilamide	Phospham (phosphonitrilimide)	Triphosphorus pentanitride

* "The prefix 'holo' for fully hydrated acids beyond the 'ortho' stage was proposed in one of the earlier papers on which the I.U.C. rules for naming inorganic compounds are based. If $P(OH)_5$ needs to be named, it can be called *holophosphoric* acid . . . then holophosphoramide can be used for $P(NH_2)_5$. Phosphopentamide is not bad. I am not sure whether I like this more or less than phosphorus pentamide."—A. M. P.

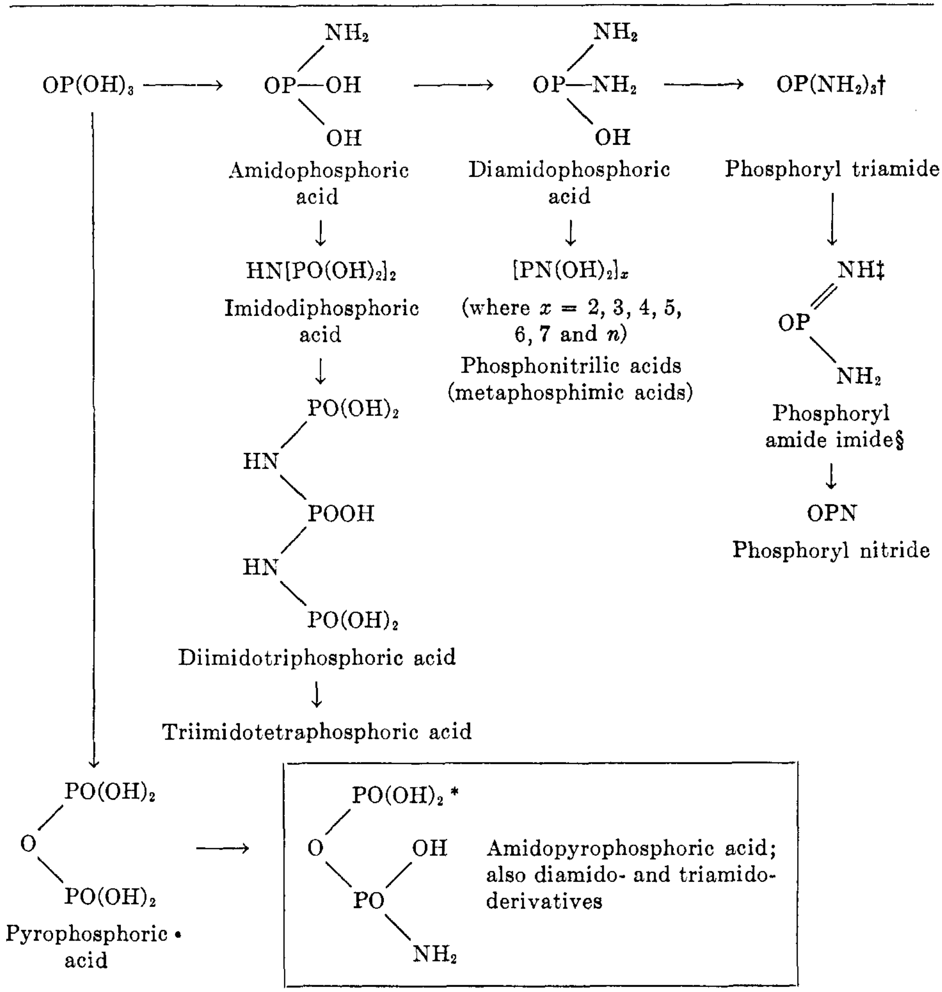
At the suggestion of J. D. S., the authors have decided to adopt the latter name.

† "It is unfortunate . . . that the same prefixes are used for the series of acids formed by loss of water and for the series of polymers of the meta acid. However, since the names for the first series conform to the International Committee Rules for indicating the number of atoms of the significant element (P) in the molecule . . . the system might as well be carried over to the aquo ammono derivatives."—J. D. S.

This difficulty is done away with by use of the system proposed by A. M. Patterson. "The prefixes di-, tri-, etc. should not be used to indicate polymeric forms. It not only conflicts with their use to indicate forms resulting from loss of water but may be misleading in other ways. It seems to me to be safer and more logical to use 'dimeric', 'trimeric', etc., or else 'dimer of', 'trimer of'. The name for $(HPO_3)_3$ would be trimeric, or trimer of, metaphosphoric acid."

TABLE 2

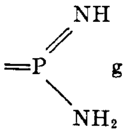
Nomenclature of mixed ammonoaquo derivatives of phosphoric acid



---

* The prefix *amido* here indicates that a hydroxyl group in pyrophosphoric acid has been replaced by an NH_2 group.

† *Phosphorus oxy* has been used in the past by *Chemical Abstracts* for the PO group. This terminology could be carried over to all of the compounds in the last column, *viz.*, *phosphorus oxytriamide* for $PO(NH_2)_3$. The name phosphoramide has also been suggested for the latter compound (A.M.P.), but does not seem sufficiently explicit to the authors, since there are at least three amides of phosphoric acid. This suggestion meets with the approval of Janet D. Scott, who states, "Phosphoramide should denote only the completely substituted amide of phosphoric acid (just as sulfamide denotes the diamide, not the monoamide, of sulfuric acid) and therefore be explicit enough. This nomenclature corresponds with that of organic amides. However, phosphoryl triamide (or amide) seems a simpler name to figure out."

‡ It has been suggested by A. M. Patterson that the  $=\mathrm{P}\begin{matrix}/\!\!/\mathrm{NH}\\ \diagdown\mathrm{NH_2}\end{matrix}$ grouping be designated the phosphamidine radical to correspond to the organic amidines. Where the two other substituents are organic radicals, this suggestion merits consideration.

§ "Phosphoryl amide imide (alphabetical order, which *Chemical Abstracts* uses with salts with two anions) seems to indicate better that both the —NH and $—NH_2$ groups are attached to the —PO group and not to each other."—J. D. S.

These formal analogies become a bit more complicated in the case of the mixed ammonoaquo acids. These relationships are depicted in table 2, where the gradual replacement of the OH and O groups by their isosteric ammono equivalents, the $-NH_2$ and $=NH$ (or $\equiv N$) groups, is outlined. The changes from left to right represent reactions of ammonolysis (analogous to hydrolysis), while those from the top to the bottom in each column represent reactions of deammonation.

It is proposed that the prefixes *amido* and *imido* be used generally for those derivatives of inorganic acids where the NH_2 and NH radicals replace the OH and O groups, respectively, but only in those cases where the parent substances are known to possess acidic properties in aqueous solution, or where they have been characterized in the form of salts.[2] Reference to table 2 indicates where this rule is applicable.

The compound $PO(NH_2)_3$ has been called triamidophosphoric acid. While it may have acidic character in liquid ammonia, it certainly gives no evidence of dissociating the proton in aqueous solution. Since the PO radical is known as the *phosphoryl* group, it is suggested that the compounds in the last column be called phosphoryl triamide,[3] amide imide, and nitride, respectively. In fact, there is no reason why a compound like $PO(NHC_6H_5)_3$ should not likewise be called phosphoryl trianilide.

B. The phosphonitrile radical

Difficulties arise when an attempt is made to place the nomenclature of $PNCl_2$ and its reaction products on a rational basis. Assuming that $PNCl_2$ has at least a transient existence in the monomeric form, it may be regarded as the nitrogen analog of phosphoryl trichloride, $POCl_3$. The PN radical retains its identity in all known reactions of $PNCl_2$. It is a group which corresponds to such acid radicals as sulfuryl, phosphoryl, and organic acid radicals formed from the acids by removal of OH. Most investigators have accepted the designation *phosphonitrile* for the PN group, since it is looked upon as a group resembling the CN or nitrile radical.

However, the situation is complicated by the fact that the formula $PNCl_2$ is not strictly correct, since a whole series of polymers, $(PNCl_2)_x$, where x = 3, 4, 5, 6, 7, and n, have been isolated and characterized. Each of these undergoes characteristic solvolytic reactions leading to well-defined derivatives,—

---

[2] "Greater uniformity might be attained by the use of names that do not contain the word acid in every case in which an acid hydrogen is present. For example:

Phosphoric monoamide	$OP(NH_2)(OH)_2$
Phosphoric diamide	$OP(NH_2)_2(OH)$
Diphosphoric amide	$HN[PO(OH)_2]_2$ (cf. diacetamide)."—E. H.

While such a system would lead to greater uniformity throughout the whole field of inorganic chemistry so far as the parent compounds are concerned, it would also create complications in those instances where salts of ammono acids have been isolated.

[3] "The prefix tri- for triamide is not necessary."—J. D. S. The authors feel, however, that a not too indiscriminate use of such prefixes is helpful in relating nomenclature to actual structure and composition.

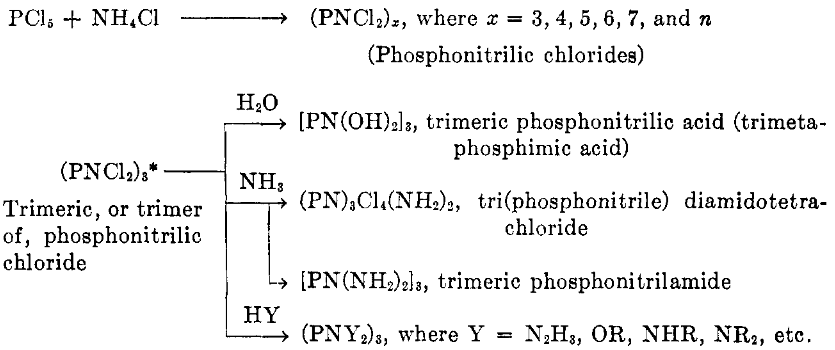
quite different from organic polymers with which the isolation of definite intermediates between the monomeric and the highly polymerized states is either difficult or impossible.

Some typical reactions of the trimer of $PNCl_2$ are given in table 3. Complete hydrolysis leads to the corresponding acid; complete ammonolysis to the amide. The chlorine atoms are partially or completely replaceable by reaction with hydrazine, *N*-substituted hydrazines, amines, alcohols, and phenols. In naming these derivatives it would seem desirable to choose a system whereby these relationships are retained.

It is therefore proposed that the PN group be called the phosphonitrile radical; the acids, the phosphonitrilic acids; the amides, the phosphonitrilamides; the hydrazides, the phosphonitrilohydrazides[4]; the chlorides, the phosphonitrilic chlorides, etc. Individual members of each class of compounds can then be differentiated, as Dr. Patterson recommends, by using *trimer of*, *tetramer of*, or *trimeric*, *tetrameric*, etc. to specify the state of polymerization. Thus, $(PNCl_2)_3$ would be called the trimer of, or trimeric, phosphonitrilic chloride. Compounds such as $P_3N_3Cl_2F_4$ would require a more specific terminology. Here use can be made of the fact that the essential identity of the PN radical is retained by speaking of this compound as tri(phosphonitrile) dichlorotetrafluoride. In fact, this same system could be applied to other phosphonitrile derivatives, such as $(PNCl_2)_3$, which would be called tri(phosphonitrile) hexachloride. Both $[PN(NH_2)_2]_3$ and $[PN(NH_2)_2]_4$ have recently been characterized and may be designated as the trimer and the tetramer of phosphonitrilamide, respectively.

TABLE 3

The phosphonitrile (PN) *radical*



* To retain the stem name phosphonitrile, this compound could be written $(PN)_3Cl_6$ and then called tri(phosphonitrile) hexachloride.

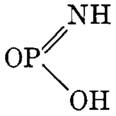
---

[4] The authors have followed in some instances the common custom of using a connecting vowel to make for greater euphony and ease in pronunciation. However, investigators in this field, including the authors, prefer to write and speak of the halogen derivatives as the *phosphonitrilic halides*, rather than the *phosphonitrilohalides*.

It is interesting in this connection to point out that $[PN(NMg)_2]_?$ has also been reported. The name magnesium phosphonitrilamide is quite in line with our proposals.

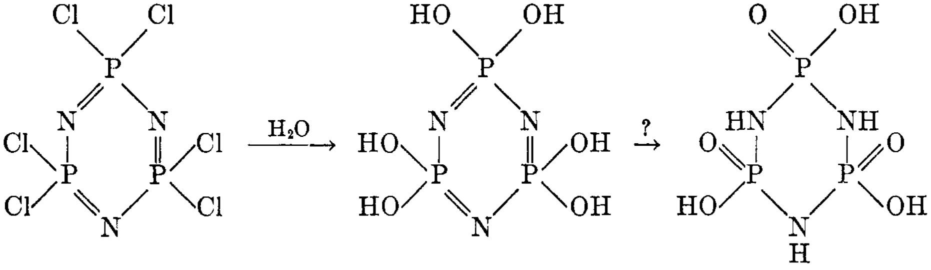
In assigning the name phosphonitrilic to the acid formed by the hydrolysis of phosphonitrilic chlorides, the present proposal runs most seriously counter to the accepted terminology. Three structures were proposed by Stokes (3)

(1) NH_2PO_2 metaphosphamic acid

(2)  $OP\begin{matrix}=NH\\-OH\end{matrix}$ metaphosphimic acid

(3) $NP(OH)_2$ phosphonitrilic acid

and were given by him what he considered appropriate names. In view of the fact that only one hydrogen atom per $PN(OH)_2$ unit could be replaced by an ordinary metallic constituent, Stokes chose to call $[PN(OH)_2]_3$ trimetaphosphimic acid.[5] While there seems little doubt that the trimeric phosphonitrilic chloride possesses structure I, the hydrolysis product is thought to undergo a tautomeric hydrogen shift from structure II to structure III.



I II III

There are, however, many cases where the maximum hydrogen replacement of an acid is not attained, as, for instance, in the heteropoly and isopoly acids. Therefore, the limited experimental evidence for formula III need not weigh too heavily in the present case, especially since the use of the name metaphosphimic would hardly make apparent the chemical relationships which exist between these acids and the corresponding phosphonitrilic chlorides. Therefore, the name phosphonitrilic acid is recommended.[6]

---

[5] Stokes did prepare the hexasilver salt of $[PN(OH)_2]_3$, but preferred to consider it an exception.

[6] The authors prefer the system outlined in this paper for the naming of the phosphonitrile derivatives. The phosphonitrile group is a distinctive radical and the effort is made by the authors to build up a system based on this name as a group name. There is another alternative which is suggested by one of the referees (E.H.) and is extended by the others. Their comments follow:

"Nitrilophosphoric would be more nearly analogous to the names in which amido and imido are used as radical names, and would suggest more clearly that the compounds are

There is certainly no justification for speaking of the phosphonitrilic acids as phosphorus *hydroxynitrides* or *hydroxide nitrides.* One does not speak of phosphorous acid as *phosphorous hydroxide,* even though its composition is sometimes represented by the formula $P(OH)_3$.

Where compounds such as $P_6N_7Cl_9$ have been reported, but not further characterized, formulas should be used, since it is obviously impossible to assign a logical name.

C. The ammonothiophosphoric acids

Only a few representatives of a large number of hypothetical ammonothiophosphoric acids have actually been isolated. These are listed in table 4 with the suggested names.

D. Nitrogen derivatives of trivalent phosphorus

A few of these compounds are known, and these are listed in table 5. These may be looked upon as ammono or mixed ammonoaquo derivatives of phosphorous acid.

---

considered as derivatives of phosphoric acid rather than as derivatives of some acid of nitrogen."—E. H.

"$PN(OH)_2$ is the stumbling block . . . but nitrilophosphoric was not considered before. The arguments for its use are good. However, nitrilophosphoric would suggest structure II (page 104). Although Webster defines nitrilo- as 'a combining form for nitrile, denoting the presence of trivalent nitrogen, $\equiv$N,' it seems strange to use it for compounds of structure III with imide groups. The authors are no doubt trying to meet a similar objection to phosphonitrilic when they say 'that the limited experimental evidence for formula III need not weigh too heavily in the present case.' If structure III is correct, an alternative name to metaphosphimic that would harmonize better with the names of the other aquo ammono acids is imidometaphosphoric (Mellor gives imidophosphoric and metaphosphimic). Perhaps it is more important to show the relationship to $(PNCl_2)_x$, as the authors maintain." —J. D. S.

"Phosphonitrile is a convenient term for the radical $=$PN, since this group does seem to preserve its identity through a series of reactions. The common name for the chlorides, phosphorus chloronitrides, is poor because the chlorine is not attached to nitrogen, and *Chemical Abstracts*' phosphorus chloride nitride is unnecessarily awkward (and the analogous name for $P_3N_3Cl_4(NH_2)_2$ would be much worse). . . . Of course, -nitrile is an unusual and therefore unfortunate ending for a radical, but I have no other to suggest except -nitrilyl. If the term phosphonitrilic acid had been introduced first, the radical should and probably would have been phosphonitrilyl. Still phosphonitrile does not seem too objectionable. . . ."—J. D. S.

"I hesitated at first about the use of 'nitrilo' . . . to denote replacement of an oxygen atom and a hydroxyl group by a nitrogen atom, but it seems to work out usefully. $NP(NH_2)_2$ would accordingly be nitrilophosphoramide and the polymeric forms would be indicated by a separate word . . . $(NPNH)_x$, or phospham, could be given a systematic name, polymeric nitrilophosphimide."—A. M. P.

"The name 'phosphonitrilyl' can conceivably be used when necessary but it is rather awkward. Is it not simpler and more consistent to use 'nitrilo' throughout? $NP(OH)_2$ would then be nitrilophosphoric acid, $NPCl_2$ nitrilophosphoryl chloride (this radical name is regularly formed so we would have to disregard the fact that 'phosphoryl' by itself means something else), . . . $NP(OC_2H_5)_2$ ethyl nitrilophosphate, etc. The higher forms would be treated as polymers without indication of structure or, where their structure is known, they might be given corresponding systematic names."—A. M. P.

TABLE 4

Nomenclature of ammonothiophosphoric acids

FORMULA	NAME
$PS(NH_2)_3$	Thiophosphoryl triamide
PSN	Thiophosphoryl nitride
$PN(SH)_2$	Dithiophosphonitrilic acid
$HNP(SH)_3$	Imidotrithiophosphoric acid

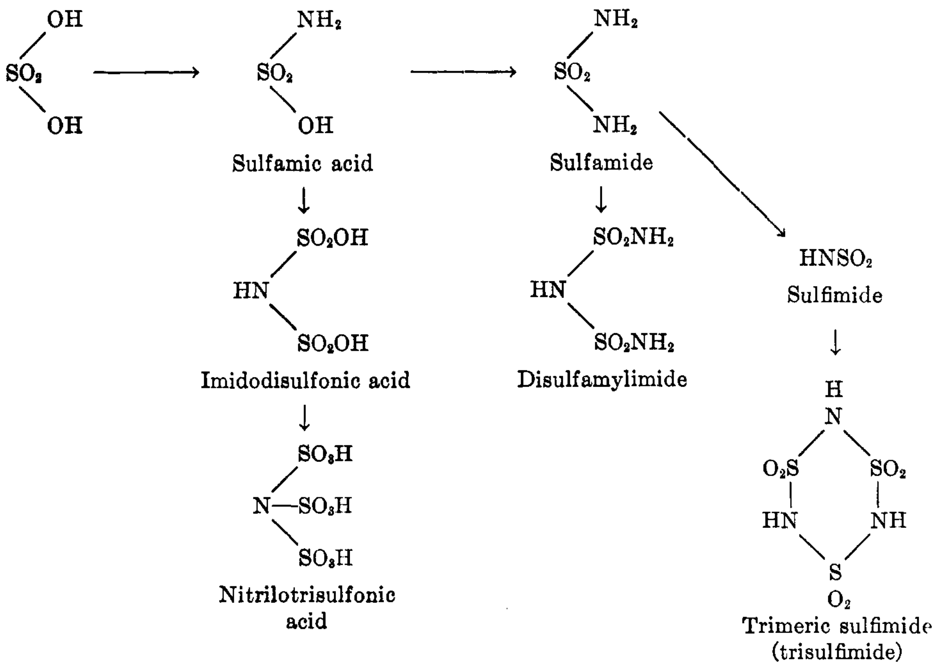
TABLE 5

Nomenclature of ammonophosphorous and ammonoaquophosphorous acids

FORMULA	NAME
$P(NH_2)_3$	Phosphorus triamide
$P(NH)(NH_2)$	Phosphorus amide imide
$P_2(NH)_3$	Diphosphorus triimide
$HOP(NH_2)_2$	Diamidophosphorous acid
$(HO)_2PNH_2$	Amidophosphorous acid
PN	Phosphorus nitride
P_4N_6	Tetraphosphorus hexanitride

TABLE 6

Nomenclature of the ammonoaquosulfuric acids



B. THE AMMONOAQUOSULFURIC ACIDS

The derivatives of the ammonoaquosulfuric acids are quite numerous and have recently been the subject of an extensive review (1). While the terminology is not consistent, it would be inadvisable to make any major changes, owing to the fact that the parent substances and their inorganic and organic derivatives have been known under given names for many years. The chemical relationships and preferred names are given in table 6.

Originally sulfamic acid was called amidosulfonic acid. Whereas the *sulfonic* terminology was given up for sulfamic acid, it is still retained for the deammonation products of sulfamic acid. Generally speaking, it would be better to use substitutive names in inorganic chemistry (J. D. S.). On this basis sulfamic acid and its deammonation products should be called amidosulfuric, imidodisulfuric, and nitridotrisulfuric[7] acids, respectively. However, usage warrants the retention of such names as imidodisulfonic and nitrilotrisulfonic, just as *chlorosulfonic* is employed rather than *chlorosulfuric.*

If the —SO_3H grouping is to be used in an additive sense in the naming of inorganic compounds, then it might be argued that *sulfonamide* be used for the —SO_2NH_2 group in naming the compound $NH(SO_2NH_2)_2$. A difficulty arises here in that the NH_2SO_2— radical has already been called sulfamyl in compounds like NH_2SO_2Cl (sulfamyl chloride), and the latter terminology is strictly in accord with accepted rules. The compounds $SO_2(NH_2)_2$ and $NH(SO_2NH_2)_2$ are related to each other, as indicated by the following deammonation reaction:

$$2SO_2(NH_2)_2 \xrightarrow{-NH_3} NH(SO_2NH_2)_2$$

$$2SO_2(OH)_2 \xrightarrow{-H_2O} O(SO_2OH)_2$$

The compound $NH(SO_2NH_2)_2$ is really a deammonated sulfamide or an amide of imidodisulfonic acid (the nitrogen analog of pyrosulfuric acid). If *diacetamide* (the authors consider this a very poor name!) is acceptable for $(CH_3CO)_2NH$, the deammonation product of acetamide, then *disulfamide* might be used in this case. It seems to the authors, however, that the name disulfamylimide is generally more consistent, and it is therefore recommended for the substance which has previously been called imidodisulfamide.

The name sulfamide for $SO_2(NH_2)_2$ meets the general approval of all referees. *Sulfamide* is a contraction for *sulfuramide* or *sulfuryl diamide,* the diamide of sulfuric acid. *Sulfimide* is likewise a contraction for *sulfuryl imide.* For the trimeric form it is recommended (A.M.P.) that the designation *trimer of,* or *trimeric, sulfimide* be employed, rather than *trisulfimide.*

---

[7] In view of the fact that *amido* and *imido* are accepted prefixes, then *nitrido,* rather than *nitrilo,* seems logical in those cases where the hydrogen atoms of ammonia have been replaced completely by substituents.

REFERENCES

(1) Audrieth, L. F., Sveda, M., Sisler, H. H., and Butler, M. J.: Chem. Rev. **26,** 49 (1940).

(2) Franklin, E. C.: *The Nitrogen System of Compounds,* American Chemical Society Monograph. Reinhold Publishing Corporation, New York (1935).

(3) Stokes, H. N.: Am. Chem. J. **18,** 629 (1896).