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ARTICLES

Nitrogen's Hydrido Oxo Acids

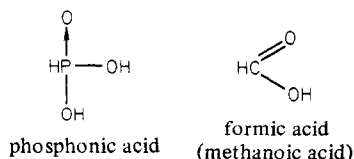
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The nomenclature of hydrido oxo acids of nitrogen is being considered by IUPAC for azinic acid ($\text{H}_2\text{NO}_2\text{H}$) and azonic acid (HNO_2H_2). The existing trivial names for methylenazinic acid, *aci*-nitromethane and methylenenitronic acid, do not have systematic origins; i.e., derivatives cannot be named by the *aci* prefix, and "nitronic acid" is systematically related to the "inic" acids such as phosphinic, arsenic, and stibinic acids. The use of the name azinic acid provides both a parent name for derivatives and a systematic relationship to the names of the hydrido oxo acids of the other group 5A elements.

An oxo acid is a compound in which a central element is bonded to oxygen and hydroxyl groups. The acid hydrogen of an oxo acid is bonded to an oxygen, for example, nitric acid. A hydrido oxo acid is a compound in which the central element is bonded to oxygen(s) and the oxygen atom(s) of the hydroxide(s) as well as directly to hydrogen(s), for example, phosphonic acid and formic acid. Hydrido oxo acids can



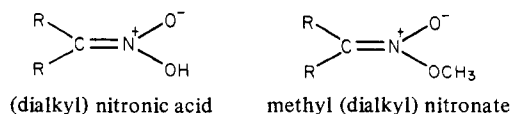
alternatively have organic groups attached to the central element by replacement of the hydrido hydrogen by an alkyl or aryl group, e.g., methylenephosphinic acid.

The first nitrogenous example of a hydrido oxo acid to

Table I. From the Original "aci" Nomenclature Proposal²

<i>aci</i> -aldehydes	<i>aci</i> -ketones
<i>aci</i> -dibenzoylacetone	<i>aci</i> -malonates
<i>aci</i> -diketopentamethylene	<i>diaci</i> -dihydroescorcinol
<i>aci</i> -formylcamphor	<i>diaci</i> -succinates

appear in the chemical literature was a tautomer of a nitroalkane called a nitronic acid by Bamberger.¹ From the original "nitronic acid" nomenclature proposal:¹



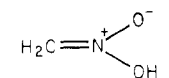
Nitronic acid can be used to name an alkylidene=NOOH group. The name nitronic acid is discussed below. The nitro tautomer of the name *aci*-nitro was originally proposed in a paper by Hantzsch.² He also described *aci*-aldehydes, *aci*-dibenzoylacetone, and the other compounds shown in Table I as well as *aci*-imides, *aci*-urethane, and *aci*-phthalimides, etc.

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Table II

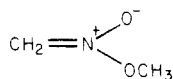
trivial name	compound	<i>aci</i> name
enols	$\begin{array}{c} \text{OH} \\ \\ \text{RC}=\text{CHR}' \end{array}$	<i>aci</i> -ketone
	$\begin{array}{c} \text{OH} \\ \\ \text{HC}=\text{CHR} \end{array}$	<i>aci</i> -aldehyde
enethiol	$\begin{array}{c} \text{SH} \\ \\ \text{RC}=\text{CHR}' \end{array}$	<i>aci</i> -thione
enamine	$\begin{array}{c} \text{NH}_2 \\ \\ \text{RC}=\text{CHR}' \end{array}$	<i>aci</i> -imine

The prefix *aci* implies a tautomeric form having acid character, that is, in *aci*-nitromethane, the acid hydrogen is

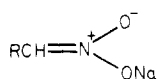
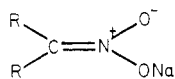
*aci*-nitromethane

formally placed on one of the nitro oxygens, though almost certainly shared between both. Likewise "*aci*-ketones" and "*aci*-aldehydes" could be used to describe enol forms of ketones and aldehydes. Other *aci*-possibilities include *aci*-thiones for enethiols and *aci*-imines for enamines (see Table II).

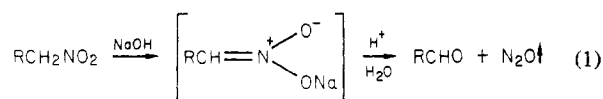
In *aci*-nitro compounds *aci* is a prefix, i.e., it describes a substituent, *aci*-nitro.⁶ The term "*aci*-nitro" cannot be used as a parent name in that it is limited to define only alkylidene nitrogen oxo acids. A true parent name can be modified to name derivatives such as esters. The *aci*-nitro nomenclature cannot be used to confer a name on the methyl ester of the *aci*-nitromethane.

methyl ester of *aci*-nitromethane
methyl nitronate

The term *aci*-nitro also derives from a discussion of the so-called isonitro compounds that are intermediates in the Nef reaction.³ Nef called the intermediates salts of nitro com-

sodium salt of a
primary nitro
compoundsodium salt of a
secondary nitro
compound

pounds. The term *aci* was introduced later, and was used in a review of the Nef reaction⁴ (eq 1).

sodium salt of "*aci* form"

Each of the examples of *aci* compounds shown above have acid hydrogens bonded to elements more electronegative than carbon. Because the *aci* prefix has not been used in any other form than for *aci*-nitro compounds, its built-in limitations allow it to be used only for very specific compounds. It has no general use. It cannot be used to name many of the compounds that resemble *aci*-nitromethane. The free alkylidene acid is the only compound that can have the *aci* name.

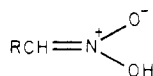
*aci*-nitroparaffins nitronic acids
(ref 4-6) (ref 7-9)

Chart I

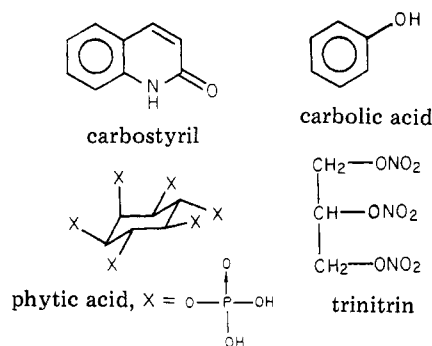
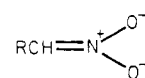
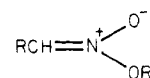


Table III

prefix	meaning	example
<i>aci</i> -	acid character	<i>aci</i> -nitromethane
apo	derived from, with removal of a group of elements	apomorphine
cyclo	cyclic	cyclopropane
de, des	removal of a specific element	desmethylmorphine
epi	bridge connection	epichlorohydrin
hypo	in a lower oxidation state	hypoboric acid
hydr	containing oxygen	hydriodic acid
hydro		hydroquinone
iso	isomeric	isonicotinic acid
	isomeric with a branched chain	isopentane
nin	a German trademark	ninhydrin
nor	homologue lower by one methylene	norcholane
oligo	a few (2-10)	oligo-N-methylmorpho- lidinopropylene oxide
per	containing the largest possible amount of a specific element	perfluoroacetic acid
seco	having an opened ring	2,3-secocholestane

The nitronic acid name must be used for the anionic and ester groups; *aci* cannot be used.

nitronate anions
(ref 10-12)nitronic esters
(ref 13-15)

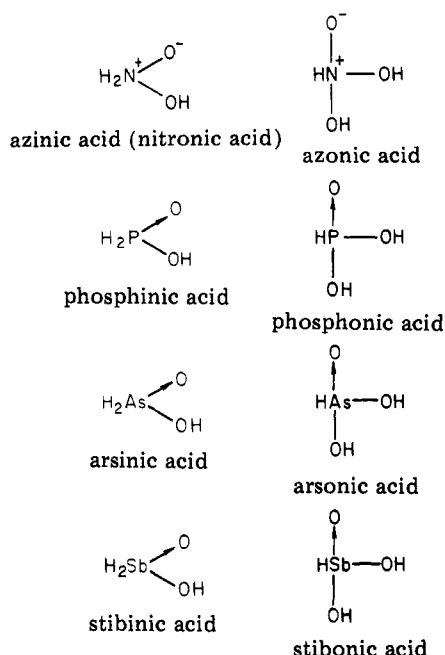
The trivial names shown above are useful only to those who can recognize them. To one unfamiliar with any of the trivial names, it is impossible to formulate the compounds from systematic nomenclature such as those compounds shown in Chart I that have not been used sufficiently by chemists to deserve mention in the chemical literature. Names such as carbostyryl, carboic acid, phytic acid, and trinitrin belong only in the Chemical Abstracts Service *Index Guide*.

In addition to *aci*, other prefixes having some use in chemistry are shown in Table III. Some are meaningful. There have been at least 45 references in *Chemical Abstracts* to "*aci*-nitro" compounds in the last 20 years. A few of them have been shown above.

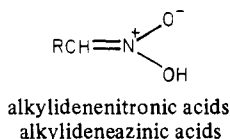
The need for a name inclusive of all *aci*-nitro-type compounds became apparent in 1902 with the introduction of the name "nitronic acid" by Bamberger.¹ This name has been used for the ester derivatives of the acids. The "nitronic acid" name had been accepted by Chemical Abstracts Service up to volume 68 in 1968. It cross-referenced the name "nitronic acid" to "see *aci*-nitro compounds". Now CAS uses only the term "*aci*-nitro compounds".

Nitrogen can have names for its oxo acids similar to the systematic oxo acid names of the other group 5A elements as shown in Chart II. "Nitronic acid", that is H_2NOOH , is analogous to phosphinic acid, arsenic acid, and stibinic acid.¹⁶

Chart II

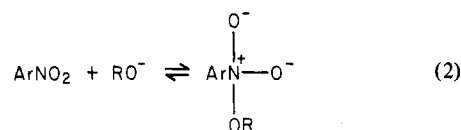


Unfortunately the term "nitronic acid" has been used in virtually all primary publications to mean alkylidene=NOOH, i.e., $\text{R}_2\text{C}=\text{NOOH}$. To attempt to change the meaning of the term "nitronic acid" at this stage would lead to confusion in both communication and indexing for many years to come. Hence, nitronic acid is recommended to be a trivial name for azinic acid. That is, the term nitronic acid becomes a trivial name for the same oxidation state that is called an "...inic acid" in which the prefix "az..." is used in lieu of "nitro...". Con-



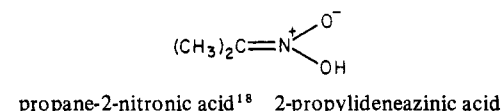
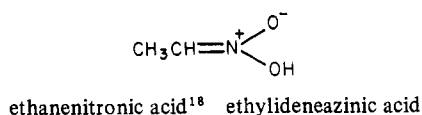
sultation with several important nitro chemists on the use of the azinic acid name has secured unanimous approval, leading to the azinic acid recommendation by the IUPAC Commission on Organic Nomenclature of Organic Chemistry.

Azonic acid is analogous to phosphonic, arsonic, and stibonic acids. Its structure, which is formally the adduct of water to a nitro compound just as carbonic acid is an adduct of water to carbon dioxide, is less well-known but has begun to receive attention in the form of the anionic monoalkyl ester derived from the addition of alkoxide to aryl nitro compounds¹⁷ (eq 2) as well as tetranitromethane. The names "azinic acid" and "azonic acid" are strictly parallel to those adopted for the other group 5A elements.



monoalkyl arylazonate anion

Other derivatives of the parent compound azinic acid, first described as nitronic acid, are shown below. Note that



Nielson¹⁸ attempted to change the name "alkylidenenitronic acid" to "alkanenitronic acid". This nomenclature presumes that all nitronic acids are tautomers of nitroalkanes, that is, *aci*-nitro compounds. It eliminates the possibility of an alkylnitronic acid in which the alkane is singly bonded to the nitrogen. This type of singly bonded alkyl-nitrogen compound has not yet been observed but can probably exist as an intermediate in several intramolecular ortho-nitro reactions.

As shown there are two kinds of chemical nomenclature: one whose meaning is understood by merely a segment of the entire chemical world and one whose meaning in fact can be part of the expression of all chemists, for example, *aci*-nitromethane and the recommended methyleneazinic acid. The IUPAC Commission would like to have your comments.

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