Some Problems in Halogen Nomenclature*

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This discussion of halogen nomenclature as originally presented at the Nomenclature Symposium reflects the thinking of the Subcommittee for Halogen Nomenclature at that time. These views are reported here to place them on record. However, more recent deliberations of the Subcommittee on the Nomenclature of Phosphorus Compounds (a subcommittee of the Committee on Inorganic Nomenclature of the Division of Inorganic Chemistry), have developed what appear to be more systematic and frequently more reasonable solutions to many of the problems considered. Consequently, the original recommendations are compared throughout this paper with those which would result from application of the rules for phosphorus nomenclature currently under consideration.

At first sight it would appear that the problems of halogen nomenclature are nowhere near so formidable as those of the other nonmetallic families. On closer examination, however, one finds that, with the possible exception of catenation compounds, most of the types of compound which cause difficulties in other families are to be found also among the halogens. Thus we have the problem of naming groups attached through different atoms, such as $-OClO_2$ and $-ClO_3$ (cf. -ONO and $-NO_2$). As with nitrito and nitryl, it has seemed advisable to use -ito or -ato to designate attachment to a ligandin-the-group atom, specifying by an appropriate letter prefix if different ligand-in-the-group atoms are possible (e.g., -ONS, O-thionitrito; -SNO, S-thionitrito) and to use -yl to designate attachment to the central atom of the group (e.g., -NOS, thionitryl). Closely related to this problem is that of the retention of the hypo-ite and per-ate affixes to designate oxygenated groups of different formal oxidation numbers. Since these groups may all occur as substituent groups in complex ions and organic molecules, it seemed advisable to retain the simple designations this system affords in order to avoid.

for example, such names as [trioxochloro(VIII)]benzene or similar jawbreaker for what is otherwise simply and euphoniously named as perchlorylbenzene or chloranoylbenzene*, C₆H₅ClO₃. Names designated by an asterisk are formulated according to the rules outlined in a preliminary report of the Phosphorus Nomenclature Subcommittee.1 As applied to the halogens, all names of compounds having covalent bonds to halogen are derived from those of the parent hydrides, e.g., IH3, ioduane; $(C_6H_5)_3I$, triphenylioduane. In the case of the oxo acids, whose names are also derived from those of the hydrides, the central atom has a coordination of four, including nonbonding pairs of electrons, in the cases of chlorine and bromine, and of six in the cases of iodine and astatine. The examples shown in Table I illustrate these principles. Names for the radicals formed from these "-oic" acids end regularly in "-oyl."

The various possibilities for naming the univalent groups derived from the common acids of chlorine are compared in Table II, along with a few other examples.

The names "iodoso" and "iodoxy" for the covalent groups –IO and –IO $_2$ do not fit into any of the systems under consideration. Especially since in the "phosphorus" system the latter name applies to the –OI group (cf. –OF, fluoroxy), the designation "–oxy" having its usual connotation of an oxygen atom linking two groups (cf. –OCH $_3$, methoxy), it is recommended that these names be dropped despite their listing by the IUPAC 1957 Rules. ^{2a} In this regard, the most recent IUPAC organic rules approve "iodoso" but replace "iodoxy" by "iodyl." These same rules approve "chlorosyl," "chloryl," and "perchloryl." The compound $C_6H_5IO_2$, for example, would be iodylbenzene or metaiodinoylbenzene*, according to the system adopted.

The problem of naming the hypofluorites (see Table III) is related.

A problem not peculiar to halogen chemistry is that of designating the degree of hydration of acids (or their anions) which systematically require a higher coordination number. With the systematic (*i.e.*, "phosphorus" system) coordination number of iodine and astatine six, in contrast

Table I Names of Hydrides and Standard Oxo Acids of Representative Halogens

ClH ₅ :ClH ₅	Chlorane Chlorinine(chlorin(e) with other suffixes)	HOClO ₃ HOClO ₂	Chloranoic acid Chlorinoic acid	$(HO)_5IO$ $(HO)_5I:$	Iodanoic acid Iodinoic acid
:ClH3	Chloruane	HOĊĴO	Chloruanoic acid	$(\mathbf{HO})_3 \ddot{\mathbf{I}} \mathbf{OH}_2$	Ioduanoic acid
:ClH	Chloruine	HOÇÌ:	Chloruinoic acid	HO'Ï'(OH ₂) ₂	Ioduinoic acid

 $^{^{\}circ}$ Adapted from the paper presented before the Divisions of Inorganic Chemistry and Chemical Literature, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 18, 1959.

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Table II Names of Radicals Derived from Oxo Acids of the Halogens

2	WP 10 2 0 4	Nomenclature	
Group	IUPAC, ² C.A., etc.	"Halogen"	"Phosphorus" *
-Cl	Chloro	Chloro	Chloro
-OCl	Hypochlorito	Hypochlorito	Chloroxy
-C1O	Chlorosyl or oxochloro(III)	Chlorosyl	Chloruanoyl
-OClO	Chlorito	Chlorito	Chloruanoyloxy
$-ClO_2$	Chloryl or dioxochloro(V)	Chloryl	Chlorinoyl
$-OClO_2$	Chlorato	Chlorato	Chlorinoyloxy
$-ClO_3$	Perchloryl or trioxochloro(VII)	Perchloryl	Chloranoyl
$-OClO_3$	Perchlorato	Perchlorato	Chloranoyloxy
-OClO ₂ OH	O-Imidoperchlorato	O-Iminoperchlorato	Iminochloranoyloxy
-NHClO ₃	N-Imidoperchlorato	N-Iminoperchlorato	Chloranoylamino
$-OIOF_2$	O-Difluoroiodato or O-dioxodifluoroiodato(V)	O-Difluoroiodato	Difluorometaiodinoyloxy
$-\mathbf{IO}_2\mathbf{F}_2$	Difluoromeso(?)periodyl or dioxodifluoroiodo	Difluoromeso(?)periodyl	Difluorometaiodanoyla
-OIS	O-Thioiodito	O-Thioiodito	Thiometaioduanoyloxy
-SIO	S-Thioiodito	S-Thioiodito	Metaioduanoylthio ^a

[&]quot;For the use of "meta," see text.

Table III

Nomenclature of Hypofluorites

Compound	"Halogen" name	"Phosphorus" name*
CF ₃ OF	Trifluoromethyl hypofluorite	Fluoroxytrifluoromethane
$\mathbf{SF}_{5}\mathbf{OF}$	Pentafluorosulfanyl* hypofluorite	Fluoroxypentafluorosulfane
NO_2OF	Nitryl hypofluorite	Fluoroxydioxonitrane
ClO ₃ OF	Perchloryl hypofluorite or chloranoyl* hypofluorite	Fluoroxytrioxochlorane
FSO ₂ OF	Fluorosulfuryl, fluorosulfonyl, or fluorosulfanoyl* hypofluorite	Fluoroxyfluorodioxosulfane

to four for chlorine and bromine, series of oxo acids differing in degree of hydration, such as the periodic acids, are possible. It is proposed to name the "standard acid," defined as that in which the central atom has a coordination number of 3 (including nonbonding electron pairs) for elements of period 2 of the periodic table, a coordination number of 4 for periods 3 and 4, and of 6 for periods 5 and 6, from the parent hydride, e.g., iodanoic acid for $OI(OH)_5 = H_5IO_6$ from iodane, IH_7 , and iodinoic acid for :I(OH)5 from iodinine, IH5. Since the lowest state of hydration to which can be given a monomeric empirical formula, e.g., HIO4, seems to be universally designated by the prefix "meta," e.g., metaperiodic acid, it is further proposed to accept this prefix to designate the monomeric acid of the lowest state of hydration. (Even this use, however, can be highly misleading, for although metaperiodic acid is monomeric, metaphosphoric, HPO3, and metatelluric, H2TeO4, represent whole series of polymers.) Such a monomeric acid or its "-oyl" radical could then be no more than difunctional: HIO_4 , $-IO_3$; H_2SO_4 , $=SO_2$; and so forth.

Monomeric acids of intermediate states of hydration would then be indicated by "deaquo," "dideaquo," etc., according to the number of molecules of water formally required to be removed from the -oic acid in order to obtain the deaquo acid. Thus H_3IO_5 would be "deaquo-iodanoic acid" and the radical $\equiv IO_2$ would be "deaquo-

iodanoyl." (Radicals such as = IO_2OH would be "hydroxydeaquoiodanoyl.") This would avoid the use of prefixes whose meanings vary from user to user and would avoid awkward alternatives such as "pentaprotic periodic acid," "triprotic periodic acid," etc., for H_5IO_5 , H_3IO_5 , etc., or (as originally recommended by the Inorganic Halogen Nomenclature Subcommittee) "periodate(1–)," "dihydrogen periodate(1–)," and "tetrahydrogen periodate(1–)" for IO_4 –, H_2IO_5 –, and H_4IO_6 –, for example, which become "metaiodanoate*," "dihydrogen deaquoiodanoate*," and "tetrahydrogen iodanoate*," respectively.

Old and suggested new names for the monomeric iodine oxo acids are compared in Table IV.

The names given to the polymeric and condensed oxo acids of iodine are in a state of utter confusion, as shown in Table V.

Again the problem of polymerized and condensed oxohalate ions is one that is not unique to halogen chemistry. In the report of the Inorganic Halogen Subcommittee, "diperiodates" such as $H_3I_2O_9^-$, $H_3I_2O_{10}^{3-}$, and $H_3I_2O_{11}^{5-}$ were considered to be best named by the Ewens and Bassett convention of designating the charge on the anion, for example, trihydrogen diperiodate(1-), diperiodate(3-), and diperiodate(5-), respectively, since a stoichiometric nomenclature would be much more awkward. Alternatively, if the structures are known, "phosphorus" nomenclature can be used to advantage, in this case by taking

Table IV Names of Iodine Oxo Acids.

Acid	Names in literature	"Phosphorus" name*
H_5IO_6	Paraperiodic, 3,4 orthoperiodic 5,6	Iodanoic
H_3IO_5	Mesoperiodic ^{6,7}	Deaquoiodanoic
HIO_4	Metaperiodic, 3.4.6.7 tetraoxoiodic(VII) 5	Metaiodanoic
$H_7IO_8(?)$	Unnamed (holoiodic?)8	
H ₅ IO ₅ (?)	Unnamed (orthoiodic?) ⁸	Iodinoic
$H_3IO_4(?)$	Unnamed (mesoiodic?) ⁸	Deaquoiodinoic
HIO_3	Iodic ^{3,6,9,10} (metaiodic?)	Metaiodinoic
$H_5IO_4(?)$	Unnamed (holoiodous?)	Ioduanoic
$H_{3}IO_{3}(?)$	Unnamed (orthoiodous?)	Deaquoioduanoic
$HIO_2(?)$	Iodous (not known ¹¹)	Metaioduanic
$H_5IO_3(?)$	Unnamed (holohypoiodous?)	Ioduinoic
$H_3IO_2(?)$	Unnamed (orthohypoiodous?)	Deaquoioduinoic
HOI	Hypoiodous ^{6,10,12,13}	Metaioduinoic

Table V

Names of Polymeric and Condensed Oxo Acids of Iodine

H₈I₂O₁₁ Diorthoperiodic⁷

 $H_4I_2O_9$ Mesodiperiodic, dimesoperiodic, pyroperiodic Unnamed (diiodic is not an appropriate name if

 $H_2I_2O_6$ Unnamed (dilodic is not an appropriate name is disulfuric is correct for $H_2S_2O_6$)

 $H_3I_3O_9$ Unnamed (same comment)

HI₃O₈ Anhydroiodic⁹

the $-\stackrel{\checkmark}{I}\!\!-\!\!O-$ (iodoxane) group as the structural unit (cf. $-\stackrel{\dagger}{Si}\!\!-\!\!O-$, siloxane). Assumed structures and corresponding names for these ions are given in Table VI.

Table VI Assumed Structures and Names of Iodine Oxo Anions and Acids

Trihydrogen 1,3-epoxycyclodiiodoxanedioate* or trihydrogen bicyclo[1.1.1]diiodoxanedioate*

$$H_3I_2O_{10}^{3-}$$
 $HO O O O O O$
 $HO O O O O O$

Trihydrogen cyclodiiodoxanedioate*

Trihydrogen diiodoxanedioate*

The stoichiometric names would be trihydrogen nona-oxodiiodate (1-), trihydrogen decaoxodiiodate (3-), and trihydrogen undecaoxodiiodate (5-), respectively.

Similarly the polymeric iodic acids might be

cyclodideaquodiiodoxinedioic acid*

cycloideaquotriiodoxinetrioic acid*

1,3,7,12-tetraoxotricyclo[8.3.1.1^{7,12}]hexaiodoxinedideaquo-5,10-dioic acid*

Substituted acids are named as though the substitution occurred in the parent hydride, as in Table VII.

According to the IUPAC rules14 "-onium" ions are "derived by addition of protons (or equivalent) to monatomic anions." This allows only one series of "-onium" ions for any family of elements, specifically R_2X^+ for the halogens (X = halogen). Ions of the sort R₄X⁺ and R₆X⁻, although theoretically possible (and possibly known as IF₄⁺ and IF₆⁺ in liquid IF₅ and IF₇, for example¹⁵), cannot be named according to the rules. Since in effect this rule implies the formation of the "-onium" ion by addition of protons (or equivalent) to the parent hydride (or equivalent), the "phosphorus" system allows naming of all these ions as derived from the various hypothetical parent hydrides. Furthermore, since the IUPAC rules16 state: "Cations formed by adding protons to nonnitrogenous bases may also be given names by adding -ium to the name of the compound to which the proton is added," names can be derived according to rule from the parent hydrides with retention of the class 94 A. F. Clifford

Table VII Names of Substituted Acids

HIO_2F_2	Difluoroiodic acid or dioxodifluoroiodic (V) acid	Difluorometaiodinoic acid*
$HIOF_2$	Difluoroiodous acid or oxodifluoroiodic(III) acid	Difluorometaioduanoic acid*
H_2ClO_3N	Perchloramide or trioxoamidochloric(VII) acid	Aminochloranoic acid*
HClO ₃ N ⁻	Trioxoamido(imido?)chlorate(VII) (hydrogen trioxonitridochlorate(VII)?)	Hydrogen aminochloranoate*
ClO_3N^{-2}	Trioxoamido(nitrido? nitrilo?)chlorate(VII)	Aminochloranoate*

distinctions (Table VIII). The term iodonium would be retained as a generic name for all of these classes of ion.

Table VIII Names of "Onium" Ions

IH_7	Iodane	IH ₈ -	Iodanium
IH₅	Iodinine	IH_6^-	Iodinium
IH_3	Ioduane	IH_4^-	Ioduanium
IH	Ioduine	IH_2^-	Ioduinium
$(CH_3)_8I^-$	Octamethylioda	nium	
$(CH_3)_3IH_3^-$	Trimethyliodini	um	
$(CH_3)_5I^{2+}$	Pentamethylioduanium(2+)17		
$(C_6H_5)_2I^{-}$	Diphenylioduini	ium	

Similarly, $p\text{-}C_6H_5IC_6H_4CO_2H$ is called $p\text{-}phenylioduiniobenzoic acid, <math>p\text{-}C_6H_5I\bar{C}_6H_4CO_2^-$, $p\text{-}phenylioduiniobenzoate, and}$

2,2'-ioduiniobiphenyl-3,3'-dicarboxylic acid, where "ioduinio" (generic: "iodonio") denotes the cationic iodine atom. This last compound is called 4,6-dicarboxydibenziodolium by *Chemical Abstracts*, 18 but the latest organic rules 19 give the name 2,2'-biphenylylenechloronium hydroxide to

Although with the exception of the polyhalide ions, catenation compounds of the halogens appear not to be known with chain lengths longer than two (e.g., O₃Cl-ClO₃), it is conceivable that catenation compounds having greater chain lengths may be prepared. Either the "halogen" or the "phosphorus" system is equipped to handle these (Table IX).

In summary, it is believed that the "halogen" system or more especially the "phosphorus" system of nomenclature is much more adaptable than "classical" inorganic nomenclature to most of the naming problems likely to arise for the more complex compounds of the halogens. It also provides systematic names for the simple compounds from which the complex ones must inevitably be derived. It is recognized, of course, that these names would undoubtedly not displace the common (trivial?) ones for simple compounds (e.g., chloruanoic acid for chlorous acid) any more than ethanoic acid has replaced acetic acid. On the other hand, the parent name, chloruane, provides a basis for a truly systematic name for its more complex derivatives, whereas the name chlorous acid does not. Furthermore, such nomenclature will be compatible in a complex name with the nomenclature of the organic groups with which it must frequently be associated, not only as side chains, but as backbone constituents. This also cannot be said for classical inorganic nomenclature.

In passing it may be noted that both subcommittees dislike the term "halogenide" as contributing nothing whatsoever in meaning which is not perfectly adequately expressed by the simpler term "halide." The maximum simplicity consistent with unambiguity should be a cardinal aim in nomenclature.

Table IX
Names of Catenation Compounds

Compound	"Phosphorus" system"	"Halogen" or alternate "Phosphorus" system
$(CH_3)_6II(CH_3)_5I(CH_3)_5I(CH_3)_6$	2,2,2,2,3,3,3,3,3,4,4,4,4,5,5,5,5,5-Icosamethyl-2,3,4,5-tetraiodahexane (icosamethyl-2,3,4,5-tetraiodahexane)	1,1,1,1,1,1,2,2,2,2,2,3,3,3,3,3,4,4,4,4- 4,4-Doicosamethyltetraiodane (doicosamethyltetraiodane)
$\mathbf{F}_{4}\mathbf{IIF}_{3}\mathbf{IF}_{3}\mathbf{IF}_{4}$	Tetradecafluorotetraiodabutine	Tetradecafluorotetraiodinine
$\mathbf{F}_{6}\mathbf{IIF}_{6}\mathbf{IF}_{5}\mathbf{IF}_{6}$	$I cos a fluoro tetra io dabut - 2-in an e^{\alpha}$	Icosafluorotetraiodane-2-(V),1,3,4- tri(VII) or 1,1,1,1,1,1,2,2,2,3,3,3- 3,3,4,4,4,4,4-icosafluorotetra- iodane
$(C_6H_5)_2\Pi(C_6H_5)_5I(C_6H_6)I(C_6H_5)_2$	Decaphenyltetraiodabutuan-2-ane ^a	Decaphenyltetraiodane-1,3,4-tri(III)- 2-(VII) or 1,1,2,2,2,2,2,3,4,4- decaphenyltetraiodane
$(C_{e}H_{5})_{2}II(C_{e}H_{5})_{3}I(C_{e}H_{5})I(C_{e}H_{5})_{3}I(C_{6}H_{5})_{2}$	Decaphenylpentaiodapentuane-2,4-diine°	Decaphenylpentaiodane-1,3,5- tri(III)-2,4-di(V) or 1,1,2,2,2,3,- 4,4,4,5,5-decaphenylpentaiodane

^a Position numbers are not given to the chain atoms of the most abundant oxidation number.

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Nomenclature Problems in Boron Chemistry*

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In its position as the only electron-deficient nonmetal, boron is involved in structural and bonding problems which are in many respects unique. They also often parallel established and sometimes opposing viewpoints from metallic and nonmetallic chemistry and nomenclature. The more difficult problems in boron nomenclature arise from the conflicting demands of simplicity for boron chemistry and compatibility with general nomenclature of other elements.

Boron seems to be always found in nature bonded to oxygen.¹ Traditional nomenclature served reasonably well for this type of compound.

 $B(OH)_3$ boric acid $(HBO_2)_n$ metaboric acid

(ortho)

 $\begin{array}{cccc} BO^{\eta_-}_{\wedge} & \text{orthoborate ion} & (BO_{2}^-)_{\pi} & \text{metaborate ion} \\ & & & & & & & & & & [\text{probably B(OH)}_{+}^-\text{in} \\ & & & & & & & & \text{aqueous systems}]^2 \end{array}$

Like other polyhydroxylic acids, boric acid condenses to form a number of complex anions. In minerals these seem to be of endless variety and states of hydration. However, they all appear to be derived from one of the three following ions by hydration and/or condensation.

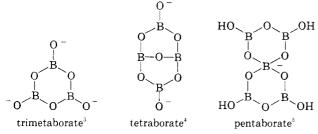


Figure 1.

In all these condensed anions the presence of the boroxin (B_3O_3) ring is noteworthy. Names completely describing these anions involve all the traditional problems of heterocyclic nomenclature, including fused and spiro ring systems as indicated above.

The nonoxygenated chemistry of boron has stemmed largely from the work of Stock on the boron hydrides during the early part of this century. The elucidation of the structures during the past decade and the evidently unusual bonding involved have contributed continuing new nomenclature demands. Chemists have in general followed Stock's lead and named the boron hydrides similarly to the silicon hydrides, *i.e.*, with a Greek prefix to indicate the number of boron atoms and the suffix ane to indicate a covalent hydride, *e.g.*

 B_2H_6 diborane B_4H_{10} tetraborane

Due to interest in the high heats of combustion of these materials, an intensive government-sponsored research effort was begun in about 1950 into the chemistry of these substances. In 1952 a group met under the prime contractors' sponsorship and the chairmanship of the late Dr. George W. Schaeffer to attempt to establish a recommended nomenclature for the burgeoning chemistry. A paper on "The Nomenclature of Boron Compounds" presented by Dr. Schaeffer and Dr. Thomas Wartik before the Division of Chemical Literature at the 125th meeting of the American Chemical Society, March 25, 1954, in Kansas City was subsequently reviewed in

*Adapted from the paper presented before the Divisions of Inorganic Chemistry and Chemical Literature, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 18, 1959.