

FREE INORGANIC RADICALS¹

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INTRODUCTION

A radical has been defined as a group of elements which, in reactions and properties, behaves as an entity. The study of *organic* radicals, beginning with the classical researches of Gomberg, Schlenk, Wieland and others (1), has long since led to many interesting results. However, the study of *inorganic* radicals, in particular of negative univalent inorganic groups, is one of the most recent developments in pure chemical science. Because of the similarity of certain of these groups to the halogens, they have been termed "halogenoids" by Browne and his co-workers (2), and "pseudo-halogens" by Birckenbach and Kellermann (3). At present we recognize as "halogenoid" radicals the thiocyanate, cyanide, azidodithiocarbonate, selenocyanate, azide, cyanate, fulminate, and tellurocyanate groups, of which the first four have been isolated in the free dimolecular form.

I. HISTORICAL

Cyanogen, $(\text{CN})_2$, was first obtained by Gay-Lussac in 1815 by heating mercuric or argentous cyanide. From the standpoint of theoretical chemistry this discovery was very important, as it is the first recorded instance of the isolation of a "radical" which could properly be classed under the definition given in 1838 by

¹ The term "free radical" is not used here in the same sense that the organic chemist speaks of "free organic radicals." (Ref. (1).) The latter, as non-saturated substances, are capable of existing in the mono-molecular state, such as triphenyl methyl, $(\text{C}_6\text{H}_5)_3\text{C}$, whereas the inorganic radicals have been obtained hitherto only in the dimeric form—just as chlorine, Cl_2 , is spoken of as "free chlorine."

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Liebig (4), who said, "We call cyanogen a radical, (a) because it does not change its constitution in a series of compounds; (b) because in these compounds it may be replaced by simple substances (elements); (c) because in its compounds with an element the latter may be liberated and replaced by its equivalent of another element."

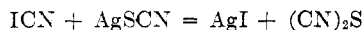
Soon after the discovery of cyanogen Liebig (5) attempted to prepare free *rhodan* or thiocyanogen by passing chlorine over dry silver or lead thiocyanate. In both cases he observed a strong evolution of heat; the compound became yellow, then increased in volume, became more viscous and finally evolved a red vapor which condensed to a red solid. The whole mass eventually hardened and became vermilion in color. The presence of sulfur chloride and cyanuric chloride in the colder portions of the tube seemed to indicate a decomposition of the thiocyanate radical. No product was found which gave even approximate analyses for thiocyanogen. Consequently Liebig concluded that the red product obtained by him was composed of a mixture of substances.

Liebig next passed chlorine through a hot concentrated solution of potassium thiocyanate and obtained a yellow amorphous precipitate, which approximated the composition of thiocyanogen. It was found to be insoluble in all common solvents, soluble, however, in concentrated sulfuric acid. In announcing the discovery of the supposed thiocyanogen, he mentioned the fact that its inert nature and non-volatility were contrary to expectations.

Other investigators worked with the same substance and found its composition to vary considerably. It was ascertained, furthermore, that the substance contained hydrogen and oxygen in addition to sulfur, carbon, and nitrogen. Liebig later (1844) admitted that the substance was probably a mixture of various compounds.

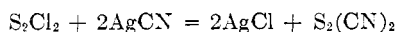
Subsequently it was found that the action of such oxidizing agents as potassium permanganate, nitric acid, hydrogen peroxide, and potassium persulfate on thiocyanates would also give similar yellow products. These were then collectively given the name "pseudothiocyanogen" (and still later "canarine").

In 1861 Linnemann (6) attempted to prepare the thioanhydride of thiocyanic acid, probably not knowing that Lassaigne (1828) had already obtained cyanogen sulfide by the interaction of sulfur chloride and mercuric cyanide. He succeeded in preparing the same substance from cyanogen iodide and silver thiocyanate:



He next allowed silver thiocyanate to react directly with an ethereal solution of iodine and obtained silver iodide and a readily volatile red-brown liquid. Because of the instability of the latter he did not pursue his investigations any further. On permitting the solution to stand for a time, large quantities of a yellow amorphous substance formed, which led him to conclude that the freshly prepared solution contained iodine thiocyanate, a statement which has never yet been denied or affirmed by any other investigator.

Schneider (7) allowed sulfur chloride in carbon disulfide solution to react with silver cyanide expecting to get a transformation in accordance with the equation:



A violent reaction took place and "white crystals with a penetrating odor invoking tears" separated out, possessing the theoretical composition $(\text{CN})_2\text{S}_2$. Microscopic study revealed the fact that the product was heterogeneous, and the assumption of the formation of the disulfide was given up. Later the substance was recognized to be a mixture of "dicyanogen mono-sulfide and dicyanogen tri-sulfide" (8).

Klason (9) oxidized thiocyanuric acid with iodine and obtained a compound to which he assigned the formula $(\text{CN})_3\text{S}_3 \cdot \text{S}_3(\text{CN})_3$, an empirical polymer of thiocyanogen. In summarizing the work which had been done up to 1901 Goldberg (10) came to the conclusion that free thiocyanogen had not yet been prepared.

Negative results of this nature seemed to make it only too evident that radicals could not be liberated from their compounds and that they existed as entities only in solution, that is, in the

ionic state. These views were expressed by Wm. Ostwald in 1895, who stated "Radicals by their inherent nature are not capable of isolation".

Thus, it was not until 1920 that thiocyanogen, the first halogenoid, was obtained by Söderbäck (13), although Sommer (11) had previously obtained azido-carbondisulfide, $(\text{SCSN}_3)_2$, without recognizing its true nature or studying it. It is the work of this brilliant Swedish investigator which gave a new impetus to the study of "inorganic radicals," and it is the appearance of his article dealing with this subject which marks the beginning of renewed interest in their characteristics and properties.

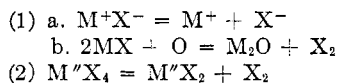
II. PROPERTIES OF THE HALOGENS

In order to bring out the halogen-like character of these substances, which we have been wont to call "halogenoids", it may be of value to discuss briefly those properties which characterize the halogens as a *group*. The great similarity existing among the latter, both as elements and in their compounds, is such that the properties of any one member can be said to typify those of any other member, even though fluorine shows a little deviation from some of these.

- (1) The halogens, in general, show pronounced volatility.
- (2) The solid substances are apparently isomorphous, belonging to the rhombic system.
- (3) They show great affinity towards metals, combining directly in many cases to form salts. Their silver, mercurous, and lead salts are to a varying degree insoluble in water. They are, however, soluble in potassium cyanide and sodium thiosulfate solutions.
- (4) With hydrogen they form hydracids, compounds which in aqueous solution are usually highly ionized.
- (5) They are capable of forming inter-halogen compounds, such as ClI , ClI_3 , BrCl , etc.
- (6) They form polyhalide complexes, such as CsCl_2I , $\text{CsI} \cdot \text{I}_4$.
- (7) Oxyacids have been prepared of which the most notable series is that of chlorine.

(8) They form characteristic double and complex salts, such as $\text{CuCl}_2 \cdot 2\text{KCl}$ and K_2PtCl_6 , respectively.

(9) The free halogens may be prepared in general, (1) by chemical or electrochemical oxidation of the hydric acids or their salts, or (2) by decomposition of the perhalides.



III. THE HALOGENOIDS

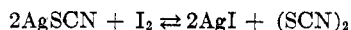
Let us apply these criteria to those substances which we have termed "halogenoids." This name has been used to designate any univalent chemical aggregate composed of two or more electronegative atoms, which shows in the free state certain characteristics of the halogens, and which combines with hydrogen to form an acid, and with silver to form a salt insoluble in water. The halogenoid salts and hydric acids have been known to science for many years. The silver, lead, and mercurous salts are insoluble in water. These few similarities could hardly be considered sufficient basis for further generalizations. However, the fact that the radicals, in so far as they have been obtained in the free state, do simulate the halogens in behavior, makes such an analogy permissible.

As determined from a study of the electrical conductivity of some of their salts in aqueous and alcoholic solutions, halogen and halogenoid ions have been arranged in the following activity or electromotive series (3), viz.: F^- , ONC^- , OCN^- , Cl^- , N_3^- , Br^- , CN^- , SCN^- , SCSN_3^- , I^- , SeCN^- , TeCN^- . It is of interest to note the explanation which Birckenbach and Kellermann offer in accounting for the halogenoid properties of these substances. On the basis of the octet theory if one considers the sum of the valence electrons of the atoms comprising the halogenoid group, rather than the individual valence electrons, it is possible to formulate an arrangement of saturated shells of eight electrons (octets), and an additional structure of seven electrons, similar to that of the halogen atoms. For example, the azide group will have a total of fifteen ($8 + 7$); the selenocyanate again a

total of fifteen ($8 + 7$); the azidodithiocarbonate group 31 ($8 + 8 + 8 + 7$). The exact configuration of the electrons is not made plain. Although such an explanation might be extended to account for the observed similarities it would unquestionably lead to wrong conclusions, *e.g.* the nitrate radical which has a total of twenty-three electrons ($23 = 2 \times 8 + 7$), and the hydroxyl radical which has a total of seven. Darrow's (12) statement might properly be cited here: "Undoubtedly the most prudent policy is to consider atoms as being creations of the scientific imagination, mental mechanisms designed to copy particular restricted sets of phenomena."

To bring out the halogenoid analogy, let us discuss: methods of preparation, physical and chemical properties of those which have been isolated in the free state; formation of compounds with the halogens (interhalogen-halogenoids) and among themselves (interhalogenoids); compounds corresponding to the polyhalides.

I. *Thiocyanogen*, $(SCN)_2$. Free thiocyanogen was first obtained by Söderbäck (13) who allowed iodine to react with an ethereal suspension of silver thiocyanate. Various solvents were tried; bromine was used in place of iodine, and various other metallic thiocyanates in place of the silver salt. Bromine was found to be much more satisfactory than iodine, as reaction with the latter comes to an equilibrium and does not go to completion.

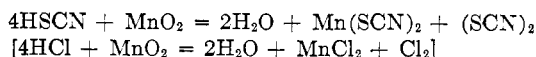


The velocity of the reaction is markedly influenced by the solvent employed; thus a $N/10$ bromine solution in carbon disulfide is decolorized in a few minutes by lead thiocyanate, while a considerably longer period of time is necessary when bromine is dissolved in ether. Other factors also enter into the reaction. If the carbon disulfide is dried over phosphorous pentoxide, the bromine is not decolorized by the lead salt even after an hour, although the reaction is immediate when silver or mercuric thiocyanates are used. Solutions of thiocyanogen so obtained liberate iodine from iodides, oxidize copper from the cuprous to the cupric state, and combine directly with metals to form the corresponding thiocyanates.

Solid thiocyanogen is prepared by evaporating a $N/2$ solution in ethyl chloride, ethyl bromide, or ether, over sulfuric acid, and cooling the concentrated solution in a special filtering apparatus to -70° . The thiocyanogen is precipitated out, filtered, and dried at this temperature and is obtained as a crystalline substance composed of "cruciform aggregates" which melts at -2 to -3° to a viscous yellow oil which may be supercooled to -20°C . It always solidifies at about -30° to small rhombic plates. If liquid thiocyanogen is warmed to room temperatures it gradually becomes less viscous and changes in color to a dark red-brown. At a certain stage a yellow vapor is given off with the evolution of a good deal of heat, and the material solidifies to a brick-red, amorphous mass. Analysis seems to indicate that it is fairly pure polymeric thiocyanogen or "parathiocyanogen," a product which is insoluble in all ordinary solvents and has, thus far, defied definite experimental treatment. Potassium cyanide converts it into a black compound, which is soluble in alkalies. Analysis of the black compound indicates the formula $(\text{CN})_2\text{SOH}$.

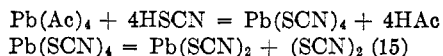
Previous to its isolation, the existence of thiocyanogen as a product of decomposition of gold thiocyanates was demonstrated by Bjerrum and Kirschner (14). By electrometric measurements these investigators determined it to be an unstable halogen-"oid," intermediate between bromine and iodine. They found that bromine was instantly reduced by an acidified solution of sodium thiocyanate, and that the resulting colorless solution set free iodine from potassium iodide.

Solutions of thiocyanogen may also be prepared by oxidation of the free acid in ethereal solution by manganese dioxide (15). This method is not suggested as feasible since the yields are extremely small. The reaction is of interest, however, since it parallels the one which is used in the laboratory preparation of chlorine:



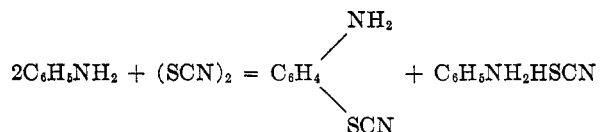
Like the halogens, thiocyanogen may also be prepared by electrolysis of thiocyanates, preferably in alcoholic solution (16). Inter-

action of lead tetracetate and thiocyanic acid in ethereal solution presumably takes place in accordance with the following equations:



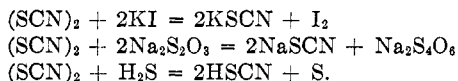
The molecular weight of thiocyanogen in bromoform has been determined by Lecher and Goebel (17). Cryoscopic measurements for solutions less than half-normal indicate it to be dissolved as $(\text{SCN})_2$. In solutions greater than half-normal there are evidences of polymerization.

Many reactions indicate the similarity of thiocyanogen with the halogens. In addition to those mentioned previously it has been found that thiocyanogen reacts with mercury diphenyl to yield phenyl mercuric thiocyanate and with aniline to give p-thiocyananiline and aniline thiocyanate:



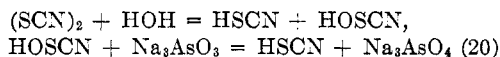
The action of ethyl nitrite upon thiocyanic acid yields a nitrosyl thiocyanate (analogous to NOCl), which is unstable above -17°C ., decomposing above that temperature into nitric oxide and thiocyanogen (18).

Kaufmann and Gaertner (19) have worked out a series of thiocyanometric determinations, which make it possible to titrate solutions of thiocyanogen in organic solvents with aqueous solutions of potassium iodide, hydrogen sulfide, and sodium thiosulfate.

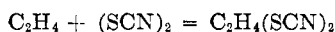


In the presence of a sufficient quantity of salts, hydrolysis of thiocyanogen is reduced to such an extent that the above reactions take place. The first reaction is most suitable for the quantitative determination of thiocyanogen in organic solvents.

Sodium arsenite is oxidized by thiocyanogen to sodium arsenate. The intermediate formation of hypothiocyanous acid is postulated:



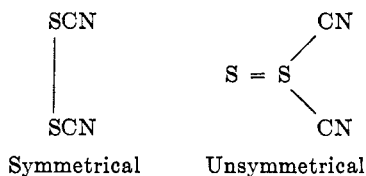
Like the halogens, thiocyanogen reacts directly with unsaturated hydrocarbons to form addition products (21):



From their work on the gold thiocyanates, Bjerrum and Kirschner conclude that the hydrolysis of thiocyanogen proceeds in accordance with the equations:

- (1) $(\text{SCN})_2 + \text{HOH} = \text{H}^+ + \text{SCN}^- + \text{HOSCN}$ (instantaneous)
- (2) $2\text{HOSCN} = \text{HSCNO}_2 + \text{H}^+ + \text{SCN}^-$ (rapid)
- (3) $2\text{HSCNO}_2 = \text{HSCNO} + \text{HSCNO}_3$ (instantaneous)
- (4) $\text{HSCNO}_3 + \text{HOH} = \text{H}_2\text{SO}_4 + \text{HCN}$ (instantaneous)
- (5) $3(\text{SCN})_2 + 4\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{HCN} + 5\text{HSCN}$

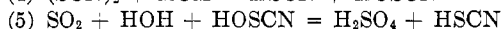
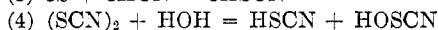
However, Lecher and his co-workers have recently found that the reaction does not proceed quantitatively in accordance with equation (5). In view of the fact that the polymerization of thiocyanogen has been found to take place with formation of small quantities of cyanogen thiocyanate and dithiocyanogen mono-sulfide (22), it has been assumed that the halogenoid is capable of existing in two tautomeric forms, viz;



Based on analogy with sulfur chloride, $\text{S} = \text{S} \begin{array}{l} \swarrow \text{Cl} \\ \searrow \text{Cl} \end{array}$, unsymmetrical

thiocyanogen with the disulfide structure might be expected to *hydrolyze* in accordance with the equations:

- (1) $2(\text{S}=\text{S}(\text{CN})_2) + 4\text{HOH} = 4\text{HCN} + 2\text{H}_2\text{S} + 2\text{SO}_2$
- (2) $\text{SO}_2 + 2\text{H}_2\text{S} = 2\text{H}_2\text{O} + 3\text{S}$



Equation (1) is based upon analogy to the sulfur halides, (2) and (3) are well known, while (4) is indicated from the reaction between sodium arsenite and thiocyanogen. The sum total of all of the above reactions would lead to the same final result as postulated by Söderbäck, Bjerrum, and others, although under the circumstances it is quite probable that other complications arise which do not permit of definite quantitative expression.

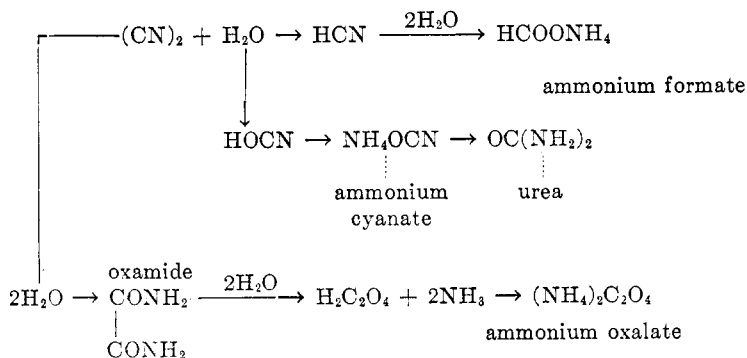
Aminolysis of thiocyanogen results in formation of compounds analogous to the chloramines:



With ammonia, thiocyanamide, $SCN \cdot NH_2$, an extremely unstable oil is obtained (23).

II. *Cyanogen*, $(CN)_2$. Cyanogen is an extremely poisonous gas, colorless and possessing a peculiar odor. It is liquefiable at ordinary pressures at $-25^\circ C$. When heated to $500^\circ C$., some of the gas is converted into the insoluble polymer, paracyanogen, $(CN)_n$. Its reactions have been common chemical knowledge for over a century—and its halogenoid characteristics have been the subject of considerable investigation, so that a detailed discussion of its various properties here would be quite superfluous. However, two interesting analogies may be brought out.

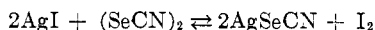
It undergoes *hydrolysis*, the course of which may be represented diagrammatically:



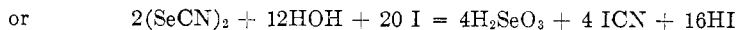
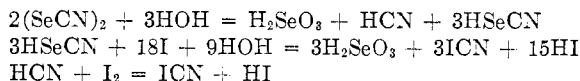
Ammonolysis results in formation of cyanamide and ammonium cyanide.

III. *Selenocyanogen*, $(\text{SeCN})_2$. Selenocyanogen is obtained as a homogeneous yellow powder, which within a very short time turns red in color. If kept dry and in a vacuum it is stable for a longer period. It is soluble in benzene, chloroform, and carbon tetrachloride. Solutions in acetic acid decompose rapidly with precipitation of selenium. Molecular weight determinations in benzene are in fair agreement with the dimeric formula $(\text{SeCN})_2$. Determinations in glacial acetic acid would seem to indicate a somewhat marked dissociation—possibly with formation of the unsaturated radical. This apparently anomalous behavior is explained by chemical interaction of solvent and solute.

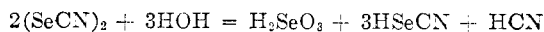
Selenocyanogen may be prepared by electrolysis of a solution of potassium selenocyanate in methyl alcohol (3), or by the decomposition of lead tetraselenocyanate (24), as formed by the interaction of selenocyanic acid and lead tetracetate in acetone. The reaction between iodine and silver selenocyanate has also been studied, and, both electrically and analytically, has been found to proceed in both directions to an equilibrium, where 86 per cent of the iodine is converted to silver iodide, and the remainder left in ethereal solution:



The strength of selenocyanogen solutions may be determined by titration with aqueous iodine. The following reactions are assumed to take place:



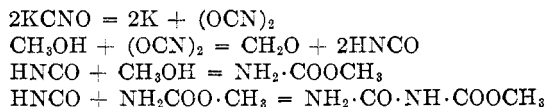
Upon *hydrolysis*, selenocyanogen yields selenous, hydrocyanic, and selenocyanic acids, presumably in accordance with the following equation:



In view of the fact that dicyanogen selenide and triselenide are formed on heating selenocyanogen in carbon disulfide, it is assumed that the latter may also, like thiocyanogen, exist in two tautomeric forms:

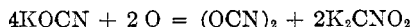


IV. *Oxycyanogen*, $(\text{OCN})_2$. The presence of this halogenoid in solution has been demonstrated by Birckenbach and Kellermann (3) who attempted to prepare it by the electrolysis of a methyl alcoholic solution of potassium cyanate. Instead of the free halogenoid they obtained methyl allophanate and detected the presence of formaldehyde, indicating that the following reactions may have taken place:



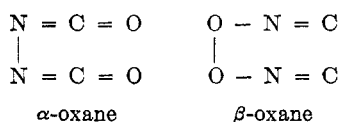
However, the presence of some free oxycyanogen was demonstrated, as the solutions obtained liberated iodine from potassium iodide, and dissolved copper, zinc and iron without gas evolution.

Lidov (25) claims to have prepared oxycyanogen or "oxane" (a) by the action of hydrogen peroxide, cupric oxide, or sodium hypobromite upon potassium cyanate:



(b) by reduction of nitrogen dioxide by carbon at 150° , and (c) by the interaction of cyanogen bromide and silver oxide. According to Lidov, oxane is a gas similar to carbon dioxide, and may be present in human exhalations. It is supposed to be the anhydride of oxanic acid, H_2CNO_2 , of which several salts have been described.

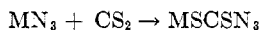
By varying the conditions of procedure, two isomeric oxanes may be produced:



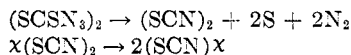
Apparently this work has either been overlooked by recent investigators, or its reliability questioned. There is no doubt but that substantiation of the above observations would be desirable.

V. *Azidocarbon disulfide*, $(\text{SCSN}_3)_2$. This substance was first studied by Browne and his co-workers (2), who prepared it by chemical and electrochemical oxidation of azidodithiocarbonic acid and its salts. It is practically insoluble in water and can therefore easily be obtained by addition of an iodine-potassium iodide solution to an aqueous azidodithiocarbonate solution. It is a white crystalline solid, very unstable, and sensitive to both shock and impact.

It is of particular interest as its preparation and decomposition involve the use and appearance of two other halogenoid radicals. The azidodithiocarbonates (26) are prepared by interaction of carbon disulfide and azides:



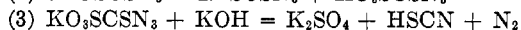
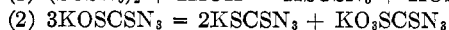
and the free halogenoid itself decomposes autocatalytically to give thiocyanogen and eventually its polymer:



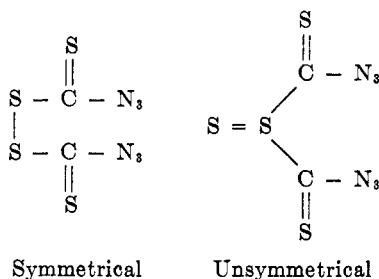
The acceleration in the rate of decomposition of the halogenoid, as noted during the course of nitrometric studies, is thought to be due to the intermediate formation of an unstable *interhalogenoid* complex, possibly $\text{SCN} \cdot \text{SCSN}_3$.

The halogenoid dissolves in alkali with formation of a greenish solution. Primary *hydrolysis* is assumed to take place in accordance with the equations (1), (2), and (3), in which the transient

formation of the hypochlorite and chlorate analogues of $(\text{SCSN}_3)_2$ are postulated.



That this reaction does not hold quantitatively has been shown by Gardner (27), who has found thiosulfates, sulfites, and sulfides among the products. Here also, it is assumed that azidocarbonyldisulfide may exist in two tautomeric forms:



Ammonolysis takes place with formation of ammonium azido-dithiocarbonate (28) and an oily, unstable product, presumably the amide derivative, NH_2SCSN_3 :



In connection with azidocarbonyldisulfide, it might be of interest to mention that thiuram disulfide $(\text{SCSNH}_2)_2$ and its substitution products, $(\text{SCSNHR})_2$ and $(\text{SCSNR}_2)_2$ are all structurally related to the halogenoid under discussion. Certain reactions and properties, such as the preparation of the dimeric radical and of the corresponding acids and salts, would make it advisable to study these substances more closely from the standpoint of the halogenoid analogy. Enough evidence is now at hand to warrant their designation as "organic halogenoids."

VI. *Other halogenoids.* Attempts have been made to prepare the other halogenoid radicals in the free form. Thus, Browne and Lundell (29) electrolyzed a solution of potassium azide in anhydrous liquid hydrogen azide, but obtained only molecular

nitrogen. *Tellurocyanogen*, $(\text{TeCN})_2$, has thus far been investigated only very superficially. It should be capable of isolation, either by the electrolysis of solutions of its potassium salt in methyl alcohol, or by the interaction of potassium tellurocyanate and lead tetracetate in acetone solution.

The free radical corresponding to the *fulminate* ion has thus far not been subjected to experimental treatment. Sufficient reasons appear to be at hand, however, to permit its classification with the halogenoid groups. It may certainly be predicted that all of these substances will some day be obtainable as "free radicals."

IV. POLYHALOGENOIDS

Compounds of the type $\text{MX}\cdot\text{X}_2$ (where M = alkali metal and X = halogen) have become firmly established and recognized as chemical individuals (30). One of the most definite supports of the halogenoid analogy is the isolation of several polyhalogenoids and evidence of the existence of others.

A compound intermediate between the polyhalides and the polyhalogenoids is cesium diiodocyanide, CsI_2CN (31), prepared by the interaction of cesium iodide and cyanogen iodide in aqueous solution as a reddish crystalline compound. The corresponding potassium compound is also known, but is much less stable.

Kerstein and Hoffman (16) have shown that complex compounds of the trithiocyanate type are possible. Ammonium trithiocyanate, $\text{NH}_4(\text{SCN})_3$, has been isolated as a clear crystalline substance, stable below -6° . The excess thiocyanogen can be removed by treatment with carbon disulfide. Electrolysis of a cold concentrated aqueous solution of potassium thiocyanate results in formation of free thiocyanogen, which is supposedly present in the form of the polyhalogenoid, $\text{KSCN}\cdot(\text{SCN})_2$. Experiment has shown that hydrolysis of thiocyanogen is retarded by the presence of a large excess of an alkali thiocyanate—presumably because of the formation of such polyhalogenoids.

Selenocyanogen is markedly more stable in solutions of potassium selenocyanate. Again it is supposed that compounds cor-

responding to polyhalides are formed, and this seems to be indicated by the work of Birckenbach and Kellermann (32), who, by electrometric titration of solutions of potassium selenocyanate and of potassium iodide with iodine, have established the existence of a series of complex salts, *e.g.* KI_3 , $K(SeCN)I_2$, $K(SeCN)_2I$, and $K(SeCN)_3$. These are all unstable in presence of water.

Verneuil (33) claims to have prepared a compound possessing the formula $K(SeCN)_3$, stable in water. It is rather questionable whether this is at all similar to the cesium tri-selenocyanate prepared by Birckenbach and Kellermann. The latter compound is a red-brown crystalline substance, stable in air, but decomposed immediately by water.

V. INTERHALOGEN-HALOGENOIDS

From the list of interhalogen compounds theoretically capable of existence as definite chemical individuals, bromine trifluoride (34), iodine pentafluoride (35), iodine monochloride and trichloride (36) and iodine monobromide (37) have been prepared.

Like their prototypes, the halogenoids are capable of entering into combination (*a*) with the halogens to form interhalogen-halogenoid compounds, and (*b*) with other halogenoids to form interhalogenoids.

The interhalogen-halogenoids include chlorazide, ClN_3 (38), bromazide, BrN_3 (39), iodoazide, IN_3 (40), the chloride, bromide, and iodide of cyanogen (all of which have been long recognized as chemical individuals), and thiocyanogen monochloride and trichloride (41).

The halides of "azine," $(N_3)_2$, are all extremely explosive substances, which undergo spontaneous decomposition at room temperatures. In so far as they have been studied they resemble the cyanogen halides very closely. They are characterized by their intense odors, and have the physiological effects of hydrazoic acid.

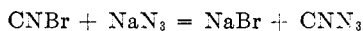
The cyanogen halides are very volatile substances whose vapors are extremely poisonous and possess a very pungent odor. They have long been known and have found wide application in synthetic organic chemistry.

There has been some question as to the molecular weight of thiocyanogen chloride, SCNCl . One might expect this substance to be an extremely volatile liquid, but, as obtained by direct combination of thiocyanogen and chlorine in chloroform, it is a white crystalline solid, non-volatile, decomposing only over 200°C . Lecher and Joseph repeated the original experiments and found the substance to possess a molecular weight corresponding to $(\text{SCNCl})_6$ in benzene. The trichloride is obtained by direct combination of chlorine and thiocyanogen in ethyl bromide, as a yellow oil, with a pungent odor, boiling at $152\text{--}153^\circ$.

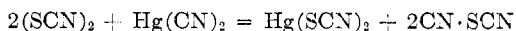
Browne and Gardner (42) have recently studied the action of the halogens on azidocarbonylsulfide and have obtained qualitative evidence of the existence of $\text{Cl}\cdot\text{SCSN}_3$, $\text{Br}\cdot\text{SCSN}_3$, and Br_3SCSN_3 . The extreme instability of these substances precludes their exact analysis and description.

VI. THE INTERHALOGENOIDS

The interhalogenoids include cyanazide, CNN_3 (43), cyanogen thiocyanate (6, 8, 13), $\text{CN}\cdot\text{SCN}$, cyanogen selenocyanate (24, 33), $\text{CN}\cdot\text{SeCN}$, and cyanogen azidodithiocarbonate (44), $\text{CN}\cdot\text{SCSN}_3$. Cyanazide is a volatile, crystalline solid melting at 36°C ., which may be prepared by the interaction of sodium azide and cyanogen bromide in suitable solvents:



Cyanogen thiocyanate was first obtained by interaction of cyanogen iodide and silver thiocyanate, and given the name dicyanogen sulfide, $(\text{CN})_2\text{S}$. Its true nature as an interhalogenoid was not recognized until Söderbäck obtained it by the interaction of mercuric cyanide and thiocyanogen:



It may also be prepared by interaction of an alkali thiocyanate and cyanogen bromide, although the yields in this case are small (44). It is a beautifully crystalline, extremely volatile solid, melting at 61°C .

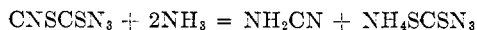
Cyanogen selenocyanate, CNSeCN , has been recognized as a

product of decomposition of selenocyanogen. It is a crystalline solid possessing properties very similar to those of cyanogen thiocyanate.

Cyanogen azidodithiocarbonate, $\text{CN}\cdot\text{SCSN}_3$, may be obtained either by interaction of potassium azidodithiocarbonate and cyanogen bromide, or by the interaction of mercuric cyanide and the free halogenoid. It is a white crystalline solid, somewhat volatile, melting with decomposition at 67° . It undergoes spontaneous decomposition in accordance with the equation:



Hydrolysis yields a variety of products, among which are hydrocyanic, cyanic, thiocyanic, sulfurous, thiosulfuric, and sulfuric acids, ammonia, sulfur, and nitrogen. *Ammonolysis* gives principally ammonium azidodithiocarbonate and cyanamide:



The existence of the interhalogenoid, $\text{SCN}\cdot\text{SCSN}_3$, has been postulated to account for the autocatalytic decomposition of azidocarbonyl disulfide (2).

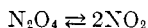
Much other experimental evidence is at hand to support the halogenoid analogy. Compounds such as sulfuryl azide, $\text{SO}_2(\text{N}_3)_2$, (45), carbonyl azide, $\text{CO}(\text{N}_3)_2$ (46), analogous to SO_2Cl_2 and COCl_2 , are known. Thiocyanogen monosulfide and disulfide, $\text{S}(\text{SCN})_2$ and $\text{S}_2(\text{SCN})_2$, have been prepared. Cyanoforn, $(\text{CN})_3\text{CH}$, analogous to chloroform is a white crystalline solid melting at 210° . Organic derivatives of the halogenoids have much in common with the corresponding halogen compounds.

Naturally, there are still many loopholes—and the opportunities for further work along this line are innumerable, particularly from the point of view of the organic chemist, be he theoretical or synthetical in aim and purpose. All general halogenic reactions should be applicable to these radicals—and, if found to be otherwise, the cause for their anomalous behavior can unquestionably be found in the structure of the radicals themselves. On the other hand, care must be taken not to apply

halogenic reactions in detail to the halogenoids, as the varied nature of the constituent atoms will be found in many cases to exercise a profound influence on the course of the reactions.

ADDENDUM

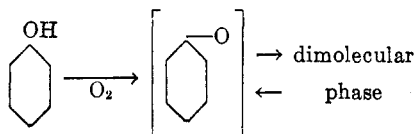
In certain respects *nitrogen tetroxide*, $(\text{NO}_2)_2$, may be thought of as an inorganic radical similar to the halogenoids. Its formation from nitrites, $\text{M} + \text{NO}_2^-$, the existence of compounds like nitroform, $(\text{NO}_2)_3\text{CH}$, nitroxyl chloride, NO_2Cl , etc., seem to bear out such an analogy. The behavior of the tetroxide,



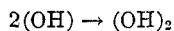
is reminiscent of the behavior of the organic radicals, which dissociate with increasing temperature. Pure nitrogen tetroxide is colorless, but with rising temperature it becomes light yellow, shading gradually into a deep brown color. Decrease in pressure also brings about the same results. These phenomena are accompanied by corresponding changes in molecular weight of the gas so that the existence of $-\text{ON}=\text{O}$ as an unsaturated radical must be assumed. In solution the dissociation of $(\text{NO}_2)_2$ also increases directly with increasing dilution, temperature, etc.

As an inorganic radical, however, it differs markedly from the halogenoids. The latter are colorless in the dimeric form and evidence of their existence in the unsaturated monomeric state is, as yet, lacking. Undoubtedly, these substances do, at the moment of formation, exist as true free (neutral or electrically charged) radicals and it is entirely probable that experimental conditions may yet be ascertained which will give indication of their existence as such to a large extent. It is a curious fact, however, that it is not dissociation, but polymerization which invokes a color change in the case of the halogenoids—exactly the opposite of the behavior of the free *organic* radicals, where appearance of color is supposed to be a sign of dissociation. The fact that the halogenoids do tend to polymerize so readily may be considered as a proof that even the dimeric structure is an unsaturated one. Comparison of inorganic radicals with the so-called “free” organic radicals is not as farfetched as it would

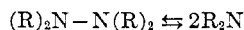
seem at first glance. As in the case of the latter, *tautomerism*⁴ must also be assumed to explain certain chemical reactions. The products formed by oxidation of phenols, the aroxyis (47),



which dissociate into a mono-molecular form, are formally related to the hydroxyl OH radical. Indeed, the latter has been obtained in the dimolecular form as hydrogen peroxide, by electrolysis of certain hydroxides, M^+OH^- (48).



The very fact that the tetra-aryl hydrazines (Wieland) dissociate to yield divalent nitrogen radicals,



would make the momentary existence of the formally analogous NH_2 group as an individual seem within the realm of plausibility. The preparation of hydrazine by interaction of chloramine (formally the interhalogen-halogenoid $\text{Cl}\cdot\text{NH}_2$) and ammonia might easily be construed as a condensation of two such free amine radicals. From an entirely similar point of view, mono-valent sulfur radicals, $-\text{SH}$ or $-\text{SR}$, should be capable of existence.

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⁴ See examples given on pages 347, 350, 351 and 352.

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