

# HYDRAZOIC ACID AND ITS INORGANIC DERIVATIVES<sup>1</sup>

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## I. INTRODUCTION<sup>2</sup>

From whatever point of view hydrazoic acid be considered, it is bound to excite and stimulate curiosity, if not wonderment and amazement. It

<sup>1</sup> This article is respectfully dedicated to Professor Arthur Wesley Browne, in appreciation of his intensive interest and his extensive investigations in the field of hydrazoic acid and its derivatives and on the occasion of completion by him of twenty-five years of service as Full Professor of Inorganic Chemistry at Cornell University.

<sup>2</sup> It is to be regretted that so much confusion exists in the literature with respect to the nomenclature of  $\text{HN}_3$  and its derivatives. Curtius used the terms "azoimide" and "Stickstoffwasserstoffsäure" (German) for the parent substance. For the organic derivatives the term "azide" and the prefix "azido-" have come into general

contains more nitrogen than any other substance with the exception of nitrogen itself. The ratio of one hydrogen to three nitrogen atoms seems to upset elementary definitions of valence. Its structure has been the subject of considerable discussion and investigation. It has been termed an *ammononitric acid* and a *hydrazonitrous acid* in its relationship to such "parent solvents" as ammonia and hydrazine. As a hydronitrogen it is one of that unique class of hydrogen and nitrogen compounds comparable with the hydrocarbons. Some of its derivatives have received considerable attention because of their explosive character. In some of its reactions it decomposes in such a way that the transitory existence of the free imine ( $\text{>NH}$ ) radical must be assumed. The azide radical has been shown to be a "halogenoid," that is, a halogen-like group, and attempts have been made to prepare free "azine," or "nitride,"  $(\text{N}_3)_2$ . It is no wonder, therefore, that the literature dealing with hydrazoic acid and its derivatives has grown so extensively and that a real need exists for its compilation. Every attempt has been made to include in this article all important and pertinent facts concerning the chemistry of hydrazoic acid and its inorganic derivatives in as brief and concise a manner as possible.

## II. SYNTHESIS OF HYDRAZOIC ACID AND AZIDES

The first compound containing the  $\text{N}_3$  group was prepared by Peter Griess (113), who obtained phenylazide (diazobenzolimide) by treatment of benzenediazonium perbromide with aqueous ammonia. Emil Fischer (97) also effected the preparation of phenylazide in 1878 by the action of potassium hydroxide or alcoholic hydrogen chloride upon phenylnitrosohydrazine. The very nature of the azide radical with its three nitrogen atoms seemed to preclude the possibility of isolating the parent compound. Its preparation was nevertheless accomplished in 1890 by Theodore Curtius (61, 62, 65) who, by treatment of benzoylazomide (benzoylazide) with sodium hydroxide or sodium ethylate, obtained the sodium salt (Stickstoffnatrium) and from the latter prepared the acid in aqueous solution. Curtius and Radenhausen (71) also prepared pure hydrogen azide, but aban-

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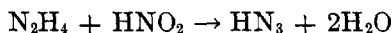
use, although the prefix "triazido-" was also employed by some of the earlier investigators. The latter connotation could not but be ambiguous and soon fell into disfavor. Many American investigators, particularly those interested in studying the inorganic derivatives and reactions of  $\text{HN}_3$ , employ the terms "hydronitric acid" and "trinitrides." English and foreign chemists favor the expressions "hydrazoic acid" and "azides" and these terms are used preferentially by Chemical Abstracts (private communication from Dr. E. J. Crane). The author, in spite of his preference for the names hydronitric acid and trinitrides, has deemed it advisable for the sake of uniformity to use the terminology adopted by the Editorial Board of Chemical Abstracts.

doned its investigation when the latter was seriously injured as the result of an explosion. It was not until 1907 that Dennis and Isham (84) isolated it in larger quantities and studied some of its physical and chemical properties.

All methods which have thus far been employed for the synthesis of hydrazoic acid and the azide group may be divided into five general classes. (These do not include the preparation of azides where the free acid, or one of its derivatives, is used.) (1) Direct synthesis. (2) Action of inorganic and organic derivatives of nitrous acid, upon hydrazine and its compounds involving diazotization of hydrazine or the "hydrazinolysis of nitrous acid." (3) Oxidation of hydrazine. (4) Interaction of certain amides, such as sodium amide, with nitrous oxide or a nitrate. (5) Oxidation of triazenes and the decomposition of higher hydronitrogens.

(1) *Direct synthesis* (160, 249). It has been shown that activated nitrogen reacts with cesium, rubidium, potassium, and sodium to form azides. Except in the case of sodium, nitride formation also takes place presumably by decomposition of the azide which is regarded as the primary product. It is interesting in this connection to note that many years before this work was reported Wendt and Grubb (273a) regarded as highly probable the existence of an ozone analog of nitrogen in the activated gas. They did not mention its possible identity with the free azide radical.

(2) *Interaction of hydrazine and nitrous acid*. This method may be represented in its simplest aspects by the general equation:



Thus, Thiele (229) found that sodium azide could be obtained in 70 per cent yield by interaction of hydrazine sulfate or hydrate with ethyl nitrite in the presence of sodium hydroxide or sodium ethylate (see also 255). Stolle (215, 216) and others (166, 255) improved the yield by using amyl nitrite in place of ethyl nitrite. Angeli (2) attempted to diazotize both amino groups of hydrazine by allowing silver nitrite to react with hydrazine sulfate, but obtained instead silver azide. Hodgkinson (135) subsequently improved this method for the direct preparation of silver azide. If solutions containing hydrazine sulfate, sodium nitrite, and an excess of sodium hydroxide are refluxed, sodium azide is formed (229). Hydrazine hydrate and sodium nitrite, when heated together in a closed tube at 150°C., give some sodium azide (229). Hydrazine sulfate and potassium nitrite (86, 134) react to give detectable quantities of hydrazoic acid. Nitrosyl chloride (238) reacts with phenylhydrazine to give phenylazide. Nitrogen trichloride (224) and the "red gases" (63) obtained by the action of nitric acid upon arsenic trioxide both react with hydrazine to give hydrazoic acid.

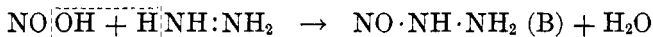
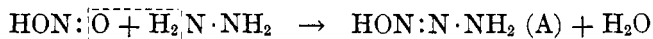
The now classical experiments of Curtius (61), which led to the isolation

of hydrazoic acid, involved the diazotization of benzoylhydrazine to give the corresponding azide. This same method was subsequently employed to synthesize numerous acyl azides ( $RCON_3$ ). The reaction of nitrosamines (210) with hydrazine hydrate, or with a hydrazine salt in the presence of sodium hydroxide or sodium carbonate, yields sodium azide. Certain monosubstituted hydrazines (97) react with nitrous acid to give the intermediate nitrosohydrazines, which in acid or alkaline solution immediately yield the azides.

Whereas Franklin (99, 100, 102, 103) and Turrentine (242) present a great deal of experimental evidence to the effect that hydrazoic acid may be looked upon as an ammonitric acid, Browne (53) concludes that "hydrazoic acid must (also) be in some way structurally related to nitrous acid . . . since . . . all of the above methods involve (the action upon nitrous acid) of some compound or derivative of hydrazine . . . a substance shown . . . to be a dissociating solvent comparable in scope and character with water and ammonia and like these substances constituting the basis of a system of acids, bases, and salts. Hydrazoic acid may therefore be looked upon as *hydrizonitrous acid* . . . experimentally obtainable by hydrazinolysis of nitrous acid and derivable by dehydrazination of normal hydrizonitrous acid."



The partial solvolytic action (5) of hydrazine upon nitrous acid leads theoretically to at least two mixed *aquohydrizonitrous acids*, at least one of which is known in the form of its organic derivatives.

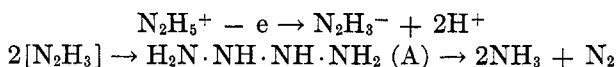


Although no derivatives of 1-hydroxytriazene (A) are known, those of nitrosohydrazine (B) form a large and interesting group. These substances break down in acid and in alkaline solution to yield the azides, whereas thermal decomposition in inert solvents results in the formation of the corresponding amines and nitrous oxide.

The reactions outlined above have been interpreted by Browne as involving initial solvolytic action of hydrazine or one of its derivatives upon nitrous acid or nitrites to give intermediate products which may formally be regarded as derivatives of the hydrazine system and which subsequently undergo desolvation to give hydrazoic acid or azides.

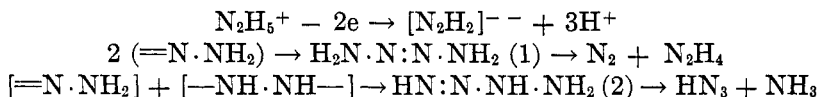
(3) *Oxidation of hydrazine.* Depending upon the oxidizing agent

(delectronator)<sup>3</sup> employed, a variety of products may be obtained from the oxidation of hydrazine (142, 47) in acid solution. Thus, monodelectronators, those active oxidizing agents which accept only one electron per active unit, act upon hydrazine to yield only nitrogen and ammonia. Here the action may be regarded as involving initial formation of the hydrazide radical, two of which subsequently unite to form the intermediate tetrazane (A), which in turn undergoes decomposition to give nitrogen and ammonia.



Such oxidizing agents as the ferric, cupric, nickelic, cobaltic (51), manganic (74), and ceric (15) ions belong to this class.

Didelectronators may bring about complete oxidation of hydrazine to give nitrogen and water, but where such action is incomplete hydrazoic acid is formed along with ammonia. Here the action is believed to involve initial formation of  $[\text{N}_2\text{H}_2]$  radicals to which may be assigned either the symmetrical  $[-\text{NH}\cdot\text{NH}-]$  structure, or the unsymmetrical  $[=\text{N}\cdot\text{NH}_2]$  form. In any case condensation may conceivably take place with formation of either (1) tetrazene, which always decomposes to give nitrogen, or (2) isotetrazene (buzylene), whose organic derivatives decompose to give azides and amines.



Thus, such didelectronators (oxidizing agents which accept two electrons per active unit) as the peroxide (35, 47, 50, 155), persulfate (47, 50), perchlorate, bromate (49), iodate (49, 123), arsenate, antimonate, selenate, and molybdate (51) ions oxidize hydrazine under suitable conditions to give water, nitrogen, hydrazoic acid, and ammonia. The reaction of hydrogen peroxide with hydrazine sulfate has been employed by Browne (35) and by Martin (155) for the preparation of very pure hydrazoic acid.

Kirk and Browne (142) have pointed out that complex delectronators such as potassium permanganate (50, 74) and ammonium metavanadate (48), which undergo reduction in two or more stages, give products indicative of both types of reactions. These oxidants give small quantities of hydrazoic acid when allowed to react with hydrazine in acid solution.

<sup>3</sup> The term "delectronator" has been proposed by Kirk and Browne (142) to cover all oxidizing agents where the action is due to the removal of electrons. Oxidation, augmentation, and delectronation are synonymous terms.

(4) *Ammonolysis of nitrous oxide and sodium nitrate.* Fused sodium amide reacts with nitrous oxide in accordance with the equation:



This reaction was first discovered by Wislicenus (257), but was modified and improved by Dennis and Browne (80) and others (156, 157, 223, 138). It has become the basis of the modern method for the manufacture of sodium azide. This reaction is of particular interest since it represents a clear-cut case of ammonolysis and is further evidence of the fact that "all methods that have hitherto been used for . . . hydrazoic acid may be considered to involve initial solvolysis of an oxyacid of nitrogen or one of its derivatives with potential formation of a solvo-acid belonging to the ammonia system, to the hydrazine system, or to both, and subsequent desolvation of this acid" (53). The substitution of the imide group for its aquo-equivalent, that is, oxygen, in nitrous oxide is strictly ammonolytic in nature. Related to this synthesis is the interesting fact that nitrous oxide, when passed into a liquid ammonia solution of potassium, yields potassium azide (139).

Stolle (217) has extended this method to other amide derivatives and has obtained sodium azide by treating disodium cyanamide with nitrous oxide at temperatures between 300–400°C.

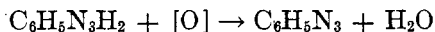
That hydrazoic acid is indeed an ammononitric acid, the ammonia analog of nitric acid, is shown by the fact that sodium nitrate and sodium amide react not only in liquid ammonia (103), but also in the fused state (53), to give sodium azide in accordance with the equation:



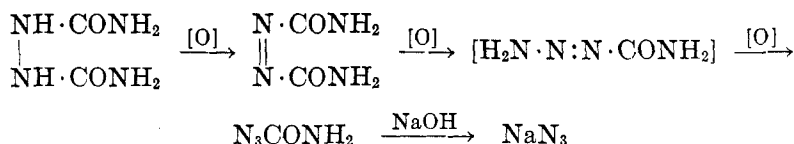
An 80 per cent yield of lead azide can be obtained by the action of an excess of potassium amide upon lead nitrate in liquid ammonia (100). These reactions have been interpreted as involving the conversion of an aquonitrate into an ammononitrate.

(5) *Oxidation of triazenes and the decomposition of higher hydronitrogens* (6). A large number of apparently unrelated reactions may be grouped together under this heading. Most of these are distinctly organic in nature.

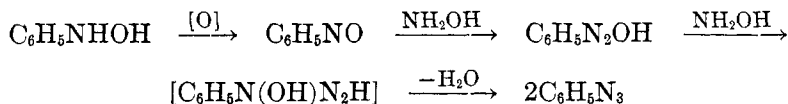
Thus, phenyltriazene in ethereal solution is oxidized to phenylazide by means of sodium hypobromite (88).



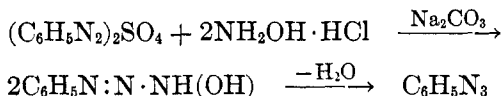
Darapsky (75) obtained sodium azide by oxidation of hydrazidicarbamide with sodium hypochlorite. This method presumably involves the formation of an intermediate triazene derivative.



Bamberger (10) obtained phenylazide by treatment of  $\beta$ -phenylhydroxylamine with hydroxylamine in the presence of oxygen. Here again the formation of a hydroxytriazene derivative is assumed, which then breaks down to give the azide and water.



Hydroxylamine salts and diazonium salts (97) react in the presence of sodium carbonate to give the respective azides by way of the intermediate hydroxytriazenes.

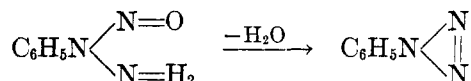


Diazo compounds and hydrazine or hydrazine derivatives react to give the intermediate isotetrazenes (buzylenes) which, under appropriate conditions, break down as indicated by the equation (64):



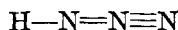
### III. STRUCTURE OF HYDROGEN AZIDE AND THE AZIDES

The structure of hydrazoic acid and its various derivatives has been the subject of considerable discussion and dispute ever since the discovery of the first representative of this class of compounds by Griess (113) in 1866. Emil Fischer (97) prepared phenylazide by the action of dilute alkalis upon the corresponding nitrosohydrazine

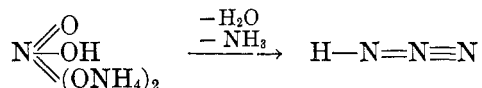


and on the basis of this reaction promulgated the so-called cyclic or ring structure for the azide group. This structure was subsequently accepted by Curtius (61), the discoverer of the parent hydronitrogen.

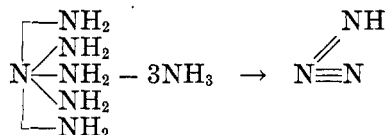
More detailed investigation of the properties of hydrazoic acid and its derivatives soon caused a decided shift in opinion to the chain structure.



Turrentine (242) was one of the first to advocate such a chain structure on the basis of similarity between nitric and hydrazoic acids. If nitric acid be assumed to possess a pentavalent nitrogen atom, it was regarded as highly probable that one of the nitrogens in hydrazoic acid must also be pentavalent. Mendelejeff (158) considered hydrazoic acid as derived from a secondary ammonium orthonitrate, and here again desolvation with loss of water and ammonia



could lead only to a chain structure. From a consideration of hydrazoic acid as a desolvation product of an ammonioorthonitric acid, Franklin (99, 100, 102) also came to the same conclusion.



Thiele (231, 1), reasoning from the action of the Grignard reagent upon hydrazoic acid and its organic compounds, by which diazoamino compounds are formed, also decided in favor of the straight chain formula. It was argued that the formation of such open chains from ring structures could take place only if the ring broke, not at the double link, but at a single link. Sidgwick (200) has pointed out, however, that this piece of evidence is hardly conclusive, since the double link between nitrogen atoms is very strong. Any rupture in a ring containing two doubly linked nitrogen atoms most certainly would not occur at that point.

Langmuir (146) was the first to point out that the cyanate and azide groups are isosteric and that many cyanates and azides possess similar physical and chemical properties. Both potassium azide and potassium cyanate crystallize in the tetragonal system and have approximately the same axial ratios.

For  $\text{KNCO}$ ,  $a:c = 1:0.5766$

For  $\text{KN}_3$ ,  $a:c = 1:0.5798$

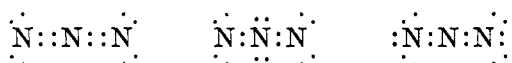
Certainly one might expect isomorphism of cyanates and azides. One might also expect both ions to possess similar structures. Langmuir discards the ring structure in favor of a chain structure which he represents as  $(\text{N}=\text{N}=\text{N})^-$  for the azide ion.



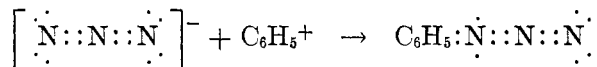
The physical properties of aqueous solutions of the isosteric pairs  $\text{KN}_3$ - $\text{KNCO}$  and  $\text{NaN}_3$ - $\text{NaNCO}$  have been determined by Cranston and Livingstone (58). The values for the refractive indices, solubilities, and equivalent conductivities were found to be so nearly alike that they concluded that the structures of the cyanate and azide ions must also be similar. Günther and Perschke (117, 179) contend, however, that it is hardly permissible to draw conclusions concerning the configuration of ions on the basis of similarity in the physical properties of their solutions. They found that the viscosities, refractive indices, and conductivities of aqueous solutions of sodium azide, thiocyanate, and nitrite were also very much alike, even though, according to them, the structures of these ions are presumably very different.

More recently a general comparison of the crystallographic and physical properties of potassium azide and potassium cyanate also led Erlenmeyer and Leo (94) to assume similarity in structure of the two radicals.

Hendricks and Pauling (130) studied the crystal structure of sodium and potassium azides by x-ray methods and definitely decided in favor of a collinear structure for the azide ion. The positions of the azide ions in the crystal lattices are such that they require centers of symmetry. They therefore discard the idea of a double and a triple link, as promulgated by Turrentine (242), and assign to the azide ion one of the following three electronic structures.

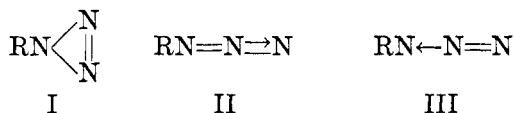


It is now generally conceded that the azide ion possesses a chain structure, but some question still existed until very recently as to those organic compounds in which the azide group is attached by a covalent bond to an organic radical. In a discussion of this problem from the standpoint of the influence of structure upon the dipole moment, Sidgwick (200) says, "We should expect the  $\text{N}_3$  group to have the same structure in the ion as it has in the covalent form. It is to be noticed, however, that the symmetry and non-polarity of the ion upon which its stability may be supposed to depend, cannot be preserved when it becomes covalent; an imaginary phenyl cation can attach itself only to one of the terminal nitrogens, since the central nitrogen has no unshared electrons



and it will then give, if the open chain is maintained, the molecule  $\text{RN}=\text{N}=\text{N}$  in which the balance is destroyed by the disappearance of one of the

two coördination moments." Three possible structures for organic azides are given by Sidgwick.



Of these I should have a small dipole moment (198, 220) owing to its symmetry, whereas II and III, since they both contain coördinate links, should be characterized by relatively large moments. "A large moment," Sidgwick (200) further states, "would hardly be compatible with the volatility of the azides." The organic azides have boiling points which lie very close to those of the corresponding bromides. Measurement of the dipole moments of a series of organic azides shows that the azide radical has a moment of about 1.5 D., also that the negative end is in a direction opposite from the point of attachment to the organic radical. Structure III is therefore out of the question since its moment is in the wrong direction, whereas II, containing a coördinate link, is not reconcilable with such a low moment as the  $\text{N}_3$  group has been found to possess. The ring structure (222) seems to be most nearly in agreement with the results of these measurements.

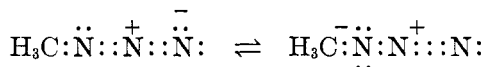
In spite of these considerations Bergman and Schütz (16, 17) feel that the results of dipole measurements are hardly conclusive. Upon analogy with the structure of the mustard oils they are inclined to favor a chain structure even for the organic azides.

The problem has been approached from still another angle by Lindemann (147, 148, 149). Parachor values for a series of organic azides agree very closely with those required for a ring structure. It should be pointed out however that these values differ but slightly from those required for chain structures with coördinate linkages.

Hantzsch (126) investigated the absorption spectra of various azides and as the result of these studies divided all derivatives of hydrazoic acid into two groups. The first group is termed the *ester type*. These are non-electrolytes with discontinuous or selective absorption. They presumably possess an altogether different structure from the *true salts*. The latter class includes the alkali and ammonium azides which are typical electrolytes. Hantzsch is inclined to favor a ring structure especially for the ester type of compound.

However, the most recent work seems again to favor a chain structure for all azides. Sutton (221) studied the crystal structure of cyanuric triazide,  $(\text{CN})_3(\text{N}_3)_3$ , by means of x-rays and assigned to the molecule a

structure in which the azide groups are in the form of short chains attached to the cyanuric ring through the middle nitrogen atom. Brockway and Pauling (34) studied methyl azide,  $\text{CH}_3\text{N}_3$ , by means of the electron diffraction method, and found their results to be compatible only with a state of resonance between two linear structures having the following electronic configurations (see structures II and III suggested by Sidgwick)



Sidgwick, Sutton, and Thomas (201) seem also lately to admit of the possibility of a chain structure for the azide group and state that "dipole moments are compatible only with a ring structure or resonance between the two linear structures." In his recent discussion of this problem before the Faraday Society at Oxford in April, 1934, Sidgwick (199) points out that for such tautomerism to exist and show a reduced moment it is necessary that the time of conversion of one form into the other take place in less than  $10^{-8}$  seconds (the relaxation time for the rotation of the dipole in the field). Sidgwick also discusses the bearing of the data for the heat of formation of the  $\text{N}_3$  group as determined by Roth and Müller (195). These investigators found the heat of formation of the  $\text{N}_3$  group from its atoms to be 210 kg-cal. Now the heats of formation of the various N—N linkages can be calculated and on this basis the expected values for the three structures determined. They are:

I. $2(\text{N—N}) + (\text{N}=\text{N})$	$= (2 \times 37.6) + 95.3$	$= 170.5$
II. $2(\text{N—N})$	$= 2 \times 95.3$	$= 190.6$
III. $(\text{N—N}) + (\text{N}=\text{N})$	$= 35.7 + 208$	$= 245.6$
Observed value		$= 210.5$

The observed value lies about halfway between the two calculated values for the chain structures, but the energies of the two forms as calculated are so different as to make a resonance between them in the Pauling sense impossible—even if the ring structure is definitely excluded by these figures. Sidgwick points out that it is probable that the value assumed for structure III is much too high. By introducing a correction for the  $\text{N}=\text{N}$  linkage, a new value of 181 kg-cal. for structure III is obtained. This would then bring the calculated values for forms II and III very close to each other, thus fulfilling the necessary requisites for such a state of resonance requiring that the energy levels of the two forms be very close to each other. That the actual molecule has a value higher by some 20 kg-cal. might be expected as the result of resonance.

## IV. ANHYDROUS HYDROGEN AZIDE

Pure hydrogen azide is a colorless, extremely explosive liquid, boiling at 37°C. and melting at -80°C. Dennis and Isham (84) recommend the following method of preparation: Sulfuric acid is allowed to react, drop by drop, with solid potassium azide. The hydrogen azide formed is carried over in a stream of carbon dioxide-free air from the distilling flask through several drying columns containing calcium chloride into a receiver surrounded by an ice-salt mixture. To prevent loss of hydrogen azide, absorbing vessels containing absolute methanol are attached to the receiving vessel. The whole apparatus should be placed behind a heavy screen of 2-inch pine planking, and all manipulations of stopcocks etc. should be effected from the outside. Double windows of half-inch plate glass, suitably placed in such a screen, can be used for purposes of observation. Too much attention can not be called to the extremely treacherous nature of hydrogen azide.

The physical properties of hydrogen azide are none too well defined. Dennis and Isham (84) state that the pure compound is probably heavier than water, exhibits high vapor tension and possesses the normal vapor density twenty-five degrees above its boiling point. Hydrogen azide is soluble in water, the alcohols, and ether. It may be extracted from aqueous solution by ether, as the distribution ratio of hydrogen azide between these two solvents (water: ether) is approximately 1:7.

Like the anhydrous hydrogen halides, so liquid hydrogen azide has been found to act as a solvent for many substances. McKinney (153) investigated qualitatively the solubilities of several hundred of the more common inorganic compounds in liquid hydrogen azide. His method consisted of condensing hydrogen azide upon a small sample of the dry salt contained in a specially designed solubility cell immersed in ice water. The salt was permitted to remain in contact with the liquid for at least thirty minutes, during which time it was observed closely for evidences of physical and chemical action. The solution was then filtered and siphoned over into an electrolytic cell fitted with two platinum electrodes. The filtered liquid was subjected to electrolysis for several minutes. If nothing untoward had happened up to this point the solvent was removed by evaporation and the residual material tested qualitatively. In about ten per cent of the experiments violent explosions occurred during electrolysis of the filtered solutions.

The results of this investigation by McKinney may be summarized as follows:

Acetic acid is more or less completely displaced from ammonium, cadmium, chromium, cobalt, mercuric, nickel, and sodium acetates,

resulting in the formation of the corresponding azides and acetic acid. Ammonium acetate swells to about double its original bulk when hydrogen azide is condensed upon it. The possible formation of a solvate containing hydrogen azide of crystallization is suggested. In several instances none of the metal associated with the acetate was found in the filtered liquid, indicating that the azides of cadmium, lead, copper, and manganese are insoluble in hydrogen azide.

A similar solvolytic action is observed in the case of the arsenites. Thus, calcium, cupric, ferric, and potassium arsenites react with hydrogen azide to give solutions from which arsenic is deposited upon electrolysis. Only in the case of the ferric and potassium arsenites were the cations found in the filtered solution.

The following halides were found to be appreciably soluble in hydrogen azide at 0°C.: ammonium bromide, ammonium iodide, bismuth iodide, cobaltous chloride, magnesium chloride, manganous chloride, mercuric chloride, nickelous chloride, potassium chloride, potassium bromide, potassium iodide, sodium bromide, and sodium iodide. Mercuric chloride is very soluble in hydrogen azide and yields cathodic mercury upon electrolysis. Iodine dissolves in hydrogen azide to give a reddish solution which appears to conduct the electric current fairly well.

The nitrates are in most instances only slightly soluble. Manganous, cobaltous, and nickelous nitrates are moderately soluble. Electrolysis of a solution of bismuth nitrate gave a cathodic deposit of bismuth.

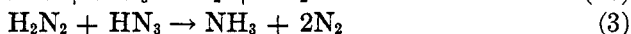
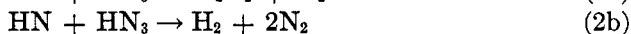
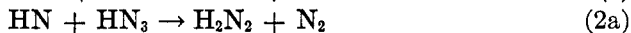
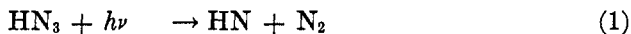
All chromates with the exception of barium chromate were found to react with or dissolve in hydrogen azide. In some instances (lead chromate, mercuric chromate, lithium chromate) a green solution was obtained indicating reduction of chromium to the trivalent state.

Cadmium, zinc, and potassium iodates react with the solvent to liberate free iodine. Sulfates, oxides, carbonates, and sulfides, in general, do not react with or dissolve in hydrogen azide.

Pure hydrogen azide is a poor conductor. However, it has been shown by Browne and Lundell (46) that the addition of potassium azide results in the formation of a conducting solution. These investigators electrolyzed solutions of potassium azide in hydrogen azide and found the ratio of hydrogen to nitrogen evolved to be approximately 1:3, but somewhat lower under certain conditions. Ammonia was usually found to be present in the residual electrolyte, but no hydrazine. The extreme explosiveness of the residual liquid after electrolysis was attributed to the possible formation of azine (nitrine, nitrazone,  $(N_3)_2$ ).

Ultra-violet light brings about decomposition of gaseous hydrogen azide with formation of nitrogen, hydrogen, and ammonium azide. Light absorption of hydrogen azide sets in at 2200 A. U. and decomposition

certainly takes place at wave-lengths below 2400 A. U. The mechanism offered tentatively by Beckman and Dickinson (11, 12) is given by the following equations.



At low pressures (4 cm.) hydrogen azide decomposes with measurable rapidity at 290°C. (181). Under these conditions about 9 to 11 per cent of  $\text{HN}_3$  is decomposed in 25 minutes. A white solid, presumably ammonium azide, is formed along with gases non-condensable in liquid air. Thermal decomposition appears to be influenced catalytically by the walls of the Pyrex glass reaction chamber.

The molecular heat of decomposition of pure liquid hydrogen azide into nitrogen and hydrogen at constant pressure has been calculated by Roth and Müller (195) from the heat of combustion of the phenyl azide and ethyl azidoacetate. By subtraction of the heat values for specific groups associated with hydrogen azide in both of these molecules the values 64.3 kg-cal. and 70.6 kg-cal. are obtained. An average value of 67 kg-cal. per mole is assigned as the heat of decomposition of liquid hydrogen azide into nitrogen and hydrogen at constant pressure.

## V. HYDRAZOIC ACID (AQUEOUS HYDROGEN AZIDE)

### A. Preparation

Hydrazoic acid is obtained in solutions of varying concentrations by treatment of aqueous solutions of potassium or sodium azides with dilute sulfuric acid. Because of the high volatility of hydrogen azide, it is advisable to bring the solution of the azide to the boiling point and then add sulfuric acid drop by drop. If this is not done a very concentrated solution of hydrazoic acid comes over at first, which because of its explosibility is apt to be hazardous.

The interaction of sodium azide with aqueous solutions of fluosilicic (138) or oxalic acids (93, 138) has been suggested for the preparation of hydrazoic acid. Pure hydrazoic acid has also been obtained by interaction of barium azide with dilute sulfuric acid (138).

The methods outlined under the oxidation of hydrazine in acid solution result in the formation of hydrazoic acid as an aqueous distillate. Thus, oxidation of hydrazine in the presence of sulfuric acid by hydrogen peroxide gives pure hydrazoic acid (35, 155).

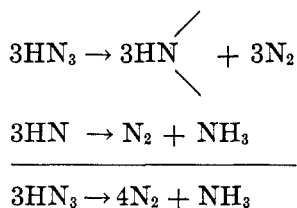
If aqueous solutions of hydrazoic acid are distilled, some hydrogen azide

comes over first in the gaseous form; this is followed at temperatures between 90–100°C. by a very concentrated aqueous distillate, the first fractions of which approximate a 27 per cent solution of  $\text{HN}_3$ . Continued distillation finally causes an equilibrium to set in, after which a very dilute solution is obtained to the last drop. These findings would seem to indicate the existence of a constant-boiling mixture of hydrogen azide and water, but no experimental work to verify this supposition has been reported.

### B. General properties

Pure aqueous solutions of hydrazoic acid may be kept indefinitely. The solutions are characterized by an intense, penetrating odor and the vapor when inhaled even in small concentrations induces decidedly unpleasant physiological effects. Headaches and dizziness are produced, with a clogging of the mucous membrane, giving all the effects of a severe head cold. The acid and its salts act as protoplasmic poisons. Subcutaneous injection of small doses of the sodium salt (0.03 g.) into mammals produces spasms and symptoms of heart and lung paralysis (150). In the case of frogs, respiration is arrested, followed by convulsions (20, 21). Growth of plants is inhibited and the germination of seedlings is prevented (197). Several cases of poisoning by hydrazoic acid have been reported (143, 211). It has been suggested that sodium azide be used as an agent for poisoning harmful animals (251).

Platinum black, platinum sponge, and platinum foil (168) decompose solutions of hydrazoic acid with the formation of ammonia and nitrogen. Occluded hydrogen or oxygen accelerate this decomposition. The catalytic decomposition of hydrazoic acid presumably involves the intermediate formation of free "imino" radicals which decompose further to give more nitrogen and ammonia.



Curiously enough, however, colloidal platinum, which might be expected to produce the greatest effect, does not decompose hydrazoic acid under any conditions. All salts of hydrazoic acid (with the exception of  $\text{Fe}(\text{N}_3)_3$ ), as well as the acid itself, inhibit the catalytic decomposition of hydrogen peroxide by colloidal platinum (171, 172, 174). Colloidal palladium does

not affect sodium azide solutions, but in the presence of hydrogen brings about reduction with evolution of nitrogen and ammonia (254).

Hydrazoic acid is decomposed by ultra-violet light (111) to give a variety of products depending upon conditions. In dilute acid solutions hydroxylamine and nitrogen are the main products, along with some ammonia. In alkaline solutions hydrazine is also formed, along with ammonia and hydroxylamine. Primary decomposition to yield "imine" radicals again seems highly probable. (See pp. 187 and 194.)

Hydrazoic acid is a monobasic acid and in many of its properties and reactions shows a striking similarity with the halogen hydracids. Birkenbach and Kellermann (34) have shown that the azide radical lies between chlorine and bromine in the relative order of reactivity of various halogen and halogenoid groups. For that reason hydrazoic acid has been termed a "halogenoid" (248) hydracid. When added to solutions of soluble silver, lead, and mercurous salts the corresponding azides are precipitated. Many of its salts, such as those of aluminum, chromium, and ferric iron, are appreciably hydrolyzed in aqueous solution. When solutions of these azides are heated the corresponding hydroxides are precipitated, indicating that hydrazoic acid is a very weak acid indeed.

These findings have also been checked by conductivity measurements. The results tabulated below, taken from determinations by West (252), indicate that at 25°C. hydrazoic acid is somewhat stronger than acetic acid (71). ( $V$  = dilution in liters per mole,  $\mu$  = molecular conductivity,  $K$  = dissociation constant.)

$V$	$\mu$	$K \times 10^{-5}$
10	5.38	1.98
100	15.98	1.80
1000	45.97	1.66

West determined the conductance of sodium azide at various dilutions and extrapolated these results to infinite dilution obtaining a  $\Lambda_{\infty}$  value for  $\text{NaN}_3 = 109$ . To determine the dissociation constant  $K$  for hydrazoic acid it was necessary to have the limiting value for  $\text{HN}_3$ , which was calculated on the basis of the equation

$$\Lambda_{\infty \text{HN}_3} = \Lambda_{\infty \text{NaN}_3} + l_{\text{H}^+} - l_{\text{Na}^+} = 109 + 320.5 - 44.5 = 385$$

The value for the dissociation constant,  $K$ , was also determined from the rate of inversion of cane sugar, as induced by hydrazoic acid, and was found to be  $1.86 \times 10^{-5}$ . No experimental details are given by West.

Very few other physical constants for hydrazoic acid have been determined. Berthelot and Matignon (18) calculated the heat of formation from the heat of combustion of the ammonium salt.





Roth and Müller (195) recalculated the data and introduced certain corrections giving a value for the heat of formation of hydrazoic acid of  $-53.4$  kg-cal. These figures are quite in accord with the extreme explosiveness of the substance. The heat of solution at  $11^{\circ}\text{C}$ . was found to be  $-7.08$  kg-cal. The heat of neutralization by barium hydroxide was found to be  $10.0$  kg-cal.; by ammonia,  $8.2$  kg-cal. This latter figure agrees well with an independent observation by Bach (9), who obtained the value  $8.3$  kg-cal.

*C. Electrolysis of solutions of hydrazoic acid and its compounds*

Many attempts have been made to discharge the azide ion directly by electrolysis, both in aqueous and non-aqueous solutions (183). While the presence of free  $(\text{N}_3)_2$  as a product of electrolytic oxidation has never been demonstrated conclusively, it is very probable that the triatomic  $\text{N}_3$  group (245) is the primary electrolytic product. Its existence is only transient, since it breaks down rapidly to give ordinary nitrogen. In all cases electrolysis of aqueous solutions of sodium azide (32, 177, 178, 223), ammonium azide (133), and hydrazoic acid (177, 178, 223), using inert electrodes, results in the discharge of cathodic hydrogen and anodic nitrogen. The ratio of the volumes of hydrogen to nitrogen formed is usually about 1:3, as might be expected theoretically. Ammonia and hydrazine are very often found in the residual electrolyte, indicating that partial reduction has also taken place.

Turrentine (240) electrolyzed 3 per cent sodium azide solutions using various metals as anodes and in the case of magnesium, aluminum, zinc, and cadmium obtained corrosion efficiencies exceeding 100 per cent. He accounted for this by assuming that these metals dissolved at a valence lower than usual and were subsequently oxidized. Ammonia was usually found to be present in the residual electrolyte.

Electrolyses of solutions of hydrogen azide in liquid ammonia (43)—solutions prepared by dissolving ammonium azide in liquid ammonia—give varying results, depending upon the electrode materials employed. When smooth platinum electrodes are used the ratio of  $\text{H}_2:\text{N}_2$  averages 1.93:1.00, instead of 1:3 as might be expected if the azide ion only is discharged. It must therefore be assumed that either the discharged azide ion reacts with the solvent to liberate nitrogen and regenerate ammonium azide (43), or that amide ions (from ammonia as solvent) are also discharged when a platinum anode is used. In either case, the ratio of  $\text{H}_2:\text{N}_2$  would then be 3:1. The experimentally determined ratio is a smaller one, indicating that some azide ions are also discharged. When graphite electrodes

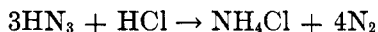
are employed a ratio of  $H_2:N_2$  equal to 1:3 is obtained, indicating that under these conditions only the azide ion is discharged.



When other anodes (44) are used in the electrolysis of ammonium azide in liquid ammonia electrolytic corrosion takes place. With copper anodes, cuprous and cupric azides are obtained. With silver, cadmium, lead, and antimony the normal azides,  $AgN_3$ ,  $CdN_6$ ,  $PbN_6$ , and  $SbN_9$ , are formed without liberation of gas at the anode. Aluminum, iron, and nickel anodes also undergo electrolytic corrosion accompanied by liberation of nitrogen gas and formation of the corresponding ammono-basic azides.

#### D. Reaction with acids

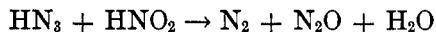
Hydrochloric acid reacts slowly with hydrazoic acid in accordance with the equation (83):



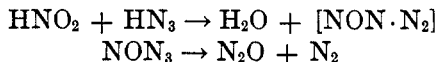
When a mixture of the two acids is boiled some chlorine is also evolved (40). Dry hydrogen azide in contact with dry hydrogen chloride reacts rapidly with formation of solid ammonium chloride (83). It is interesting to note that freshly prepared mixtures (242) of the two acids have the ability to dissolve such noble metals as platinum and gold.

Hydriodic acid (40, 137) reduces hydrazoic acid to give free iodine, nitrogen, and ammonia. Hydrobromic acid is nitridized with liberation of bromine (100).

According to Werner (250) and to Thiele (229), nitrous acid reacts with hydrazoic acid to give nitrogen, nitrous oxide, and water. This reaction has been shown to proceed quantitatively in accordance with the equation (206):



It has been suggested as a method for the determination of nitrites in the presence of nitrates. The reaction is essentially one characteristic of all secondary amines. Thus, it is assumed that the two substances react first to give nitrosyl azide, which then breaks down to give nitrous oxide and nitrogen. The intermediate compound has never been isolated.

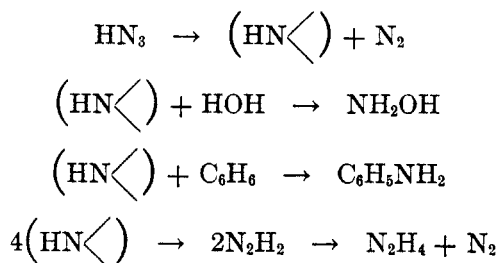


The reaction with sulfuric acid has been the subject of considerable investigation. Hantzsch (125) carried out molecular weight determina-

tions of hydrogen azide in 100 per cent sulfuric acid and concluded that a compound of hydrogen azide with three molecules of sulfuric acid,  $\text{HN}_3 \cdot 3\text{H}_2\text{SO}_4$ , was formed. When hydrogen azide is passed into concentrated sulfuric acid a white crystalline product (83) is obtained which is decomposed by water to give hydrazine sulfate.<sup>4</sup> The original white product has been shown to be hydrazine disulfate (152),  $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{SO}_4$ , a substance first prepared by Sommer (208) in an entirely different fashion. Treatment with water gives the normal sulfate and free sulfuric acid.

The interaction of sulfuric acid with hydrazoic acid has also been investigated by Schmidt (196). If these two substances are heated together in a fairly concentrated solution considerable quantities of hydroxylamine and some ammonia, but no hydrazine, are formed. The presence of the sulfite radical in the residual solution indicated partial reduction of the sulfuric acid. If sulfuric acid be permitted to react with a benzene solution of hydrogen azide at room temperatures, gas evolution takes place until all of the hydrogen azide has disappeared. Large quantities of hydrazine sulfate and some hydroxylamine and aniline sulfate form under these conditions. If this decomposition be allowed to take place at 60°C., the main product is aniline sulfate, with little or no hydrazine sulfate.

Schmidt regards these reactions as being due to the primary formation of the "imino" ( $\text{HN}\langle$ ) residue, which may combine with water to form hydroxylamine (see p. 194) or with benzene to form aniline. Two imino residues may also combine to form diimide, which disproportionates itself to give nitrogen and hydrazine.

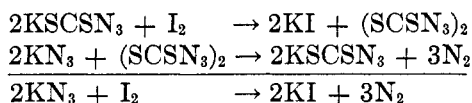


#### *E. Oxidation*

Depending upon conditions a variety of products is obtained by the action of various oxidizing agents upon hydrazoic acid and azides. In

<sup>4</sup> Browne and Wilcoxon (53) have called attention to this fact as a basis for their contention that sulfuric acid may be considered not only a dehydrating agent, but a desolvating agent in general. The reaction with hydrogen azide is an example of "dehydrazination" by virtue of the fact that it may be interpreted as the removal of hydrazine from the hydrazonitrous acid,  $\text{HN}_3$ .

*neutral* solution iodine reacts with azides in the presence of thiosulfates (185), sulfides (185), azidodithiocarbonates (39), and carbon disulfide (39, 95) to liberate nitrogen. Iodine itself does not affect solutions of azides, but the tetrathionate ion formed by the interaction of iodine with the thiosulfate catalyzes the reaction. In the case of the azidodithiocarbonates it has been shown by Browne and Hoel (39) that the formation of azidocarbon disulfide,  $(SCSN_3)_2$  (see p. 196), catalyzes the reaction. The azidodithiocarbonate and the halogenoid radical undergo repeated mutual conversion into each other, constituting what has been termed a reciprocal catalytic pair. The reaction may be represented by the following series of equations:

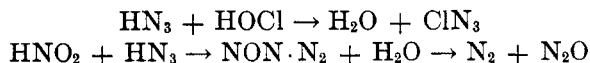


The oxidation of azides by iodine in the presence of carbon disulfide (95) is of course due to the formation of some azidodithiocarbonate, which then catalyzes the reaction as indicated above. These reactions permit the quantitative determination of alkali azides, either gas-volumetrically (185) or by the determination of the excess of standard iodine solution by means of arsenite solutions (95). It should be pointed out in this connection that the action of iodine upon silver azide results in the formation of iodine azide (124).

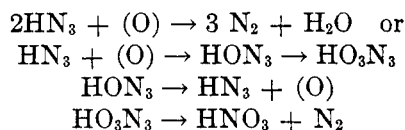
In acid solution such oxidizing agents (194) as ferric salts, iodates, and hydrogen peroxide have no appreciable effect. Potassium chlorate and manganese dioxide react only slightly, while potassium permanganate and persulfates are more vigorous in their action. Complete and rapid reaction is obtained only when the ceric salts (207), hypochlorous acid (184), or nitrous acid (206, 207, 230, 169) are used. Oxidation with complete conversion of the azide group into molecular nitrogen is obtained only in the case of ceric salts, in accordance with the equation:



This reaction is used for the quantitative determination of azides. Either the volume of nitrogen (207) evolved is measured directly, or the excess of standard ceric salt solution determined iodimetrically (155). In the case of hypochlorous acid and of nitrous acid, condensation takes place to give in the first instance chlorazide, and in the second case nitrosylazide (207), which decomposes into nitrogen and nitrous oxide.



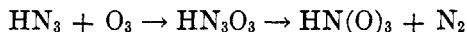
Dennis and Browne (80, 81) investigated potassium permanganate as an oxidizing agent in the hope that it might lead to a quantitative method for the determination of hydrazoic acid. They found the relationships to be very complex and were unable to assign any definite stoichiometric ratios to the amounts of permanganate and hydrazoic acid used. The gases evolved contained oxygen in addition to nitrogen. Nitric acid was also found to be present in the residual solution. Raschig (182a) subsequently studied this reaction and found that the addition of potassium iodide to the decolorized solution resulted in the liberation of iodine. The iodine set free was titrated with standard thiosulfate solution, but curiously enough, such a solution would shortly again turn blue, owing to the liberation of more iodine, requiring the further addition of thiosulfate. This seemed to indicate the presence of some oxidizing agent which acted but slowly upon hydriodic acid, possibly a hypoazidous acid ( $\text{HON}_3$ ), the analog of hypochlorous acid. Such oxyacids had already been discussed by Dennis and Browne (80, 81), who argued that the halogenoid character of the azide radical might lead one to expect at least the transient formation of such substances. Raschig assumed that the hypoazidous acid would decompose to give either oxygen and hydrazoic acid, or undergo autooxidation with formation of some of the chlorite and chlorate analogs of hydrazoic acid,  $\text{HO}_2\text{N}_3$  and  $\text{HO}_3\text{N}_3$ . The oxidation of hydrazoic acid by permanganate may therefore be summarized by the following series of equations:



Such a mechanism would account for the complex character of the reaction.

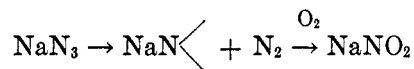
Most oxidizing agents have no effect upon alkaline solutions of azides. However, if a 10 per cent ozone-oxygen mixture is passed into a sodium azide solution, the latter turns yellow, eventually assumes a deep orange color, and finally fades again on long-continued action. Complete ozonation results in the disappearance of all traces of the azide ion. The residual solution becomes more strongly alkaline and possesses powerful oxidizing properties. Acidification immediately destroys any color, whereas increase in alkalinity stabilizes the orange compound formed under these conditions. Gleu and Roell (112) attempted to isolate this colored compound, but were unsuccessful. Heating of the ozonized solutions resulted in the liberation of considerable quantities of oxygen. If any unreacted azide was still present, nitrogen and nitrous oxide were also obtained. The addition of bicarbonate solution resulted in the discharge of the color, but evolution of little oxygen. Nitrite and nitrate were found in such solutions. In many

respects these ozonized solutions behaved as though a salt of a per-acid were present. Gleu and Roell assume the direct addition of ozone to the azide with formation of a compound which might be regarded as one of the hypothetical oxyacids mentioned before. This substance is thought to decompose to give nitrogen and pernitrite, that is, a salt of a *pernitrous* acid to which the formula  $\text{H}-\text{O}-\text{ONO}$  is assigned. In acid solution this substance immediately decomposes with formation of some nitric acid.



It might be mentioned in this connection that the direct addition of ozone is not unexpected, particularly since all structures for the azide ion assume the presence of a double bond. Ozone adds very easily to organic compounds containing a double bond.

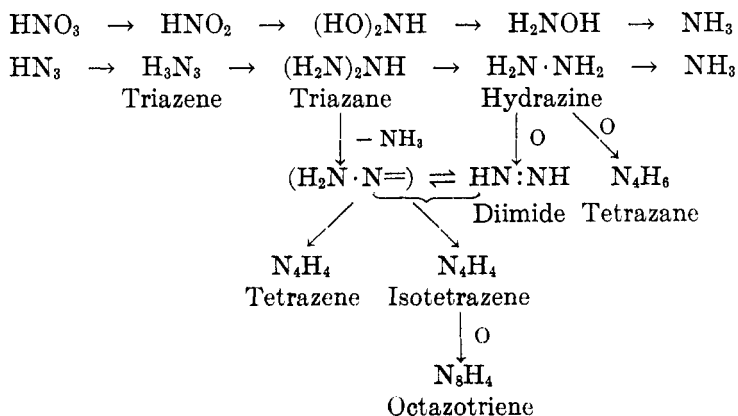
K. A. Hofmann and U. Hofmann (136) studied the action of molecular oxygen on sodium azide-sodium hydroxide melts and observed the formation of sodium nitrite. They assumed the direct addition of oxygen to the imide radical with formation of the nitrite. Gleu and Roell, however, are not inclined



to accept this mechanism for the reaction studied by them, since ozonization of other substances containing the imide grouping does not result in the formation of pernitrous acid.

#### F. Reduction

From a consideration of hydrazoic acid as ammononitric acid it is possible to represent the action of reducing agents diagrammatically (6, 264) as indicated by the following scheme:



Naturally, the reverse series of reactions points to the possible nitridation of other hydronitrogens to hydrazoic acid. Thus, nitridation of hydrazine to hydrazoic acid is quite analogous to the complete oxidation of hydroxylamine to nitric acid.

The mechanism outlined above is interesting in that it brings out the interrelationship of no less than ten different hydronitrogens (6). It also serves to characterize all of these as ammonio compounds from the Franklin (99) point of view.

Investigators are generally agreed that triazene is the first step in the reduction of hydrazoic acid. Certain organic azides, such as phenylazide, may be reduced in ethereal solution by means of stannous chloride and hydrogen chloride to the corresponding monosubstituted triazenes (88). Although triazene itself has never been isolated, indications of its existence in aqueous solution have been obtained. Dimroth and Pfister (89) treated a concentrated solution of potassium azide, containing some ammonium chloride and free ammonia, with zinc-copper powder at  $-10^{\circ}\text{C}$ . and found that immediate reduction took place. Filtration gave a solution which continued to evolve gas for some time in spite of the fact that the reducing agent had been removed. This behavior they assumed was due to the transitory existence of very unstable triazene.

Many reactions which might be expected to give triazene yield only ammonia and nitrogen. In water such reducing agents as stannous chloride-hydrogen chloride (89), hydriodic acid (40), sodium bisulfite (180b), and cuprous oxide (241) give these products. It may therefore be assumed that under the conditions employed in these cases reduction to triazene is followed by decomposition into nitrogen and ammonia.



A few trisubstituted triazenes have been reduced to the corresponding triazanes (234), a group of rather ill-defined substances and derivatives of the hydronitrogen,  $\text{N}_3\text{H}_5$ . From analogy with the corresponding reduction product of nitric acid, dihydroxylimine, which undergoes desolvation through the nitroxyl radical to give the dimer, hyponitrous acid, triazene might be expected to lose ammonia with formation of the  $[\text{=N}\cdot\text{NH}_2]$  radical or its tautomer, diimide. The reverse procedure, that of solvation, has been carried out in the preparation of certain organic derivatives of triazene, which are obtained by condensation of azo compounds with amines (87).

These considerations immediately call to mind the reduction of sodium azide in alkaline solution by metallic aluminum. Raschig (182b) found that one-third of the nitrogen is obtained in the form of ammonia and that variable quantities of hydrazine are obtained along with hydrogen and

nitrogen in approximately equivalent volumes. Raschig assumes that the decomposition of triazene yields nitrogen in an active form which is reduced to diimide, only to reappear again immediately in the form of free nitrogen and hydrogen. That diimide is actually an intermediate reduction product seems quite likely, especially since nitrogen and hydrogen have always been obtained in those cases where attempts have been made to prepare diimide.

However, it seems much more probable that reduction by aluminum yields principally triazane, which may then desolvate to give diimide, the latter decomposing into nitrogen and hydrogen. It should be pointed out that the  $[=N \cdot NH_2]$  radical might conceivably polymerize to give the dimer, tetrazene, which, as has been noted previously, decomposes to give hydrazine and nitrogen. The mechanism outlined here suggests the possibility of preparing these two hydronitrogens as such by the reduction of hydrazoic acid.

Ammonia and hydrazine are the common reduction products of hydrazoic acid. Metals (241, 244) react with hydrazoic acid to give nitrogen, ammonia, and variable quantities of hydrazine. Larger yields of hydrazine are obtained in those cases where reduction results in the separation of an insoluble hydrazine compound. Thus, reduction with zinc and sulfuric acid (56) results in the formation of an insoluble precipitate of the double salt,  $ZnSO_4 \cdot (N_2H_4)_2 \cdot H_2SO_4$ . Electrochemical reduction (241, 244) yields small quantities of these same substances. It is quite probable that the discrepancies in the theoretical ratios of nitrogen to hydrogen formed in the electrolysis of solutions of hydrazoic acid and azides, may be accounted for in this way. Sodium amalgam (56, 68), sodium polysulfide (56), and ferrous hydroxide (56) give mainly ammonia and little hydrazine. Both titanous and chromous chlorides (180) yield exactly 1 mole of ammonia per mole of hydrazoic acid used. Molecular and active hydrogen in the presence of colloidal palladium give ammonia and hydrazine. There is no appreciable reduction under these conditions in alkaline solution (191).

A critical survey of the chemistry of hydrazoic acid certainly indicates that the information concerning its behavior towards reducing agents, while prolific, is nevertheless fragmentary and in need of more extended study and investigation. Especially should the reduction of hydrogen azide in non-aqueous solvents be studied with the possible stabilization of such products as triazene and diimide in mind.

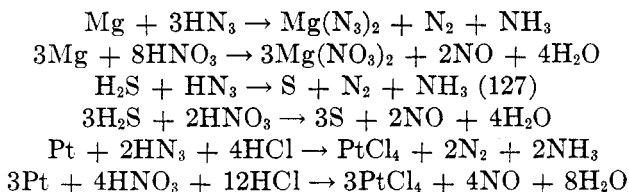
#### G. Behavior as a nitridizing agent

Attention has already been called to the fact that hydrazoic acid may be considered an *ammononitric* acid. It is formally derivable from ortho-

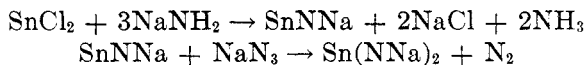


ammononitric acid by a process of deammonation (see p. 176). Potassium azide, an ammononitrate, is obtainable by the ammonolysis of potassium aquonitrate (100). Fused sodium amide reacts with sodium nitrate to give good yields of sodium azide (53). Lead azide can be obtained in 80 per cent yield by the action of an excess of potassium amide upon lead nitrate in liquid ammonia (100). All of these reactions may be considered to involve the conversion of an *aquonitrate*, a derivative of nitric acid, into an *ammononitrate*, a derivative of hydrazoic acid.

Just as nitric acid is characterized by its powerful oxidizing properties, so hydrazoic acid has been shown to be a powerful nitridizing agent. When effecting nitridation (a specific case of deelectronation), it undergoes reduction to give products which are analogous to the reduction products of nitric acid (see p. 190). Reaction with metals rarely gives hydrogen, but yields the corresponding metallic azides along with variable quantities of nitrogen, ammonia, and hydrazine (see p. 192). Turrentine (242) offers a series of parallel reactions to bring out the similarities between hydrazoic and nitric acids as deelectronators.

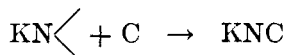
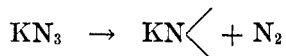


In a recently published article Franklin (100) summarizes various other experimental facts to support the assumption that hydrazoic acid is a powerful oxidizing agent. Ferrous azide is oxidized to ferric azide by warming with an excess of hydrazoic acid. Sulfur is converted to sulfuric acid by hot aqueous hydrazoic acid. Sodium ammonostannite, prepared by dissolving stannous chloride in fused sodium amide, is converted to the ammonostannate by action of sodium azide.

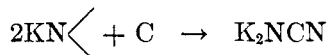


Fused potassium azide, like potassium nitrate, is a very efficient deelectronator. Carbon and potassium azide give potassium cyanide (101); in the presence of an excess of potassium azide the dipotassium salt of cyanamide (101) is obtained. This reaction is considered to involve the nitridation of an ammonocarbonite to an ammonocarbonate. In all of these reactions

the primary formation of the highly reactive  $\text{>NH}$  (or  $\text{>NK}$ ) group may be assumed. Thus



or



Nitridation of methylamine, an ammonioalcohol, to guanidine, an ammonocarbonic acid, is effected by heating methylamine with a liquid ammonia solution of ammonium azide. Numerous other cases involving nitridation of organic compounds are reported by Franklin (105) and by Schmidt (196).

#### H. Detection and determination

The most sensitive qualitative test for hydrazoic acid and azides in general is the blood-red coloration produced upon the addition of a solution of a ferric salt (72). This color, due to the formation of ferric azide, will last indefinitely, provided the ferric salt is present in excess. The test is sensitive to one part in 100,000 (80, 81) and has been made the basis of a colorimetric method for the quantitative determination of azides (145). The ferric azide color is distinguishable from that produced by ferric thiocyanate in two ways (80, 81). Dilute mineral acids cause the color of ferric azide to be discharged readily. The addition of mercuric chloride causes the color of ferric thiocyanate to fade very much more readily than that of the azide. Even insoluble metallic azides respond to the ferric azide test.

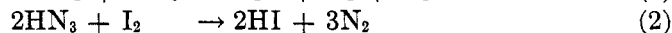
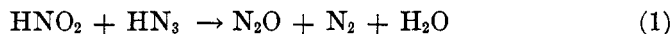
In the absence of other halogen or halogenoid ions, the addition of silver nitrate to a solution of a soluble azide causes precipitation of the extremely explosive silver azide.

A variety of methods has been used and proposed for the quantitative determination of azides. Curtius (72) used the absolute Dumas method for those azides which were not too explosive or too volatile. In their study of the reduction of hydrazoic acid Dennis and Isham (83) investigated the Kjeldahl method, but found that results were invariably low, probably because of loss of hydrogen azide upon contact of the sample with concentrated sulfuric acid. Since only one-third of the azide nitrogen is obtained as ammonia, this method is hardly to be recommended, even if loss of hydrogen azide could be avoided.

Curtius (72) analyzed soluble azides by precipitation as silver azide from

solutions made slightly acid with nitric acid. The precipitate was washed and then dried at 100°C. Results were usually low, owing to the fact, as Dennis (83) pointed out later, that silver azide is appreciably soluble in nitric acid. However, silver azide can be precipitated quantitatively from neutral solutions, or from solutions containing free acetic acid (83). Owing to the extremely treacherous nature of silver azide, Dennis and coworkers (78, 79, 82) converted the silver azide to silver nitrate by the action of nitric acid and then precipitated the silver in solution as silver chloride (31).

These difficult and hazardous methods have been displaced by simpler and more practical ones, involving either (1) the interaction of nitrous acid with hydrazoic acid, (2) the oxidation of azides by iodine in the presence of certain catalysts, or (3) oxidation by ceric salts.



In carrying out the analysis of azides according to equation 1, the sodium nitrite and the azide are allowed to react in a solution made acid with dilute sulfuric acid and the resulting gases are collected and measured (206, 207, 229, 250). Since nitrous oxide is appreciably soluble in water, results are apt to be low. A recently published method makes use of this same reaction, with the modification that the slightly acid solution of the azide is titrated with standard nitrite solution (187). Ferric chloride is used as the indicator and the end point is shown by a change from the deep red color of ferric azide to yellow.

One of the most useful gas-volumetric methods is based upon the oxidation of azides by iodine solutions in the presence of sulfides (185), thiosulfates (185), azidodithiocarbonates (39), or carbon disulfide (95). This method does not give accurate results when very dilute solutions are to be analyzed. However the procedure is very simple, involving only the addition of one of the above substances to a mixture of a potassium iodide-iodine solution and the azide to be analyzed under such conditions that the nitrogen gas formed may be collected and measured. If a standard iodine solution is used, the excess may also be determined by titration with standard sodium arsenite (119, 120).

Ceric salts also oxidize the azide nitrogen quantitatively to molecular nitrogen. The nitrogen gas may be collected and measured (57, 207), or the excess standard ceric salt solution may be determined, for instance, by the addition of potassium iodide and subsequent titration of the liberated iodine with standard thiosulfate using starch as indicator (155).

The acid character of hydrazoic acid has also been made the basis of

several analytical methods. Curtius (72) decomposed various inorganic azides with dilute sulfuric acid, collected the aqueous distillate of hydrazoic acid, and titrated the latter with a standard solution of potassium hydroxide using phenolphthalein as an indicator. West (252) varied this procedure by decomposing the salt with an excess of decinormal sulfuric acid, boiling off the hydrogen azide, and titrating the excess of sulfuric acid with standard alkali. Naturally, the hydrazoic acid distillate may be caught in standard alkali and the excess of the latter determined by titration with standard acid (57, 31).

#### VI. AZIDODITHIOCARBONIC ACID AND AZIDOCARBONDISULFIDE

Sommer (206) was the first to point out that, regardless of which structural formula is assigned to hydrazoic acid, the presence of the imide grouping should give to it properties characteristic of the secondary amines. Thus, hydrazoic acid and its salts (60) react with carbon disulfide to give azidodithiocarbonic acid and azidodithiocarbonates.



The acid and its salts are of particular interest since their oxidation leads to the formation of the free halogenoid (248) radical, azidocarbonbisulfide,  $(\text{SCSN}_3)_2$ , one of a group of inorganic radicals possessing halogen-like characteristics. Most of our knowledge concerning azidodithiocarbonic acid and its derivatives is the result of investigations by A. W. Browne and his coworkers.

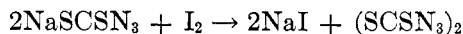
*Azidodithiocarbonic acid* may be prepared either by direct interaction of hydrazoic acid with carbon disulfide (170), or, better, by treatment of a concentrated solution of sodium azidodithiocarbonate with concentrated hydrochloric acid (205). In the latter case the free acid is obtained as a white crystalline solid, fairly soluble in water, but more soluble in the common organic solvents. It has been found to be a fairly strong acid in aqueous solutions and may be titrated (52) with standard alkali using methyl orange or methyl red as indicator. Measurement of the electrical conductance (203) of azidodithiocarbonic acid places the compound in acid strength above hydrofluoric, hydrazoic, and hydrocyanic acids, but below the halogen hydracids. Potentiometric titration shows that it is comparable in strength with sulfuric acid. The dry substance is very sensitive to both shock and heat and decomposes at room temperatures. In aqueous solution it is much more stable. In either case primary decomposition proceeds in accordance with the equation:



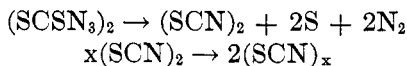
The thiocyanic acid formed rapidly undergoes polymerization and reaction to give products of indefinite composition and structure.

A whole series of salts (8, 36, 37, 41, 204) of azidodithiocarbonic acid has been prepared either (1) by direct interaction of the corresponding azides with carbon disulfide, (2) by the action of the acid upon the oxides and carbonates, or (3) by precipitation of the insoluble salts from aqueous solution. The silver, mercurous, and lead salts are insoluble in water (204). Not only are the heavy metal salts extremely explosive (186), but even such water-soluble salts as cesium azidodithiocarbonate are apt to decompose violently merely by contact during the process of crystallization from aqueous solution. Like the acid these salts undergo slow decomposition with formation of the corresponding thiocyanates, free nitrogen, and sulfur. The ammonium and substituted ammonium (8), as well as the potassium, rubidium, and cesium salts (36) are characterized by their peculiar sensitivity to light. All of these salts change color when exposed to sunlight. In some cases (cesium and rubidium salts) this color change is completely reversible. This phototropic effect is particularly noticeable in the case of the cesium salt, which turns a deep purple in strong sunlight. Investigation has shown that a rather limited region in the near ultra-violet (3750–3950 A. U.) causes this change to take place.

*Azidocarbondisulfide*,  $(SCSN_3)_2$  (39, 206), may be prepared by chemical or electrochemical oxidation of the free acid or one of its soluble salts. An iodine-potassium iodide solution is immediately decolorized when added to a solution of sodium azidodithiocarbonate with the resultant precipitation of the free dimeric radical as a white, microcrystalline, explosive solid (42).



Azidocarbondisulfide decomposes at room temperatures fairly rapidly, at higher temperatures with explosive violence, to yield as final products nitrogen and an intimate mixture of polymeric thiocyanogen and sulfur. Since this decomposition (38)

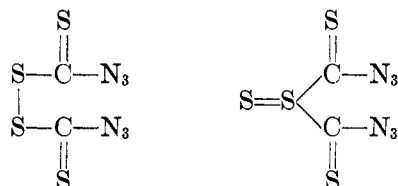


has been found to be autocatalytic, it is thought that the acceleration in the rate of decomposition of the halogenoid, as noted during the course of nitrometric studies, is due to the intermediate formation of an unstable interhalogenoid complex, possibly  $SCN \cdot SCSN_3$ . The halogenoid dissolves in potassium hydroxide to give a solution which upon acidification reprecipitates the original compound. On the basis of this and other chemical

evidence it has been assumed that the reaction occurring under these conditions is analogous to the well-known reaction which takes place when chlorine is dissolved in alkaline solution.



The oxyazidodithiocarbonate is not stable and such solutions gradually decompose with formation of a host of products, among which the thiocyanate, sulfate, thiosulfate, sulfide, and sulfite ions, in addition to free nitrogen and sulfur, have been identified. Azidocarbonyl disulfide in contact with water slowly undergoes simultaneous hydrolysis and decomposition to give similar products. The halogenoid is assumed to exist in two tautomeric forms, a disulfide and a monosulfide, to which the following structures have been assigned:



That azidocarbonyl disulfide does indeed possess halogenoid characteristics is further demonstrated by the fact that it forms the exceedingly unstable halogen derivatives,  $\text{ClSCSN}_3$ ,  $\text{BrSCSN}_3$ , and  $\text{Br}_3\text{SCSN}_3$  (107). The interhalogenoid, *cyanogen azidodithiocarbonate*,  $\text{CNSCSN}_3$  (7), has also been prepared either by the interaction of the potassium salt with ethereal cyanogen bromide, or by the action of the halogenoid upon mercuric cyanide. It is a white crystalline solid which melts with decomposition at  $67^\circ\text{C}$ . It undergoes decomposition to form polymerized cyanogen thiocyanate, nitrogen, and sulfur. When heated in inert solvents some cyanogen thiocyanate can be obtained.

Azidocarbonyl disulfide oxidizes hydrogen azide (256) in ethereal solution to give nitrogen. It undergoes simultaneous decomposition with formation of thiocyanogen, sulfur, and a variety of other products.

## VII. METALLIC AZIDES: AZIDES, TRINITRIDES, PERNITRIDES, AZOIMIDES, TRIAZOATES

### A. Preparation and general properties

Direct methods for the preparation of certain metallic azides have already been described in section II dealing with the synthesis of the azide radical. However, only two of these have been adapted to laboratory or

larger scale production; namely, the nitrous oxide-sodium amide method (80, 81, 257, 223, 138) and the alkyl nitrite-hydrazine synthesis (255, 166, 229, 215, 216). Both of these methods are used chiefly in the preparation of sodium azide, although they may be modified to obtain other azides. Thus, directions are given by Hoth and Pyl (138) for the preparation of potassium azide from potassium amide and nitrous oxide. These investigators also obtained 30 per cent yields of barium azide from ethyl nitrite, hydrazine hydrate, and barium hydroxide. In most instances, however, sodium azide must serve as the starting material for the preparation of all other salts.

Solutions of sodium azide react metathetically with solutions of soluble copper (72), silver (61), lead (62), mercurous (61, 62), and thallos (82) salts to precipitate the corresponding azides. All other common metallic azides are soluble in water and are obtainable (1) by the action of hydrazoic acid upon the metals, oxides, hydroxides, or carbonates, (2) by metathesis of barium azide with soluble sulfates, and (3) by double decomposition of potassium azide with a soluble perchlorate. Since silver azide is much more soluble than silver iodide, Friedlander (104) was able to use the reaction between tetramethylammonium iodide and silver azide to obtain tetramethylammonium azide. The extremely treacherous character of silver azide militates seriously against the general adoption of this method.

In many cases metallic salts are not obtainable from aqueous solution as such, but give on standing or evaporation insoluble basic salts, some of extremely variable composition. Such azides as those of magnesium (72), zinc (72), yttrium (68), lanthanum (68), cerous cerium (68), chromium (68), manganese (68, 72), and cobalt and nickel (72) yield basic compounds upon evaporation of aqueous solutions of the corresponding salts. In the case of aluminum (72), zirconium (68), and thorium<sup>5</sup> (68) precipitation of the corresponding hydroxides takes place even in the cold when sodium azide is added to solutions of salts of these metals in water. Quantitative

<sup>5</sup> Dennis and Kortright (85, 78) made use of potassium azide for the separation of thorium from the rare earths of the cerium and yttrium group, and recommend this reagent as one which may be used both for the qualitative detection of thorium and for its quantitative determination either alone or in the presence of other rare earths. Recently, this method has been extended to the separation of the rare earths themselves (3). Cerium can be oxidized to the ceric state readily by hydrogen peroxide. Addition of sodium azide is said to result in the quantitative separation of ceric hydroxide, leaving the other rare earths in solution. If such a solution is boiled the less basic rare earths precipitate first, with the result that the residual solution is gradually enriched with respect to the more basic members. J. Ant-Vuorinen (3) claims to have prepared pure lanthanum material in this manner. This same investigator has also shown that samarium hydroxide is precipitated quantitatively when solutions containing samarium salts and sodium azide in excess are boiled (144).

precipitation of ferric hydroxide (68) is effected when a solution of the azide is boiled. Hahn (121) recommends the use of sodium azide-sodium nitrite solutions for the precipitation of the hydroxides of iron, aluminum, and chromium in a granular and easily filterable form.

Non-aqueous media have been used successfully in the preparation of certain azides. Thus, ammonium (106), ethylammonium, and diethylammonium (129) azides may be obtained by interaction of ethereal solutions of hydrogen azide with the corresponding anhydrobases in ether or alcohol. Dihydroxylammonium azide,  $(\text{NH}_2\text{OH})_2 \cdot \text{HN}_3$  (83), is best prepared in alcoholic solution from its components. Zinc azide,  $\text{Zn}(\text{N}_3)_2$  (263), is obtained by action of ethereal hydrogen azide upon metallic zinc. Chromium azide,  $\text{Cr}(\text{N}_3)_3$  (173), may be prepared by the reaction of anhydrous chromium nitrate with sodium azide in anhydrous alcohol. Ferric azide,  $\text{Fe}(\text{N}_3)_3$  (263), is obtainable when dry ferric sulfate and sodium azide are shaken together in absolute methanol. The precipitated sodium sulfate is removed by filtration and the solution of ferric azide concentrated in a vacuum desiccator. Reaction of cobaltous carbonate with ethereal hydrogen azide gives the anhydrous cobaltous azide,  $\text{Co}(\text{N}_3)_2$  (263).

The alkali and alkaline earth metals react with ammonium azide in liquid ammonia to give the corresponding azides (45, 98). Browne and his coworkers (44) have prepared various metallic azides by electrolyzing solutions of ammonium azide in liquid ammonia, using the respective metals as anodes. No analyses are recorded for the products obtained, but they claim to have prepared the normal azides of silver, cadmium, lead, and antimony by this method. With aluminum, iron, and nickel anodes ammono-basic azides are presumably obtained.

Stabilization of some metallic azides is effected by converting them into ammonates, pyridinates, and even hydrazinates (90). Thus, zinc azide dipyridinate,  $\text{Zn}(\text{N}_3)_2 \cdot 2\text{C}_5\text{H}_5\text{N}$  (83), which is precipitated upon addition of pyridine to an aqueous solution of the azide, is much more stable than zinc azide itself. Pyridinates of cadmium, cobaltous, and nickelous azides have been prepared in a similar manner.

Double salts, such as  $\text{Ni}(\text{N}_3)_2 \cdot \text{NH}_4\text{N}_3$  and  $\text{Ni}(\text{N}_3)_2 \cdot \text{KN}_3$  (72, 263), are obtained by adding the calculated quantities of the ammonium or potassium azides to concentrated aqueous solutions of nickelous azide. The corresponding cobaltous salts (72) have also been prepared.

It is rather questionable whether the compound  $\text{Cr}(\text{N}_3)_3 \cdot 3\text{NaN}_3$  (173) is to be considered a double salt. It is probably the sodium salt of a complex chromihydrazoic acid,  $\text{H}_3\text{Cr}(\text{N}_3)_6$ , since it yields with silver nitrate solution not silver azide, but a precipitate whose composition has not been determined because of its highly explosive nature. It is significant in this



connection that Mendelejeff (158) predicted the existence of complexes of this type some forty years ago, shortly after the discovery of hydrazoic acid by Curtius.

Only recently, however, has an attempt been made to prepare and describe cobalt complexes containing the azido grouping, although reference to such an investigation may be found in Mellor.<sup>6</sup> Strecker and Oxenius (218) were unable to apply the usual methods for the preparation of such complexes, because of the tendency for cobalt azide to hydrolyze. However, interaction of hexamminocobaltic sulfate with barium azide in aqueous solution yields hexamminocobaltic azide,  $[\text{Co}(\text{NH}_3)_6](\text{N}_3)_3$ . From chloropentamminocobaltic sulfate and barium azide is obtained chloropentamminocobaltic azide,  $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{N}_3)_2$ . These compounds are both soluble in water. Treatment of tetramminocarbonatocobaltic chloride with hydrazoic acid gives tetramminodiazidocobaltic azide,  $[\text{Co}(\text{NH}_3)_4(\text{N}_3)_2]\text{N}_3$ . The corresponding compound, diethylenediamminodiazidocobaltic azide,  $[\text{Coen}_2(\text{N}_3)_2]\text{N}_3$ , is prepared in a similar manner. Several other compounds of this type are described by Strecker and Oxenius.

Ricca and Pirrone (192) have prepared a series of addition compounds of azides with mercuric cyanide having the general formula  $\text{Hg}(\text{CN})_2 \cdot \text{Me}(\text{N}_3)_2$  (where  $\text{Me} = \text{Cu}^{++}, \text{Zn}^{++}, \text{Co}^{++}, \text{Ni}^{++}$ ). Vournasos has also prepared several rather remarkable compounds of the complex type by allowing sodium azide to react with antimony tribromide in acetone to give  $\text{NaSb}_3\text{Br}_9\text{N}_3$  (247) and with arsenic tribromide in methyl alcohol to give  $\text{Na}_8(\text{AsBr}_3\text{N}_3)_8$  (246).

### B. Properties

While the chemical properties of the metallic azides are fairly well known, since they resemble in most respects those characteristics of the azide radical discussed under hydrazoic acid, little is known of the physical properties of these compounds. Only the alkali and alkaline earth azides have been the subjects of more than a cursory examination. The physical properties of these azides have been collected in table 1. The physical properties of those heavy metal azides which have found application as detonators are included under the discussion of the explosive properties of azides (see p. 207).

<sup>6</sup> Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume VIII, p. 355. The preparation of a series of cobalt complexes by S. Lorie is noted from information obtained from a publication by this author entitled "Stickstoffwasserstoffsäure und ihre anorganischen Verbindungen," Zürich (1912).

FORMULA	MELTING POINT	DECOMPOSITION TEMPERATURE	DECOMPOSITION TEMPERATURE* (235)	SOLUBILITY IN 100 G. WATER†	SOLUBILITY‡ IN OTHER SOLVENTS
	<i>degrees C.</i>	<i>degrees C.</i>	<i>degrees C.</i>	<i>grams</i>	<i>grams</i>
LiN <sub>3</sub> .....				66.41 <sup>16</sup> °	C <sub>2</sub> H <sub>5</sub> OH: 20.26 <sup>16</sup> Insoluble in eth
NaN <sub>3</sub> .....		330 (235) 275 (219) 300 (162)	280	41.7 <sup>17</sup> °	C <sub>2</sub> H <sub>5</sub> OH: 0.22 <sup>20</sup> ° Soluble in liquid
KN <sub>3</sub> .....	343 (219) 350 (135)	355 (219) 320 (235)	360	49.6 <sup>17</sup> °	C <sub>2</sub> H <sub>5</sub> OH: 0.14 <sup>16</sup> ° Soluble in liquid
RbN <sub>3</sub> .....	300 (235) 321 (219) 330 (72)	260 (235) 395 (219)	310	114.1 <sup>17</sup> °	Slightly soluble Insoluble in eth
CsN <sub>3</sub> .....	320 (235) 326 (219)	290 (235) 390 (219)	350	307.4 <sup>16</sup> °	C <sub>2</sub> H <sub>5</sub> OH: 1.04 <sup>16</sup> ° Insoluble in eth
NH <sub>4</sub> N <sub>3</sub> §.....	Sublimes (106, 72)			13.8 <sup>0</sup> ° 20.16 <sup>20</sup> ° 27.07 <sup>40</sup> ° (106)	CH <sub>3</sub> OH: 3.27 <sup>20</sup> ° C <sub>2</sub> H <sub>5</sub> OH: 1.06 <sup>20</sup> ° Insoluble in eth Very soluble in
N(CH <sub>3</sub> ) <sub>4</sub> N <sub>3</sub> (104).....		125		Very soluble	Soluble CH <sub>3</sub> OH, Slightly soluble ether
(NH <sub>2</sub> OH) <sub>2</sub> ·HN <sub>3</sub> (83).....	66			Very soluble	Soluble in C <sub>2</sub> H <sub>5</sub> OH Insoluble in eth
N <sub>2</sub> H <sub>4</sub> ·HN <sub>3</sub> .....	75.4 (91)			Very soluble	N <sub>2</sub> H <sub>4</sub> : 190 <sup>23</sup> ° CH <sub>3</sub> OH: 6.1 <sup>23</sup> ° C <sub>2</sub> H <sub>5</sub> OH: 1.6 <sup>23</sup> °
Ca(N <sub>3</sub> ) <sub>2</sub> .....		110 (235)	100	45 <sup>15, 22</sup> °	C <sub>2</sub> H <sub>5</sub> OH: 0.211
Sr(N <sub>3</sub> ) <sub>2</sub> .....		140 (235)	110	45.83 <sup>16</sup> °	Slightly soluble
Ba(N <sub>3</sub> ) <sub>2</sub> .....		160 (235)	120	16.7 <sup>15</sup> °	Slightly soluble

\* The figures given in column 3 refer to those temperatures at which regular nitrogen evolution begins.

† Unless otherwise noted all solubilities were determined by Curtius and Rissom (72).

‡ Indicates an x-ray crystal structure study.

§ Solubilities of ammonium azide, both in water and in other solvents, refer to grams per 100 grams of solvent.

*inorganic azides*

PER	CRYSTAL FORM	OTHER PHYSICAL PROPERTIES	SOLVATES
			LiN <sub>3</sub> ·H <sub>2</sub> O (79) LiN <sub>3</sub> ·2H <sub>2</sub> O (270) LiN <sub>3</sub> ·4H <sub>2</sub> O (270)
	Hexagonal (72, 130)‡	d <sup>25°</sup> = 1.8473 (161, 58, 130) Refractive index, aqueous solution (58) Conductivity, aqueous solution (58) Density, aqueous solution (31) Viscosity, aqueous solution (31)	
	Tetragonal (79, 130)‡	d = 2.056 (58, 130) Refractive index, aqueous solution (58) Conductivity, aqueous solution (58)	
	Tetragonal (79, 176, ‡ 54†)	d = 2.9365 (118)	
	Tetragonal (79)		
(106)	Rhombic (72)	d <sub>D</sub> <sup>20°</sup> = 1.3459 (106) Vapor pressure of solid (106) Density of saturated solutions (106) Thermal data (18, 19)	NH <sub>4</sub> N <sub>3</sub> ·NH <sub>3</sub> NH <sub>4</sub> N <sub>3</sub> ·5NH <sub>3</sub> (91)
HCl <sub>3</sub> ,	Tetragonal		
	Rhombic (91)		N <sub>2</sub> H <sub>5</sub> N <sub>3</sub> ·N <sub>2</sub> H <sub>4</sub> (91, 193, 53)
	Rhombic (79)		Ca(N <sub>3</sub> ) <sub>2</sub> ·2N <sub>2</sub> H <sub>4</sub> Ca(N <sub>3</sub> ) <sub>2</sub> ·N <sub>2</sub> H <sub>4</sub> (90)
	Rhombic (79)		
	Monoclinic (118)‡		Ba(N <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O (80, 81)

after decomposition has begun (see p. 205).

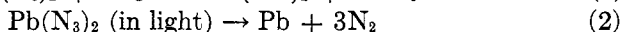
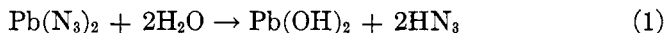
tion

### C. Photochemical decomposition of azides

In his first description of silver azide, Curtius (61) stated that it was possible to distinguish this compound from the halides of silver by the fact that it was not light-sensitive. Subsequent investigations by Wöhler and Krupko (260, 261) and by Bekk (13, 14) showed that this was not the case. Not only silver azide but several other metallic azides undergo distinct decomposition upon exposure to light. Silver azide darkens slowly with formation of metallic silver and evolution of nitrogen, a process which may be followed both microscopically where particles of silver may be detected readily, and also gasometrically, by measuring the volume of nitrogen gas evolved. Bekk (13, 14) prepared dry emulsions of the silver salt and found that they were insensitive to shock and could be manipulated without danger. It is claimed that such an emulsion is much more easily reduced by developing solutions than the corresponding halides, and that it is characterized by its relatively high sensitivity to the red portion of the spectrum. More recently (4), however, it has been found that emulsions of silver azide absorb light in the same regions as silver chloride. This absorption does not parallel that of the chloride, but decreases in the region of shorter wave length.

Mercurous azide is extremely light-sensitive and takes on a superficial yellow coloration within a few minutes. The formation of droplets of free mercury is readily discernible under the microscope. Cuprous azide is also decomposed by sunlight.

Dry lead azide assumes a grayish yellow color on exposure to light. Under water the color changes are much more marked, and decomposition takes place with formation of appreciable quantities of ammonia. This reaction does not take place in the dark, so that the reduction of hydrazoic acid liberated by hydrolysis of the lead salt may be said to be due to the action of the metallic lead formed by the photochemical decomposition of the azide. The following reactions probably take place.



Sodium azide is decomposed by ultra-violet light at wave-lengths below 4050 Å. U. (163). When barium azide is exposed to soft x-rays decomposition takes place with formation of barium nitride (116).<sup>7</sup>

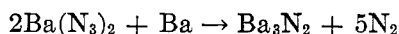
<sup>7</sup> Müller and Brous (163, 164) have studied the decomposition of sodium azide by bombardment with a stream of electrons. Decomposition with evolution of nitrogen does not take place until the electrons have assumed an energy of  $12 \pm 0.1$  volts. Muraour and Trillat (269) observed darkening of lead azide upon bombardment with electrons.

*D. Thermal decomposition of azides*

All azides are characterized by their relative instability towards heat. At higher temperatures all of them decompose with more or less violence to give free nitrogen and the corresponding metal, sometimes with varying quantities of the nitride. Very few azides are stable at their melting points, and even these undergo decomposition if kept in the fused state over longer periods of time. In table 1 are given the melting points and decomposition temperatures of the alkali and alkaline earth azides. In the third column are noted the temperatures at which, according to Tiede (235), regular evolution of nitrogen takes place once decomposition has begun. The temperatures given by Tiede and by Suhrmann and Clusius (219) refer to observations made in a vacuum. Determinations of the melting points and decomposition temperatures made by other authors were carried out at atmospheric pressures.

It is quite evident that the temperature required to initiate decomposition of certain azides is higher than that required to carry it forward, once it has begun. Tiede ascribed this behavior to the catalytic effect of the liberated metals. This assumption has since been verified by Günther, Andreev, and Ringbom (115), who were able to prove that the explosive decomposition of barium azide is due, not necessarily to direct dissociation of the azide into metal and nitrogen, but rather to the secondary reaction of metallic barium with barium azide to give the nitride and free nitrogen.

Garner and Moon (109), as well as Harvey (128), have shown that the small particles of metallic barium first formed on heating barium azide act as nuclei and catalyze the further decomposition in accordance with the equation:



Curiously enough, exposure of crystals of barium azide to radium emanation shortens very appreciably the time required to bring about initial decomposition. An induction period (109) is necessary to start decomposition even under ordinary conditions, but according to Garner and Moon (109) the time is reduced at 110°C. from 110 to 55 minutes and the speed of decomposition tripled by exposure to radium emanation of intensity of 1 millicurie.

The heavy metal azides tend to undergo sudden and explosive dissociation over a range of temperatures depending upon crystal size, purity, rate of heating, and the presence or absence of admixed substances. Their explosive properties will be discussed later. Hitch (132) carried out a series of experiments effecting slow decomposition by using extremely small quantities (0.05 g.) of various metallic azides. The initial decomposition

temperatures and explosion temperatures as determined by Hitch are given in table 2.

Tiede (235, 237) recommends the thermal decomposition of the alkali and alkaline earth azides as a method for the preparation of very pure nitrogen. Justi (140) also decomposed sodium azide to prepare very pure nitrogen. Booth (30) determined the atomic weight of nitrogen by decomposing silver azide. An average of fourteen determinations of the silver-nitrogen ratio gave an atomic weight of 14.007 for nitrogen. Hitch (132) determined the atomic weight of silver from the silver azide-silver ratio obtaining values varying between 107.93 and 107.98. Moles (162) used sodium azide for the determination of the atomic weight of sodium and obtained values whose extremes were 23.024 and 23.10. The fact that both Moles and Hitch obtained values higher than those generally accepted indicates that both determinations were subject to a common error.

TABLE 2  
*Decomposition temperatures of some heavy metal azides*

AZIDE	INITIAL DECOMPOSITION TEMPERATURE	EXPLOSION TEMPERATURE
	<i>degrees C.</i>	<i>degrees C.</i>
HgN <sub>3</sub> .....	215	270
Hg(N <sub>3</sub> ) <sub>2</sub> .....	215	300
Pb(N <sub>3</sub> ) <sub>2</sub> .....	250	360
TlN <sub>3</sub> .....	Melts at 330; sublimes at 340	430
Ba(N <sub>3</sub> ) <sub>2</sub> .....	180	225

The thermal decomposition of azides (92, 188, 219, 202, 27) has been used for the preparation of various metals in a state of high purity. Ebler (92) prepared a barium azide containing approximately 2 per cent radium azide and decomposed this preparation, obtaining a metallic mirror which had lost but little of its activity. Suhrmann and Clusius (219) studied the decomposition of the alkali azides as a means for preparing the alkali metals in very pure form. The azides were allowed to decompose slowly in a high vacuum over periods of three to four days at temperatures noted in table 1. Under these conditions the liberated metals distilled away from the residual masses in the decomposition vessel giving the following yields of pure alkali metal:

Azide.....	NaN <sub>3</sub>	KN <sub>3</sub>	RbN <sub>3</sub>	CsN <sub>3</sub>
Per cent yield.....	100	80	60	90

The residues remaining in the case of potassium, rubidium, and cesium yielded considerable quantities of ammonia upon treatment with water,

indicating that nitrides had been formed under these conditions. These residues were subsequently analyzed by Clusius (55), who verified this supposition. Since the stability of the azides rises with increasing atomic weight of the alkali metal, Suhrman and Clusius assumed that the nitrides probably exhibited a reverse order of stability, thus accounting for the relatively large amount of  $\text{Rb}_3\text{N}$  formed under the temperature conditions employed. Wattenberg (249) decomposed sodium azide partially and observed limited nitride formation under these circumstances. Tiede observed high percentage of nitride formation in the decomposition of the alkaline earth azides. Günther and his coworkers (115) found that yields of nitride as high as 75 per cent could be obtained by careful decomposition of barium azide.

De Boer, Clausing, and Zecher (77) decomposed mixtures of cesium chloride and barium azide thermally in a vacuum, and were able to obtain mirrors of metallic cesium by this method.

If the alkali and alkaline earth azides are decomposed in an atmosphere of hydrogen the corresponding hydrides may be prepared. Wattenberg (249) obtained sodium hydride in this manner, and Tiede (236) applied this method to the preparation of barium hydride.

#### *E. Explosive properties of azides*

While it is not the purpose of this article to discuss in detail the use of certain azides as initiators for the detonation of secondary explosives, it is nevertheless worth while to point out some of the interesting facts upon which these applications rest. The great sensitivity of various metallic azides to heat, impact, and friction suggested their possible use as detonants soon after the discovery of hydrazoic acid and the preparation of its inorganic derivatives by Curtius (62). As early as 1893 (154b, 258) the Prussian government investigated the azides of lead, silver, and mercury from this point of view, but a fatal accident resulted in the discontinuance of these experiments. Shortly thereafter, Berthelot and Vieille (19) directed attention to the explosive properties of mercurous and ammonium azides, pointing out that the latter compared favorably with guncotton insofar as temperature ( $1400^\circ\text{C}.$ ) attained during explosion and the pressure developed was concerned. One kilogram of ammonium azide upon decomposition yields 1148 liters of gas measured at standard conditions. However, nothing was done concerning the possible utilization of azides until Wöhler called attention to them about 1907 as possible substitutes for mercuric fulminate. After considerable investigation by Wöhler (258, 262), the manufacture of lead azide was begun in Germany about 1914 (189). It was not until the Italian advance upon Gorizia brought the Austrian mercury mines within range of the Allied guns that the Central

powers were forced to consider seriously the use of lead azide detonants (190). It is therefore fairly certain that lead azide was used during the World War by the Germans, who seem also to have been the only ones to have considered it seriously as a substitute for mercuric fulminate. Since 1920 the use of lead azide has developed considerably (253, 213, 225, 122). A large and extensive patent and technical literature is evidence of this growing interest in and application of azide detonators (274 to 279).

While mercuric fulminate is still the most important constituent of primers<sup>8</sup> it is not satisfactory in all respects. It deteriorates on long storage, especially if kept under unusual temperature conditions. It is somewhat hygroscopic and its effectiveness is very much decreased by the presence of moisture. It does not function satisfactorily when highly compressed. Even though lead azide has received most attention as a substitute for mercuric fulminate, it is superseded in initiatory power by

TABLE 3  
*Effectiveness of various azides and fulminates*

METAL	AZIDE	FULMINATE
Cadmium.....	1	2
Silver.....	3	4
Lead.....	5	—
Cuprous.....	6	7
Mercurous.....	8	—
Mercuric.....	—	9

several others. Marshall (154b) gives numbers to show in descending order the effectiveness of various azides and fulminates (see table 3).

Both Wöhler (211) and Birckenbach (23) have emphasized the extremely sensitive character of cadmium azide. It can not be employed as a detonant on account of its solubility in water and its hygroscopicity. The cost and extreme explosiveness of silver azide have acted as serious deterrents to its extended use. However, Taylor and Rinkenbach (226) have found that precipitation of silver azide from concentrated solutions of sodium

<sup>8</sup> In a private communication to the author L. V. Clark states, "The term 'primer' according to accepted nomenclature designates those devices used to effect the ignition of the propellant charge in small arms or large caliber military ammunition, or, in the case of high explosive shell, is the device which, acting through a booster charge of tetryl, effects the detonation of the main charge of explosive within the shell. It is true that mercuric fulminate is still the most important constituent of primers for the larger caliber military ammunition. However, in the case of primers for small arms ammunition, there has been a definite effort on the part of manufacturers to eliminate mercuric fulminate from their compositions."



azide and silver nitrate produces a semicolloidal material which is much safer to handle, much less hygroscopic, and more stable toward temperature changes, than the more crystalline material obtained from dilute solutions (see also 29). Silver azide is much more sensitive than either mercuric or silver fulminate and develops a higher initial impulse. This is true of several of the more sensitive azides, thus making it possible to use a much smaller quantity of azide than fulminate to detonate a given quantity of high explosive (see table 4).

Although lead azide (59, 141) (1) withstands unusual temperature conditions in storage, (2) is not appreciably affected by moisture, (3) develops a higher initial impulse than mercuric fulminate, and (4) does not become "dead pressed," its commercial development was retarded by the fact that it is slowly attacked by wet carbon dioxide and hydrogen sulfide (273) with the resultant liberation of hydrazoic acid, which in turn attacks

TABLE 4  
*Minimum detonating charge (154c)*

INITIATOR	MINIMUM CHARGES IN GRAMS WHICH WILL DETONATE 0.5 G. OF			
	Tetryl	Picric acid	T.N.T	Trinitroanisole
Hg(ONC) <sub>2</sub> .....	0.29	0.30	0.36	0.37
HgN <sub>3</sub> .....	0.05	0.08	0.15	0.55
Pb(N <sub>3</sub> ) <sub>2</sub> .....	0.03	0.03	0.09	0.28
AgN <sub>3</sub> .....	0.02	0.04	0.07	0.26
Cd(N <sub>3</sub> ) <sub>2</sub> .....	0.01	0.02	0.04	0.10

copper or brass detonator capsules to form the extremely treacherous cuprous azide. It has been found that if sufficient care is taken to dry thoroughly the ingredients entering into a detonator composition, the danger of decomposition of lead azide is eliminated.<sup>9</sup> The difficulty has also been overcome by use of aluminum or aluminum alloy materials as containers (276). Lead azide is also more difficult to ignite, although it is claimed that careful purification of the sodium azide and the water used in its preparation yields a better product. This difficulty has largely been overcome either by the use of composite azide detonators, where other ingredients are added to lower the ignition temperature, or an ignition mixture designed to develop a high temperature is superimposed upon the azide charge. Practically all patent specifications now call for the admixture of other substances in the manufacture of azide detonators (275). Efforts to use basic lead azide (258) or double salts of lead azide (26) have not been particularly successful.

<sup>9</sup> Private communication from Dr. L. V. Clark.

Only recently has it been shown that lead azide exists in two crystalline modifications (108, 159). The ordinary form (denoted as the  $\alpha$ -form) crystallizes in the orthorhombic system ( $d = 4.71$ ). It is much more stable and less sensitive to shock and friction than the  $\beta$ -form ( $d = 4.93$ ), which is monoclinic. This observation has been checked by determining the rate of decomposition of both forms from 210°C. to the explosion temperature (295°C.). The unstable  $\beta$ -form has a much lower critical increment than the  $\alpha$ -form (47,600 calories). Furthermore, it has been found that the  $\beta$ -form often explodes spontaneously, which may be the cause for some of the accidents which have occurred in the manufacture of lead azide. The  $\beta$ -form undergoes transition into the  $\alpha$ -form by contact with a solution of a lead salt.

Lead azide, like lead chloride, is appreciably soluble in warm water. Upon cooling lead azide sometimes comes out in the form of large crystals (probably the  $\beta$ -form (159)), which are extremely sensitive.<sup>10</sup> This fact is in accord with previous observation that, owing to internal strains, large crystals of various fulminates and azides are inherently much less stable than the finely divided product. Present technical methods and patent specifications call for the precipitation of lead azide in finely divided or colloidal form (151, 131, 214).

Mercurous azide (114) has also been proposed as a constituent of composite detonators. It is claimed that mercurous azide is not affected by carbon dioxide and may be used in copper detonator tubes. Mercuric azide, like lead azide, appears to exist in two crystalline modifications (159). The  $\beta$ -form is even less stable than the  $\beta$ -lead azide. Its solubility in water will probably prevent its consideration for use as a priming agent.

In addition to the azides of silver and lead and mercury, cyanuric triazide,  $(\text{CN})_3(\text{N}_3)_3$ , (175, 227, 141, 228, 259) has been mentioned prominently as a possible detonating agent. According to Kast and Haid (141) it develops a maximum detonation velocity of approximately 7500 meters per second when compressed to a density of 1.54, whereas the figure for lead azide with density of 4.6 is 5300 meters per second. Taylor and Rinkenbach (228) have studied the sensitiveness of various detonating compounds to frictional impact, impact, and heat. A glance at their figures (see table 5) will indicate immediately that cyanuric triazide possesses interesting possibilities. It is, however, relatively expensive to manufacture and rather volatile.

The sand-crushing strength test (see table 6) shows very clearly that

<sup>10</sup> The mechanism of and the various phenomena accompanying the explosion of lead azide under varying conditions have been the subjects of considerable study by Muraour and his coworkers (267, 268) as well as others (265, 271, 272).

cyanuric azide is probably the most brisant of the proposed and commercial initiators.

A comparative study by Muraour (165) of lead and cyanuric azides and mercuric fulminate is reproduced in table 7, in which the distinctive physical properties of these substances are listed.

TABLE 5  
*Sensitiveness to friction (228)*

AZIDE	PENDULUM FRICTION			IMPACT FALL 500 G. WEIGHT	EXPLOSION TEMPERA- TURE
	Added weight in kilograms	Fall	Number of swings		
Pb(N <sub>3</sub> ) <sub>2</sub> .....	0.45	37.5	12	43	383
AgN <sub>3</sub> .....	4.35	33.0	30	41	273
HgN <sub>3</sub> .....	1.00	50.0	16	6	298
(CN) <sub>3</sub> (N <sub>3</sub> ) <sub>3</sub> .....	0.00	12.5	3	7	252

TABLE 6  
*Sand-crushing strength of certain of the azides*

WEIGHT OF CHARGE OF EXPLOSIVE	WEIGHT OF SAND CRUSHED FINER THAN 30 MESH BY			
	Mercury fulminate	Lead azide	Silver azide	Cyanuric triazide
<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
0.10	—	—	3.3	4.8
0.20	3.8	5.9	6.8	12.2
0.30	8.0	—	10.4	—
0.40	12.2	12.7	—	33.2
0.50	16.0	16.1	18.9	—
0.60	20.1	20.9	—	54.4
0.75	—	—	30.0	—
0.80	28.2	28.5	—	68.9
1.00	36.8	33.6	41.1	78.6

The use of sodium azide as a constituent of a priming charge has been patented (279). A recent study of the explosive properties of the alkaline earth azides has shown that calcium azide is the most sensitive (266).

An interesting study dealing with the sensitivity of various salts of hydrazoic acid to heat has been carried out by Wöhler and Martin (273). The data show very clearly the dependence of the true point of deflagration of the azides upon the quantity of substance. By plotting the minimum temperatures at which no explosion took place in 5 minutes against the

TABLE 7  
*Characteristics of certain explosives (165)*

EXPLOSIVE	H.F.M. calories per molecule	H.F.G. calories per gram	$T_d$ degrees C.	CHARGE LIMITS grams	Q kg.-cal. Hg vapor	Q <sub>i</sub> kg.- cal.	V <sub>0</sub> liters	VOL. liters	T <sub>A</sub>	P 5630	P <sub>i</sub>	CO- VOL- UME cm. <sup>3</sup>	V <sub>E</sub> cm. <sup>3</sup>	RATE OF DETONA- TION	
														Density	Meters per Second
Mercury fulminate.....	-64.3	-223	169-175		368 Hg vapor	1360	liters 315 Hg vapor	4720	5630	24941	226	315	226	1.66	2730
d = 4.43 (density of crystals).....				0.80(A)		1306				19986			282	3.30	4500
d = 3.55 (350 atmospheres per cm. <sup>2</sup> ).....				0.29(B)		1214				18579			303		
d = 3.30 (200 atmospheres per cm. <sup>2</sup> ).....															
Lead azide.....	-110.8	-380	305-320		260 Pb vapor		308 Pb vapor	3720	4339			308			
d = 4.79 (density of crystals).....				0.10(A)		1245				20784			209	2.80	4500
d = 3.50 (800 atmospheres per cm. <sup>2</sup> ).....				0.19(A)		1078				15186			286	3.80	4500
d = 2.90 (200 atmospheres per cm. <sup>2</sup> ).....						893				12583			345		
Cyanuric triazide.....	-219	-1073	197-206		1140* 700†		659*†	4220* 3320†	10590* 8286†			659			
d = 1.4 (200 atmospheres per cm. <sup>2</sup> ).....				0.12(A)		1596*		923		14742*			714	1.15	5550
d = 1.5 (800 atmospheres).....				0.08(B)		980†				11600†					
				0.20(A)		1710*		988		15795*			667		
						1050†				12429†					

H.F.M. = heat of formation from the elements in large calories per molecule.

H.F.G. = heat of formation from the elements in small calories per gram.

$T_d$  = temperature of decomposition—the temperature at which the explosive decomposes on an oil bath.

Charge limit = minimum weight of the explosive which is able to detonate T.N.T. compressed to a density of 1.35 in a copper tube of the type used for the preparation of No. 8 detonators, the initiating explosive having been compressed on top of the T.N.T. The letter A signifies that the upper surface of the initiating explosive is free; the letter B signifies that on this upper surface has been placed a metallic capsule.

$Q$  = the number of large calories given off by 1 kg. of the explosive.

$Q_t$  = the number of large calories given off by the decomposition of 1 liter of the explosive.

$V_0$  = gaseous volume measured at 0° and 760 mm. (water vapor) given off by 1 kg. of the explosive.

Vol. = the volume of gas given off by the decomposition of 1 liter of the explosive.

$T_A$  = the absolute temperature attained by the gas on explosion.

$P$  = force of the explosive. The pressure which is developed by the gas given off by the decomposition of 1 kg. of the explosive in a volume of 1 liter if this gas follows the laws of a perfect gas at high pressure.

$P_t$  = the pressure which would be generated by the gas liberated by the decomposition of 1 liter of explosive detonated in its own volume if the gas again follows the laws of perfect gas.

Covolume of the gas of the explosion. Covolume has been given, according to Sarrau, to be 1/1000 of  $V_0$ .

$V_E$  = volume occupied by 1 kg. of the explosive.

Rate of detonation = rate of detonation, in meters per second, of the explosive compressed at the density "d."

\* Indicates decomposition in accordance with the equation:  $C_3N_{12} = 3C + 6N_2$ .

† Is based on products actually observed:  $C_3N_{12} = 1.27C_2N_2 + 4.79N_2 + 0.46C$  (amorphous).

quantity of substance used, Wöhler and Martin obtained a series of curves asymptotic to the weight axis, from which the true explosion temperature of the compound was determined. Their results are given in table 8 and compared with standard values for the corresponding fulminates. There appears to be no regularity in the temperature of explosion. The azides of silver, cadmium, and lead detonate at a high temperature, while the azides of cobalt and manganese detonate at a much lower temperature. It should be pointed out that protracted heating at temperatures even

TABLE 8  
*Detonation temperatures of azides and fulminates*

AZIDES AND FULMINATES	DETONATION TEMPERATURES OF	
	Azides	Fulminates
	<i>degrees C.</i>	<i>degrees C.</i>
Silver.....	297	170
Lead.....	327	—
Mercurous.....	281	215
Cadmium.....	291	—
Zinc.....	289	205
Cuprous.....	174	—
Nickel*.....	200	—
Cobalt†.....	148	—
Manganese.....	203	—
Barium.....	152	—
Strontium.....	169	—
Calcium.....	158	—
Lithium.....	245	—
Thallium.....	320	—
Mercuric.....	—	215

\* Hydrated salt.

† Contained 13 per cent water.

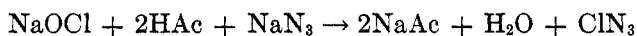
considerably lower than those noted in the table results in decomposition of these compounds (see page 205).

Wöhler and Martin also give data for the sensitivity of these azides to impact. Their results show that no apparent regularity exists between weights of substance employed and their sensitivity to shock. Some azides, such as mercurous, silver, and lead azides, become more sensitive as the quantity of substance is increased. In the case of nickel and cobalt azides the sensitivity increases up to a certain weight and then falls off again as the quantity of material is increased. Zinc and manganous azides, on the other hand, become less sensitive as the amount of substance is increased.

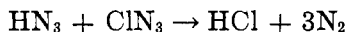
## VIII. NON-METALLIC AZIDES

The halogenoid (248) character of the azide radical is further substantiated by the fact that, like the halogens, it (1) forms compounds with other halogen or halogenoid groups and (2) replaces the halogens to form inorganic acyl azides. The few known members of both groups are described below.

*Chlorine azide*,  $\text{ClN}_3$  (184), is a colorless gas with a sweetish odor which is obtained by acidification, with acetic or boric acid, of a mixture of sodium hypochlorite and sodium azide in aqueous solution.



It dissolves in sodium hydroxide to give the hypochlorite and azide, and reacts with hydrazoic acid to give nitrogen and hydrochloric acid (183).



It is a tremendously explosive substance. It decomposes at  $400^\circ\text{C}$ . at 2 mm. pressure into the elements (110).

*Bromine azide*,  $\text{BrN}_3$  (209), may be prepared by passing bromine vapor over absolutely dry sodium azide. It also forms when silver and sodium azides are treated with bromine dissolved in ether, benzene, or ligroin. It is a mobile, very volatile, orange-red liquid which changes to a dark red solid at about  $-45^\circ\text{C}$ . It is instantly hydrolyzed, giving a mixture of hydrazoic and hypobromous acids which subsequently react to give nitrogen. It liberates iodine from a potassium iodide solution in quantities equivalent to the hypobromous acid formed.

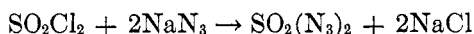
*Iodine azide*,  $\text{IN}_3$  (124), is obtained as a light yellow solid by interaction of an aqueous suspension of silver azide with iodine in ether or benzene. It is somewhat soluble in water and is decomposed largely even at  $0^\circ\text{C}$ . into the elements. It is hydrolyzed by alkaline solutions to give the azide, iodide, and iodate. With silver azide iodine azide gives molecular nitrogen, not the free dimeric azide radical as had been hoped. Metallic sodium yields sodium iodide and sodium azide; in insufficient quantity it yields sodium azide and free iodine, demonstrating that the azide radical is more electronegative than iodine. Iodine azide (as well as chlorine azide) is immediately decolorized by a sodium arsenite solution; sodium arsenate and sodium azide are formed (119, 120).

*Dicyandiazide*,  $(\text{CNN}_3)_2$ , was first isolated by Darzens (76), who believed the compound obtained by the action of cyanogen bromide upon sodium azide to be the monomer, cyanogen azide or carbon pernitride. Hart (127) showed that this could hardly be the case (although no molecular

weight determinations were made), since the compound reacted with ammonia in ethereal solution to give *dicyanamidazide*,  $\text{NCN}(\text{NH}_2)\text{N}_3$ , and ammonium azide. Dicyandiazide hydrolyzes in aqueous solution to yield carbon dioxide, hydrazoic acid, and cyanamide. It melts at  $40.3^\circ\text{C}$ ., begins to decompose at  $70^\circ\text{C}$ ., and explodes violently above  $170^\circ\text{C}$ . It is soluble in water, alcohol, ether, and chloroform, but insoluble in petroleum ether.

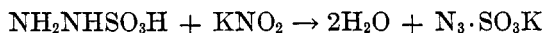
*Cyanuric triazide*,  $(\text{CN})_3(\text{N}_3)_3$ , may be obtained either from cyanuric chloride and sodium azide (175), or by diazotization of the corresponding hydrazide (96). The compound crystallizes in the hexagonal system (221), melts at  $94^\circ\text{C}$ ., and explodes when heated above  $170^\circ\text{C}$ . It has been prominently mentioned as a possible detonant (see p. 210).

*Sulfuryl azide*,  $\text{SO}_2\text{N}_6$ , was first prepared by Curtius and Schmidt (73) by the interaction of sulfuryl chloride and finely divided, slightly moist sodium azide.



After the reaction has gone to completion, the sodium chloride is dissolved out by the addition of ice water and the azide settles to the bottom as a water-white liquid. It is separated from the supernatant liquid and dried over anhydrous sodium sulfate. It explodes violently when heated, and often spontaneously at room temperatures. It has a suffocating odor and the pronounced physiological after-effects of hydrogen azide. It is hydrolyzed slowly in the cold by alcohol and water, but more quickly on warming. Alcoholic silver nitrate reacts with it instantaneously with the formation of silver azide. When heated in certain organic aromatic hydrocarbons, such as *p*-xylene, it undergoes decomposition with transient formation of the  $\left[ \text{>NSO}_2\text{N} < \right]$  residue which then breaks down further with liberation of sulfur dioxide.

Related to sulfuryl azide are the salts of *azidosulfonic acid*,  $\text{HSO}_3\text{N}_3$ , the analog of chlorosulfonic acid. Potassium azidosulfonate,  $\text{KSO}_3\text{N}_3$  (239), may be prepared by the treatment of a concentrated aqueous solution of potassium nitrite with finely powdered hydrazinesulfonic acid.



It crystallizes from solution in the form of large flat prisms which explode on heating. The addition of mineral acids probably causes the intermediate formation of azidosulfonic acid,  $\text{HSO}_3\text{N}_3$ , since hydrolysis of the product yields hydrazoic and sulfuric acids. The ammonium, sodium, and barium salts have been prepared, but their properties are not described.

*Carbonylazide*,  $\text{CO}(\text{N}_3)_2$ , is prepared by diazotization of carbohydrazide



dihydrochloride with sodium nitrite (69, 70). It is an extremely explosive, easily volatile, crystalline solid, very soluble in water, alcohol, and ether, but insoluble in petroleum ether. It undergoes hydrolysis to yield carbon dioxide and hydrazoic acid. Like sulfuryl azide, it decomposes in such solvents as benzene and xylene with probable transient formation of the  $\text{CO}(\text{N} \langle \rangle)_2$  residue (67).

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