The greater the concentration of the acid, the greater we should expect the variation of this reaction constant. Data in Table I show this to be true.

The effect of the neutral salt on the rate of hydrolysis may be shown by calculating the ratio of the time required with the acid sulfate plus the neutral salt for producing 75 and 150 cc. of carbon dioxide, to the time required with the acid salt alone for producing the same quantity of carbon dioxide. In this manner the constituents in the solution will be the same at the time of comparison. These calculations are given in Table VIII for potassium salts and calculations for sodium salts give very similar results.

Summary

An apparatus has been devised for accurately measuring the velocity of reactions at higher temperatures and over a long period of time with substances evolving a gas.

The effects of normal sodium and potassium sulfates on their corresponding acid sulfates in the hydrolysis of ethyl acetoacetate have been studied at the temperatures of 80°, 90° and 95°.

ROLLA, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

CARBONIC ACID AZIDES

BY CHARLES VINTON HART[1]

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Accepting the view of Franklin and his collaborators to the effect that guanidine, cyanamide, dicyandiamide and melamine are ammono carbonic acids,[2] then the compounds named and formulated as follows: (1) guanylazide, $HNC(NH_2)N_3$, (2) cyanazide, NCN_3, (3) dicyanamidazide, $NCNC(NH_2)N_3$, (4) dicyandiazide, $NCNC(N_3)_2$, (5) cyanuramiddiazide, $C_3N_3(N_3)_2NH_2$ and (6) cyanurtriazide, $C_3N_3(N_3)_3$, are to be looked upon as carbonic acid azides.

Dicyandiazide, $NCNC(N_3)_2$, and Dicyanamidazide, $NCNC(NH_2)N_3$.— By the action of cyanogen bromide on sodium azide in water solution, Darzens[3] obtained a crystalline product, formed as he believed in accordance with the equation, $NCBr + NaN_3 = NCN_3 + NaBr$, to which he gave the name carbon pernitride.

[1] An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Stanford University, 1927. Dr. Hart died at Berkeley, California, April 12, 1928. This paper, for the most part, is in the form written by the author. (E. C. Franklin.)

[2] Franklin, THIS JOURNAL, **44**, 486 (1922); **46**, 2137 (1924); Burdick, *ibid.*, **47**, 1485 (1925); Blair, *ibid.*, **48**, 87, 96 (1926). See also Pinck and Blair, *ibid.*, **49**, 509 (1927).

[3] Darzens, *Compt. rend.*, **154**, 1232 (1912).

Looking upon cyanogen bromide and sodium azide as a carbonic acid bromide and sodium ammono nitrate, respectively, then Darzens' compound, represented by the formula, $N\equiv\ddagger C+ -N\equiv\ddagger N\ddagger\equiv N$, would be a mixed carbonic-nitric anammonide.[4]

It was in an attempt to determine whether Darzens' compound would be converted into a mixture of cyanamide and hydrazoic acid by the action of ammonia that the investigation described in this paper had its origin.

When, accordingly, a current of dry ammonia gas was passed into an ether solution of Darzens' compound, ammonium azide was obtained as expected but instead of cyanamide the other product of the reaction proved to be a hitherto unknown compound of the formula, $NCN(NH_2)N_3$, to which the name dicyanamidazide has been given.

The formation of this carbonic acid azide is readily explained on the assumption that Darzens had the dimer of cyanazide in his hands, which under the action of ammonia is ammonolyzed as represented by the equation, $NCNC(N_3)_2 + NH_3 = NCNC(NH_2)N_3$, into dicyanamidazide and hydrazoic acid.

Hydrolysis of Dicyandiazide.—Darzens states that when his azide is hydrolyzed with boiling water, carbamic acid azide is first formed, which, being unstable, decomposes to give carbon dioxide and hydrazoic acid. The present investigation showed the hydrolysis to proceed in conformity with the equation

$$NCNC(N_3)_2 + H_2O = NCNC(OH)_2 + 2HN_3 = CO_2 + 2HN_3 + H_2NCN$$

The hydrazoic acid and cyanamide were not formed quantitatively for the reason that a certain portion of each disappeared to form 5-aminotetrazole.[5] When a sodium hydroxide solution was used in place of pure water for the hydrolysis, sodium azide and sodium cyanamide were formed almost quantitatively.

Reduction of Dicyandiazide and Dicyanamidazide.—Dicyandiazide is reduced to dicyandiamide in accordance with the equation, $NCNC(N_3)_2 + 2H_2S = NCNC(NH_2)_2 + 2S + 2N_2$, when treated with hydrogen sulfide. It is interesting to interpret the reactions involved as consisting in the reduction of a mixed carbonic-nitric anammonide to a mixed carbonic-nitrous acid which breaks down into a carbonic acid and nitrous anammonide, $NCNC\ddagger(-N\equiv\ddagger N\ddagger\equiv N)_2 + 4H = NCNC\ddagger(-N\equiv\ddagger N+ -NH_2)_2$ or $NCNC\ddagger(-NH- +N\ddagger\equiv NH)_2 = NCNC(NH_2)_2 + 2N_2$.

Dicyanamidazide is reduced to dicyandiamide in a similar manner.

Tests for the Presence of Azide Groups.—During the early part of

[4] An ammonia analog of a purely hypothetical carbonic-nitric anhydride, $OC(ONO_2)_2$.

[5] Hantzsch and Vagt, *Ann.*, **314**, 362 (1900).

this investigation, some doubt was entertained as to whether or not we were dealing with azide groups in these compounds since azides tend to revert to the more stable isomeric tetrazoles. Although sodium azide is formed when dicyandiazide and dicyanamidazide, respectively, are warmed with sodium hydroxide solution, yet the literature concerning tetrazoles does not seem to exclude similarly acting substances from being ring compounds.[6] Tetrazoles are generally very resistant to the action of alkali or acid, so the formation of sodium azide by treating a compound with sodium hydroxide solution would strongly indicate the presence of a free azide group and not a stable ring compound. It is highly desirable that we have some other test to substantiate this one.

Turrentine[7] has shown that hydrogen sulfide reduces hydrazoic acid in the cold to nitrogen and ammonia. Thiele[8] in his investigation of guanyl-azide reduced this compound to guanidine with hydrogen sulfide, sulfur being precipitated and nitrogen evolved while in a similar manner Hantzsch and Vagt[9] reduced carbamic azide to urea.

These reactions together with experience to the effect that all the azides described in this paper readily undergo reduction when treated with hydrogen sulfide lead us to emphasize two tests for proving the presence of azide groups, (1) heating the substance with sodium hydroxide solution to form sodium azide and (2) the reduction of the azide group to the amino group by means of hydrogen sulfide with simultaneous evolution of nitrogen and the precipitation of sulfur.

Dicyanphenylamidazide and Phenyldicyandiamide.—When an alcoholic solution of dicyandiazide is treated with aniline, dicyanphenyl-amidazide is formed as represented by the equation, $NCNC(N_2)_2 + C_6H_5NH_2 = NCNC(N_3)NHC_6H_5 + HN_3$.

Dicyanphenylamidazide is a phenyl ester of a carbonic acid azide containing one unreplaced acid hydrogen atom in consequence of which it should show distinctly the properties of an acid. A sodium salt, stable in the presence of water, has been prepared.

When treated with hydrogen sulfide dicyanphenylamidazide is reduced to phenyldicyandiamide, $NCNC(NH_2)NHC_6H_5$, which is probably identical with phenylcyanguanidine.[10]

α-Naphthylamine, methylamine, ethylamine and phenylhydrazine were found to enter into reactions with dicyandiazide. With the exception of dicyan-α-naphthylamidazide the products formed were not purified and analyzed.

[6] See, for example, (a) Thiele and Ingle, *Ann.*, **287**, 233 (1895), and (b) Freund and Schander, *Ber.*, **29**, 2500 (1896); (c) Ott and Ohse, *Ber.*, **54**, 179 (1921).

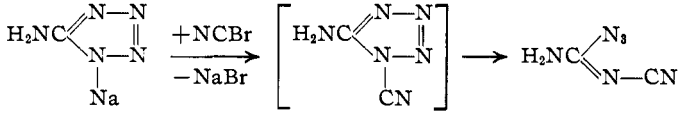
[7] Turrentine, THIS JOURNAL, **34**, 285 (1912).

[8] Thiele, *Ann. Chem.*, **270**, 48 (1892).

[9] Ref. 5, p. 355.

[10] Wheeler and Jamieson, THIS JOURNAL, **25**, 721 (1903).

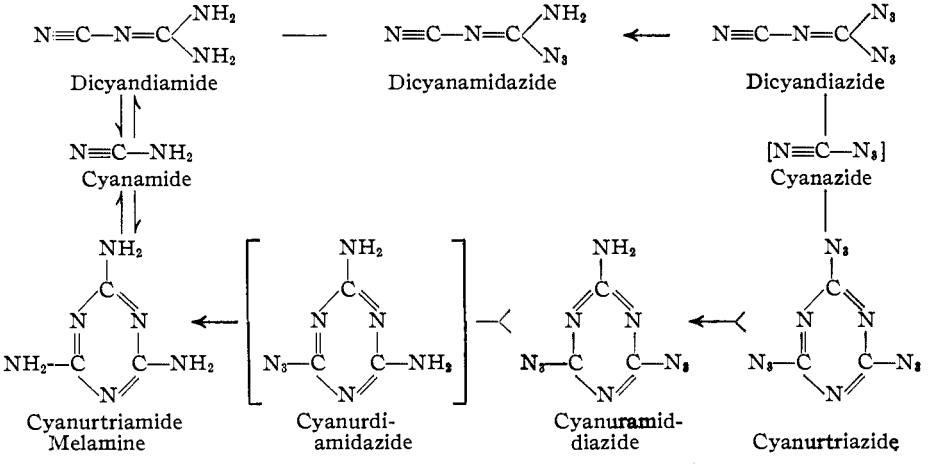
The Opening of a Tetrazole Ring.—An attempt was made to prepare 1-cyan-5-aminotetrazole, a tetrazole isomer of dicyanamidoazide (formula in bracket below) by treating the sodium salt of aminotetrazole with cyanogen bromide. Instead of the expected compound dicyanamidazide was obtained, the reaction taking the course represented by the scheme



Since aminotetrazole is formed from guanylazide by isomerization and the former is converted to dicyanamidazide by replacement of a hydrogen atom by a cyanogen group, the transformation of a compound possessing an azide group to a tetrazole, and from a tetrazole again to a compound having an azide group, has been effected.

Cyanurtriazide, $C_3N_3(N_3)_3$.—It will be recalled that cyanamide is capable of forming a trimolecular polymer known as melamine from which cyclic ammono carbonic acid three azides are theoretically derivable, depending upon whether it is considered as reacting with one, two or three molecules of hydrazoic acid.

Certain considerations led Ott, who first prepared this triazide, to assume that one or more tetrazole groupings might be present in the cyanurtriazide configuration. Referring to the two general tests already mentioned in this paper for the identification of azide groups, it is seen that the hydrolysis of cyanurtriazide into sodium azide and cyanuric acid by the action of hydroxide solution[6c] indicates the presence of three azide groups. In order to strengthen the evidence that cyanurtriazide contains three azide groups, it was subjected to the action of hydrogen sulfide, whereupon melamine was formed in accordance with the equation, $C_3H_3(N_3)_3 + 3H_2S =$



$C_3N_3(NH_2)_3 + 3S + 3N_2$. It must therefore be concluded that cyanurtriazide does not contain a single tetrazole group.

Cyanuramiddiazide, $C_3N_3(NH_2)(N_3)_2$ and Cyanurdichlorazide, $C_3N_3(Cl_2)N_3$.—The first compound was prepared by passing gaseous ammonia into an ether solution of cyanurtriazide; the second was obtained by treating one mole of cyanurtrichloride with one mole of sodium azide. Cyanuramiddiazide was reduced to melamine by the action of hydrogen sulfide.

Carbonic Acid Azides.—The scheme given above summarizes the relationships which have been established between three ammono carbonic acids and their azides.

Experimental Part

Preparation of Dicyandiazide.—To a solution of 25 g. of sodium azide in 100 cc. of water maintained at 0°, 45 g. of freshly prepared cyanogen bromide was added in small amounts with continuous stirring. After all of the cyanogen bromide was dissolved, the flask was removed from the ice-bath and allowed to stand three or four hours at room temperature, whereupon a colorless or slightly yellow oil separated at the bottom of the flask. The oil was extracted with alcohol free ether, washed once with a little water and then dried over anhydrous sodium sulfate. After one hour the ether solution was filtered into several evaporating dishes and the ether removed by a current of dry air. Some crystals usually formed on the sides of the dish and were carefully removed with a piece of filter paper and saved for future seeding. As a rule after the ether had disappeared, an oil remained to which a crystal of the substance had to be added in order to start the crystallization. After washing with a very small amount of anhydrous ether, the product was obtained in the form of needle-like crystals by recrystallization from pure, dry ether. The crystals were removed from the dish to a filter paper by the use of a horn spatula and dried *in vacuo* over phosphorus pentoxide. The yield was about 55%.

The purest reagents were used in this preparation since small amounts of impurities prevented crystallization even after seeding. If the crystals were not pure, or in case they were allowed to stand in contact with the mother liquor, a substance was formed after a time which was insoluble in ether and water, and was not exploded by shock. This fact was noted by Darzens, and believed by him to be evidence of the formation of a polymer of cyanogen azide. Furthermore, a well crystallized, explosive, water soluble compound showing no definite melting point was isolated from the reaction mixture. Unfortunately neither of these compounds was further investigated.

Dicyandiazide, especially when impure, is dangerously explosive. It is soluble in water, ether, chloroform and alcohol, but insoluble in petroleum ether. The purest crystals obtained in this investigation melted at 40.3° (corr.). Darzens gives the melting point, 35.5–36.0°. At a temperature of about 70°, it commences to decompose, and it explodes with extreme violence at about 170°.

The analysis of this compound was made by mixing the powdered sample intimately with powdered cupric oxide and so regulating the combustion that the substance decomposed at a little above 100°.

Anal. Calcd. for C_2N_8: C, 17.7; H, 0.0; N, 82.4. Found: C, 17.9; H, 0.02; N (Dumas), 82.0.

Mol. wt. of dicyandiazide, calcd. for C_2N_8: 136. Calcd. from the following data, 137.

Substance	Solvent	Depression	Mol. wt.
0.1014	($C_6H_5NO_2$), 17.33	0.293°	141
.1073	($C_6H_5NO_2$), 18.40	.308°	134
.1175	($C_6H_5NO_2$), 18.40	.341°	132
.1135	(C_6H_6), 11.83	.347°	141

Hydrolysis of Dicyandiazide by Boiling Water.—The apparatus and procedure used were essentially those used in the determination of carbon dioxide in rock analyses with the exception that a tube containing a 5% solution of silver nitrate was interposed between the reflux condenser and the drying tubes in order to absorb the hydrazoic acid. In solution in boiling water decomposition of the compound was rapid. The silver azide formed was filtered on a Gooch crucible and weighed as such. The carbon dioxide evolved was absorbed in a soda-lime tube at the end of the apparatus. The cyanamide remaining in solution in the reaction flask was determined by precipitation as the silver salt from a slightly ammoniacal solution. When the filtrate from this salt was acidified with dilute nitric acid, a gelatinous silver precipitate was formed which was not further investigated (dicyandiamide).

Anal. Calcd. for CO_2: 32.3. Found: 29.0. Calcd. for HN_3: 63.2. Found: 43.4. Calcd. for $NCNH_2$: 30.9. Found: 21.0.

Although the analytical data show the carbon dioxide which was formed to approximate the theoretical, the hydrazoic acid and the cyanamide obtained are far below the calculated amount.[5]

Hydrolysis of Dicyandiazide with Sodium Hydroxide Solution.—To a suspension of 0.1 g. in 10 cc. of water, 0.6 g. of sodium hydroxide was added and the solution was heated to about 70° for some two minutes. After dilution to about 100 cc., the cyanamide was precipitated from the slightly ammoniacal solution by adding a solution of silver nitrate. The silver azide was precipitated from the filtrate by acidifying with dilute nitric acid.

Anal. Subs., 0.1000: Ag_2NCN, 0.1926; AgN_3, 0.2115. Calcd. for $NCNH_2$: 30.9. Found: 31.6. Calcd. for HN_3: 63.2. Found: 60.7. 0.1926 g. of Ag_2NCN gave 0.2137 AgCl. Calcd. for Ag: 84.3. Found: 83.5. 0.2115 g. of AgN_3 gave 0.1971 AgCl. Calcd. for Ag: 71.9. Found: 70.2.

Reduction of Dicyandiazide to Dicyandiamide.—One gram of dicyandiazide was dissolved in about 5 cc. of alcohol. After diluting with 30 cc. of water, hydrogen sulfide was passed through the solution. Nitrogen was evolved and sulfur was precipitated immediately. After heating to 80° for a few minutes to coagulate the sulfur, the solution was filtered and the filtrate was evaporated with a current of dry air. The crystals of dicyandiamide thus obtained were, after recrystallization, found to melt at 207.4°. When mixed with pure crystals of dicyandiamide melting at 207.8° the mixture melted at 207.5°.

Ammonolysis of Dicyandiazide to Dicyanamidazide.—A slow current of ammonia was passed into a cold solution of 0.39 g. of dicyandiazide in about 150 cc. of dry ether. Ammonium azide separated as a white, flocculent precipitate. After filtration and removal of the ether, colorless, plate-like crystals of dicyanamidazide remained, which after recrystallization from ether melted at 151–152° with evolution of a gas; yield, 0.30 g.

Anal. Calcd. for $NCNC(NH_2)N_3$: C, 21.8; H, 1.8; N, 76.3. Found: C, 21.8; H, 1.8; N (Dumas), 76.2.

Dicyanamidazide is sparingly soluble in water and ether and is very soluble in alcohol and acetone. It is only slightly soluble in chloroform and hot benzene and it is insoluble in petroleum ether. When an aqueous solution of dicyanamidazide is boiled, hydrazoic acid is given off gradually. When heated with a concentrated solution of

sodium hydroxide, sodium azide, sodium carbonate, cyanamide and ammonia are formed. When heated in a tube it decomposes with a flash leaving a light brown residue (melon).

Dicyanamidazide from Aminotetrazole (the Opening of a Tetrazole Ring).—Aminotetrazole nitrate, 37 g., suspended in 50 cc. of water, was brought into solution and neutralized by adding a concentrated solution of sodium hydroxide, using phenolphthalein as an indicator. After cooling to about zero degrees, 27 g. of pulverized cyanogen bromide was added in small quantities while agitating. In order to increase the solubility of the cyanogen bromide, about 40 cc. of acetone was advantageously added at this point. Some heat was evolved. After standing for several hours, the solution was extracted with ether and the ether solution was dried with anhydrous sodium sulfate. Pure dicyanamidazide was obtained after evaporation and recrystallization from ether.[11] The crystals gave all the reactions characteristic of dicyanamidazide; melting point, 151–152°. A mixed melting point gave 151°.

Anal. Calcd. for $C_2H_2N_6$: C, 21.8; H, 1.8. Found: C, 21.8, H, 2.1.

Reduction of Dicyanamidazide to Dicyandiamide.—One gram of finely powdered dicyanamidazide was suspended in 30 cc. of cold water, and hydrogen sulfide was passed through the solution for half an hour. Nitrogen was evolved and sulfur was precipitated. The solution was heated almost to boiling in order to precipitate the sulfur and was then filtered. The cold solution was evaporated in a current of air to a small volume. After purification by three recrystallizations, the substance melted at 207.5°. When mixed with pure dicyandiamide melting at 207.8°, the mixture melted at 207.7°.

Dicyanamidazide Hydrochloride, $NCNC(NH_2)N_3 \cdot HCl \cdot H_2O$.—One gram of pure powdered dicyanamidazide was dissolved in 5 cc. of concentrated hydrochloric acid. Within a few minutes needle-like crystals separated out. The excess of acid was absorbed on a porous plate and after air-drying the crystals were dried for a short time in a desiccator. The hydrochloride containing one molecule of water gradually decomposes when heated, losing its crystalline appearance above 150°.

Anal. Calcd. for $C_2H_2N_6 \cdot HCl \cdot H_2O$: Cl, 21.6. Found: 21.7.

Dicyanphenylamidazide, $NCNC(N_3)NHC_6H_5$.—To a solution of 0.55 g. of dicyandiazide in 10 cc. of alcohol, a solution of 0.35 g. of aniline in 10 cc. of alcohol was added and thoroughly mixed. Hydrazoic acid was freely evolved and within half an hour needle-like crystals separated from the solution. After filtration the crystals were washed with a little alcohol. They were recrystallized from alcohol.

Anal. Calcd. for $C_8H_6N_6$: C, 51.6; H, 3.2. Found: C, 51.2; H, 3.2.

Dicyanphenylamidazide decomposes suddenly with evolution of a gas when heated above 145°. It is insoluble in most of the common solvents. It dissolves in concentrated hydrochloric acid, but it is reprecipitated upon dilution. When heated with concentrated sodium hydroxide solution, sodium azide and aniline are two of the products formed.

Sodium Dicyanphenylamidazide, $NCNC(N_3)N(Na)C_6H_5$.—Dicyanphenylamidazide, 0.5 g., was suspended in 3 cc. of water and a normal solution of sodium hydroxide was added until most of the azide dissolved. After filtration, the solution was concentrated to a small volume by a current of dry air. The crystals separated as very minute needles. They were dried in a desiccator.

Anal. Calcd. for $C_8H_5N_6Na$: Na, 11.1. Found: 11.0.

Reduction of Dicyanphenylamidazide to Phenyldicyandiamide.—Approximately 0.5 g. of dicyanphenylamidazide was suspended in a mixture of 5 cc. of alcohol and 5 cc. of water. After warming to 70°, hydrogen sulfide was passed into the solution. At the

[11] The yield was good (E. C. F.).

end of the reaction the solution was brought to boiling in order to coagulate the sulfur. After filtration, the solution was evaporated to a small volume by dry air. Plate crystals were obtained which after recrystallization from water melted at 195–196°. Phenylcyanguanidine[10] is described as forming needle crystals from water, melting at 190–191°.

Dicyan-α-naphthylamidazide, $NCNC(N_3)NHC_{10}H_7$.—One gram of dicyandiazide was dissolved in 15 cc. of alcohol and one gram of α-naphthylamine dissolved in an equal volume of alcohol was added. Hydrazoic acid was freely evolved and after some time beautiful needle crystals separated which were filtered and recrystallized from alcohol. The crystals decomposed slowly when heated. They were found to be insoluble in most of the common solvents. When heated with a concentrated solution of sodium hydroxide, sodium azide was formed and the odor of α-naphthylamine was observed.

Anal. Calcd. for $C_{12}H_9N_6$: C, 61.0; H, 3.4. Found: C, 60.9; H, 3.5.

Sodium Dicyan-α-naphthylamidazide, $NCNC(N_3)N(Na)C_{10}H_7$.—Dicyan-α-naphthylamidazide (0.3 g.) was suspended in 10 cc. of water and a little less than the calculated amount of normal sodium hydroxide was added. The solution was heated to boiling and filtered. Upon cooling, the sparingly soluble sodium salt crystallized out as needles.

Anal. Calcd. for $C_{12}H_7N_6Na$: Na, 8.9. Found: 8.9.

Reduction of Cyanurtriazide to Melamine.—Cyanurtriazide[6] (0.6 g.) was suspended in a mixture of 25 cc. of alcohol and 15 cc. of water and hydrogen sulfide was passed into the cold solution for about one-half hour. Nitrogen was evolved and sulfur was precipitated. After boiling and filtering, the solution was evaporated to about 7 or 8 cc. Upon cooling, melamine separated as colorless plate crystals. They were recrystallized once from hot water.

Anal. Calcd. for $C_3H_6N_6$: N, 66.6. Found: 66.2.

Cyanuramiddiazide, $C_3N_3(NH_2)(N_3)_2$.—Two grams of cyanurtriazide were dissolved in 200 cc. of anhydrous ether and a current of ammonia was passed through the solution for one hour. A white precipitate formed consisting of a mixture of ammonium azide and cyanuramiddiazide. After filtration, the mixture was treated with a little water in order to dissolve the ammonium azide. The cyanuramiddiazide remained undissolved as dense, colorless crystals which were recrystallized from a large volume of hot alcohol forming large plate-like crystals.

Anal. Calcd. for $C_3H_2N_{10}$: C, 20.2; H, 1.1. Found: C, 20.1; H, 1.2.

This substance does not melt sharply, but starts to decompose above 200°, gradually turning brown. It decomposes with great violence when heated suddenly to 210°. When treated with a solution of sodium hydroxide it dissolves and is reprecipitated when the solution is acidified. When heated with a strong sodium hydroxide solution, sodium azide, cyanamide and carbon dioxide are formed. It is insoluble in most of the common solvents.

Reduction of Cyanuramiddiazide to Melamine.—Cyanuramiddiazide (0.5 g.) was suspended in a mixture of 10 cc. of alcohol and 10 cc. of water. Hydrogen sulfide was passed into the warm solution. Notwithstanding the slight solubility of the substance the reaction took place with vigorous evolution of nitrogen and deposition of sulfur. After filtration, the solution was evaporated to a small volume, whereupon melamine separated as colorless plate crystals.

Anal. Calcd. for $C_3H_6N_6$: N, 66.6. Found: 66.1.

Cyanurdichloridazide, $C_3N_3(Cl_2)N_3$.—One gram of sodium azide was dissolved in 10 cc. of water and was slowly added to a solution of 3 g. of cyanurtrichloride in 20 cc. of acetone. After shaking for about five minutes, the solvent was allowed to evaporate spontaneously. Plate-like crystals separated which were filtered off, washed with water and recrystallized from a small amount of warm alcohol; m. p. 85°.

Anal. Calcd. for $C_2N_6Cl_2$: Cl, 37.2. Found: 37.7.

Cyanurdichloridazide is sparingly soluble in alcohol and insoluble in water. The usual tests showed the presence of an azide group.

In conclusion, the author wishes to extend his sincere thanks to Dr. Edward Curtis Franklin under whose guidance this work progressed.

Summary

1. The product previously known as cyanogen azide or carbon pernitride is shown to be dicyandiazide.

2. The azides studied are shown to be derived from the ammono carbonic acid, cyanamide and its polymers.

3. Two general tests, which show the distinction between compounds containing azide groups and their isomeric tetrazoles are described and their application demonstrated.

4. The structure of cyanurtriazide containing three azide groups is confirmed, thus eliminating the tetrazole structures which the original investigator considered.

5. A tetrazole ring is opened, revealing the free azide group from which the original tetrazole was derived.

6. The following new compounds are described: (1) dicyanamidazide, (2) dicyanamidazide hydrochloride, (3) dicyanphenylamidazide, (4) sodium dicyanphenylamidazide, (5) phenyldicyandiamide, (6) dicyan-α-naphthylamidazide, (7) sodium dicyan-α-naphthylamidazide, (8) cyanuricamiddiazide and (9) cyanuricdichloridazide.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

CATALYSIS IN THE CONVERSION OF ALLYL ALCOHOL AND ACROLEIN INTO PROPIONALDEHYDE

BY PAUL E. WESTON AND HOMER ADKINS

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F. H. Constable[1] concluded from a study of the rates of the reactions at different temperatures that allyl alcohol over copper showed two primary reactions

$$CH_2{=}CHCH_2OH = CH_2{=}CHCHO + H_2 \quad (1)$$
$$CH_2{=}CHCH_2OH = CH_3CH_2CHO \quad (2)$$

He demonstrated that propionaldehyde was not formed, as had previously been assumed, according to the reaction

$$CH_2{=}CHCHO + H_2 = CH_3CH_2CHO \quad (3)$$

For some time one of us has been greatly interested in those properties of oxide catalysts which determine the proportion of simultaneous and

[1] Constable, *Proc. Roy. Soc.* (*London*), **A113**, 254 (1926).