

TABLE II
TWISTING OF THE BENZENE RINGS IN 2-HALOBIPHENYLS

Substituent	C-halogen bond length, ^a Å.	van der Waals radius, ^b Å.	Angle ^c
H	1.04	1.20	42
F	1.35	1.35	49
Cl	1.69	1.80	64
Br	1.88	1.95	67
I	2.00	2.15	72

^a Electron Diffraction; P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950). ^b L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd ed., 1942, p. 189. ^c The distance between the rings is taken to be 1.50 Å., the carbon bond length 1.40 Å., and no deformation of the bonds is assumed.

the 2-substituent is increased. An increase in melting point would be expected with increasing molecular weight, and this is found for the 4-halobiphenyls. The melting point of the 2-halobiphenyls decreases as the molecular weight increases. This may be caused by the decreasing symmetry of the molecule as the benzene rings are twisted further out of plane. This is shown in Table III.

Conclusion

Steric repulsion, as found between the halogen

and *ortho* hydrogens in a 2-halobiphenyl, may cause a shift in the nuclear magnetic resonance absorption of the hydrogen atoms concerned. Examination

TABLE III
MELTING POINTS OF 2- AND 4-HALOBIPHENYLS^a

Substituent	M.p., °C.	M.p., °C.
H	69	69
F	71	74
Cl	34	76
Br	-20	89
I	Liquid	113

^a These values are taken from Beilstein's "Handbuch der Organischen Chemie."

tion of the spectra of model compounds makes it appear unlikely that the change in the resonance absorption is due to electronic effects.

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Some Salts of Nitrocyamide and their Efficiency as Primary Explosives

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The preparation and isolation of nitrocyamide and some of its salts are described. A number of the latter have been subjected to tests designed to determine their adaptability as initiating explosives.

Introduction

During an investigation of the use of N-alkyl-N-nitroso-N'-nitroguanidines in the preparation of diazohydrocarbons, McKay¹ isolated potassium nitrocyamide as a by-product. He noted that, when heated above its melting point on a spatula, this salt exploded and could be readily detonated by the blow of a hammer. These explosive properties of potassium nitrocyamide aroused interest in the possibility that some other salts of nitrocyamide might be even more susceptible of initiation to detonation. Considering the pressing need for more efficient primary explosives, this investigation was aimed primarily at preparing some of the heavier metal salts of nitrocyamide to test their suitability as initiating explosives.

The various salts of nitrocyamide were generally prepared by a metathetical reaction between silver nitrocyamide² and the appropriate metal chloride in a suitable solvent. Alternatively, a number of the salts were prepared by treating the solid metal carbonates with a solution of nitrocyamide in acetonitrile. This method proved particularly clean-cut.

Most of the nitrocyamide salts prepared

(1) A. F. McKay, *et al.*, *Can. J. Research*, **28B**, 683 (1950).
(2) A. F. McKay, W. G. Hatton and G. W. Taylor, unpublished data.

were readily eliminated from serious consideration as useful primary explosive compounds because they proved too insensitive to impact when tested upon the Bureau of Mines impact machine. These included all salts prepared, except those of potassium, tin, lead, barium, and silver. None of the others were detonated by the impact of a 5-kg. weight falling through a distance of 300 cm. A contributing factor to this insensitivity to impact may have been either hygroscopic moisture or water of crystallization. Each of the insensitive salts tested was hydrated, hygroscopic or both. Although the potassium salt could be consistently detonated by the impact of a 5-kg. weight falling from a height of 125 cm., this was well outside the impact sensitivity range of the commonly used primary explosives and thus it was eliminated. The tin and lead salts, though quite sensitive to impact when vacuum-dried over a desiccant, readily picked up enough moisture on short exposure to the atmosphere to greatly reduce their sensitivity to impact. This shortcoming was enough to remove them from any further consideration as practical primary explosive compounds.

A rather graphic illustration of the effect of hygroscopicity and/or water of crystallization upon impact sensitivity was obtained when the two lead salts and the tin salt of nitrocyamide were tested

in different states of dryness. When an air-dried sample of lead nitrocyanoamide tetrahydrate was tested for sensitiveness to explosion by impact on the Bureau of Mines impact machine, it was not detonated by the impact of a 5-kg. weight falling through a distance of 325 cm. This may be contrasted to its sensitivity when dried over anhydrous magnesium perchlorate before testing. Such a sample showed unit probability³ of explosion by impact at 15 cm. The dry, non-hydrated lead salt of nitrocyanoamide exhibited unit probability at a height of fall of only 10 cm. These results, along with similarly informative ones for the pentahydrated tin(II) salt of nitrocyanoamide, are summarized in Table I.

TABLE I
VARIATIONS OF SENSITIVENESS TO EXPLOSION BY IMPACT
DUE TO THE PRESENCE OF MOISTURE

Nitrocyanoamide salt	State of dryness	Minimum height of fall of 5-kg. weight, cm.	Per cent. of unit probability
Lead, tetrahydrate	Air-dried	325	0
Lead, tetrahydrate	Dried over Mg(ClO ₄) ₂	15	100
Lead, anhydrous	Dried over Mg(ClO ₄) ₂	10	100
Tin(II) pentahydrate	Air-dried	40	60
Tin(II) pentahydrate	Dried over Mg(ClO ₄) ₂	20	90

Among the salts of nitrocyanoamide prepared, only those of silver and barium are neither hygroscopic nor hydrated and appear to have any great potential for use as primary explosives. The maximum no-explosion⁴ heights as determined on the Bureau of Mines impact machine were found to be 6 and 8 cm., respectively, for the silver and barium salts. These results show that the two salts compare favorably with mercury fulminate-potassium chlorate (80-20) whose maximum no-explosion height is 5 cm.

The efficiency of an explosive in initiating detonation may be measured in terms of the minimum amount required to detonate a base charge and of the crushing power produced. When tested for efficiency of initiation according to the method of Taylor and Cope,⁵ it was found that 0.45 g. of silver nitrocyanoamide was the minimum charge necessary to detonate 1.25 g. of pressed tetryl in conventional gilding metal detonator shells. The sand crushed per unit weight of explosive charge weighed 91 g. Under the same conditions 0.40 g. of 80-20 mercury fulminate-potassium chlorate was necessary to ensure detonation crushing 80 g. of sand per unit weight of explosive charge. In Table II barium and silver nitrocyanoamide are compared in efficiency with a number of widely used primary explosive compositions on the basis of the minimum charge of each required to detonate

(3) Unit probability is here used to indicate that the compound being tested for sensitiveness to explosion by impact detonated 10 times out of 10 trials when struck by a 5-kg. weight dropped through a given minimum distance.

(4) The height of fall at which no explosion follows impact and 1 cm. above which an explosion does follow impact.

(5) G. B. Taylor and W. C. Cope, Bureau of Mines Tech. Paper 162 (1917).

a given weight of tetryl and the amount of sand crushed per gram of explosive charge in a detonator, as given by Grant and Tiffany.⁶

TABLE II
RELATIVE INITIATING VALUE OF VARIOUS PRIMARY EXPLOSIVES⁷

Primary explosive composition	Minimum charge of priming composition required to detonate 1.25 g. of tetryl, g.	Sand crushed per gram of explosive charge in detonator, g.
Lead azide-lead styphnate (80-20)	0.15	110
Diazodinitrophenol-potassium chlorate (75-25)	.25	103
Lead azide	.25	97
Mercury fulminate-potassium chlorate (80-20)	.40	83
Silver nitrocyanoamide	.45	91
Barium nitrocyanoamide	.50	80
Lead styphnate	1.50	..

It is readily apparent from the data in Table II that lead azide is the only pure explosive compound listed whose initiating efficiency is greater than that of barium and silver nitrocyanoamide on the basis of the minimum charge required to detonate a given weight of base charge and the amount of sand crushed per gram of explosive charge in the detonator.

Experimental⁸

Preparation of Silver Nitrocyanoamide.—Silver nitrocyanoamide, starting material for each preparation, was prepared by a variation of the method of McKay, *et al.*¹ A solution of 16 g. (0.4 mole) of sodium hydroxide in 600 cc. of water was cooled to -2° in a 1500-ml. beaker placed in an efficient hood. To this was added 44.1 g. (0.3 mole) of N-methyl-N-nitroso-N'-nitroguanidine over a 10-minute period. The continuously stirred reaction mixture was kept at 0° during the addition; the cooling bath was removed after the addition had been completed and the reaction mixture aged for 20 minutes, during which time it warmed to room temperature. To this mixture, which was no longer characterized by the yellow color of the nitroso compound, was added 36 ml. (0.4 mole) of concentrated nitric acid in 150 cc. of water, followed by 51 g. (0.3 mole) of silver nitrate in 150 ml. of water. The precipitate was filtered immediately and washed with hot water, giving 48.3 g. of silver nitrocyanoamide. Upon being chilled the filtrate deposited an additional 8.2 g. for an over-all 89.4% yield.

In an effort to determine the temperature at which silver nitrocyanoamide decomposes, a small amount was heated in a capillary tube placed in a beaker of oil. At approximately 115° the sample *detonated* with a sharp report and enough force to shatter both beaker and thermometer. Dry silver nitrocyanoamide *detonated with tremendous force* when a few drops of methyl iodide were added. It is therefore extremely important that great care be taken when working with the dry salt to avoid a dangerous explosion.

In an effort to demonstrate the existence of nitrocyanoamide in solution and to characterize its silver salt further by preparation of a known derivative, the following procedure was carried out: A portion of the above silver salt was dissolved in acetonitrile and treated with an equivalent amount of 1 N hydrochloric acid. After separation from the precipitate, which formed immediately, the filtrate was poured over an equivalent amount of potassium carbonate.

(6) R. L. Grant and J. E. Tiffany, *Ind. Eng. Chem.*, **37**, 661 (1945).

(7) The data on barium and silver nitrocyanoamide were obtained by R. L. Grant.

(8) All melting points were determined using a Fisher-Johns melting point apparatus (except as otherwise noted) and are uncorrected. Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill., or by Mr. Otho Harris of the Microchemical Laboratory, University of Pittsburgh, Pittsburgh, Pa.

Effervescence began immediately and continued until no solid potassium carbonate remained. Evaporation of the solvent and recrystallization of the residue from absolute ethanol gave white crystals which melted at 135–137° alone and on admixture with an authentic sample¹ of potassium nitrocyanoamide.

Ammonium Nitrocyanoamide.—To a solution of 0.54 g. (0.01 mole) of ammonium chloride in 3 ml. of water was added 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile. After standing overnight, the reaction mixture was filtered and the precipitate washed with acetonitrile and then with absolute ethanol. Vacuum-concentration of the filtrate gave a tacky white solid which was dissolved in absolute ethanol, filtered, and concentrated to about 2 ml. Addition of ether caused precipitation of a white hygroscopic solid. This product, after being vacuum-dried over Drierite, weighed 1 g. (96.2%). A sample was recrystallized several times from absolute ethanol–absolute ether to yield lustrous pearly white plates, m.p. 93–94°. Ammonium nitrocyanoamide gave a green Franchimont test⁹ with diethylaniline. It was dried to constant weight at 80° before analysis.

Anal. Calcd. for $\text{CH}_4\text{N}_4\text{O}_2$: N, 53.85. Found: N, 53.89.

Barium Nitrocyanoamide.—A solution of 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile was added to 1.2 g. (0.005 mole) of barium chloride dihydrate dissolved in 5 ml. of water. The reaction mixture was filtered after 20 minutes of intermittent shaking. The precipitated silver chloride was methanol-washed and the combined filtrates concentrated by a forced-air draft overnight. To the partly crystalline, partly liquid concentrate was added 2 ml. of methanol and 60 ml. of ether, the latter being introduced gradually. Continued trituration of the semi-solid concentrate in this medium finally led to a crystalline material which, after filtration, ether-washing, and air-drying, gave 1.60 g. (103% of the theoretical yield) of barium nitrocyanoamide. Recrystallization from methanol by the gradual addition of ether gave 1.53 g. (98.7%) of purified product, a sample of which showed no inclination to melt up to 275°. The grayish-white salt gave a dark, wine-red Franchimont test with diethylaniline.

Anal. Calcd. for $\text{C}_2\text{N}_6\text{O}_4\text{Ba}$: N, 27.17. Found: N, 27.40, 27.35.

Cadmium Nitrocyanoamide.—To 0.57 g. (0.0025 mole) of cadmium chloride, $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, in 1 ml. of distilled water was added 1.07 g. (0.006 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile. Immediately, a precipitate of silver chloride formed which was filtered off after 30 minutes. Concentration of the filtrate yielded a grayish solid which was purified by solution in acetone, filtration, and reprecipitation by the addition of petroleum ether. The grayish-white salt melted incompletely at 70–71° when heated upon the Fisher–Johns melting-point apparatus. As the temperature was raised the mass resolidified, forming a white solid which neither darkened nor remelted up to 250°.

When the melting point was determined, using a capillary tube, it was noted that the sample melted with evolution of gas at 88–90°. Cooling resulted in a product of the same color as the original. Upon reheating the residue began to melt at 88° with gradual decomposition, finally resulting in a white, high melting solid.

A sample of hygroscopic cadmium nitrocyanoamide dried to constant weight in a vacuum desiccator at room temperature prior to elemental analysis gave a nitrogen value (24.85%) considerably lower than that anticipated (29.54%) on the basis of the formula $\text{Cd}(\text{N}(\text{NO}_2)\text{CN})_2$.

Since a sample from a different batch contained an amount of nitrogen that did not differ significantly from the first, it was felt that the compound was probably hydrated, thus explaining both the low value and excellent agreement among the several results of nitrogen analyses. Analysis for carbon and hydrogen, in addition to that for nitrogen, ordinarily would give enough data to indicate whether the compound is of constant composition, thus ruling out impurities including hygroscopic moisture. Unfortunately, the samples submitted exploded during the carbon–hydrogen determination, reducing the validity of the results. The presence of a significant amount of hydrogen in a compound supposedly containing none, coupled with the excellent

agreement of the nitrogen with theoretical, strongly supports the assumption of a trihydrate. Assuming a trihydrate, the yield of purified material was 0.79 g. or 93% of the theoretical value. It gave a strong green Franchimont test with diethylaniline.

Anal. Calcd. for $\text{C}_2\text{N}_6\text{O}_4\text{Cd} \cdot 3\text{H}_2\text{O}$: C, 7.10; H, 1.78; N, 24.80. Found: C, 8.38; H, 2.68; N, 24.85.

Calcium Nitrocyanoamide.—To 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile was added 10 ml. of 1 N hydrochloric acid. The precipitated silver chloride was removed after 5 minutes of agitation and the filtrate immediately added to 0.5 g. (0.005 mole) of dry calcium carbonate. Effervescence began at once and continued until no more solid remained. The resulting solution was evaporated *in vacuo* and the remaining solid taken up in methanol. To the filtered methanol solution was added enough petroleum ether to cause an oily liquid to separate. After several days standing at room temperature, 1.2 g. (96.7%) of white solid formed. This hygroscopic salt, $\text{Ca}(\text{N}(\text{NO}_2)\text{CN})_2 \cdot 2\text{H}_2\text{O}$, melted sharply at 51–52° and gave a strong green Franchimont test with diethylaniline. The sample submitted for analysis exploded during the carbon–hydrogen determination.

Anal. Calcd. for $\text{C}_2\text{N}_6\text{O}_4\text{Ca} \cdot 2\text{H}_2\text{O}$: C, 9.68; H, 1.61; N, 33.87. Found: C, 8.42; H, 1.30; N, 34.21.

Cobalt Nitrocyanoamide.—To a solution of 1.19 g. (0.005 mole) of cobaltous chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, in 5 ml. of water was added a solution of 2.12 g. (0.11 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile. After 20 minutes aging the precipitated silver chloride was filtered off, washed with alcohol, and the filtrate was evaporated to dryness. The solid was recrystallized from absolute alcohol to yield 1.5 g. (97.5%) of reddish-brown crystals of cobalt nitrocyanoamide having 4 moles of water of crystallization. This salt gave a light-green Franchimont test with diethylaniline. It melted with decomposition at 170°.

Anal. Calcd. for $\text{C}_2\text{N}_6\text{O}_4\text{Co} \cdot 4\text{H}_2\text{O}$: C, 7.92; H, 2.64; N, 27.70. Found: C, 7.40; H, 2.10; N, 27.64.

Copper(II) Nitrocyanoamide.—To a solution of 0.85 g. (0.005 mole) of cupric chloride dihydrate in 5 ml. of water was added 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile. The reaction mixture was mechanically stirred for 20 minutes, then filtered after standing overnight. The filtrate was evaporated to near dryness and extracted successively with ethanol and methanol. After separation from an insoluble residue, the filtrate was vacuum-evaporated to yield 0.71 g. (94.6%) of pale-blue copper nitrocyanoamide containing 4 moles of water of crystallization, m.p. 132–133°. It gave the characteristic blue color of copper salts when dissolved in the acetic acid necessary for the Franchimont test. This color remained unchanged when the Franchimont reagents were added. The compound exploded during carbon–hydrogen analysis.

Anal. Calcd. for $\text{C}_2\text{N}_6\text{O}_4\text{Cu} \cdot 4\text{H}_2\text{O}$: C, 7.80; H, 2.60; N, 27.30. Found: C, 8.14; H, 2.59; N, 27.46.

Lead Nitrocyanoamide.—To 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile was added 10 ml. of 1 N hydrochloric acid. The reaction mixture was filtered and the silver chloride washed with methanol. The filtrate was added immediately to 1.90 g. (0.005 mole) of lead acetate, $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$, and the resulting solution concentrated to a small volume of slightly viscous pale yellow material. This material was treated with dioxane, filtered, and again concentrated by a forced-air draft. Crystals were finally obtained upon trituration with a small amount of dioxane. This hygroscopic cream colored solid was analyzed for nitrogen and gave a value in excellent agreement with the theoretical value for the tetrahydrate. It did not melt below 250°, but a sample decomposed when left overnight in an oven at 70°.

Anal. Calcd. for $\text{C}_2\text{N}_6\text{O}_4\text{Pb} \cdot 4\text{H}_2\text{O}$: N, 18.62. Found: N, 18.85, 18.97.

A second sample was prepared in similar fashion to the above, except that the solution of lead salt was vacuum-evaporated to dryness. This salt was vacuum-dried to constant weight over magnesium perchlorate and then analyzed for nitrogen without further attempts at purification. The analysis indicated a non-hydrated product. This salt melted with decomposition at 123–124°, leaving a white, solid residue as the temperature was increased. Both

(9) A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 226 (1897).

salts gave a dark-green Franchimont test with diethylaniline.

Anal. Calcd. for $C_2N_6O_4Pb$: N, 22.15. Found: N, 22.13, 22.34.

Lithium Nitrocyanoamide.—To 0.43 g. (0.01 mole) of lithium chloride in 2 ml. of water was added 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile. The silver chloride which formed was filtered after the reaction mixture had stood for 20 minutes. The filtrate was vacuum-concentrated to yield 0.9 g. (96.8%) of lithium nitrocyanoamide containing 2 moles of water of crystallization. This salt was purified by being dissolved in absolute alcohol, from which it separated as an oily liquid. After several washings with ether, this material, when left in a vacuum desiccator overnight, gave a hard but waxy product which was quite hygroscopic. It melted at 94–95°. One part of the sample submitted for analysis was dried to constant weight at 80°, while another was dried in a vacuum desiccator overnight at room temperature. The amounts of nitrogen found in the two specimens were not significantly different.

Anal. Calcd. for $CN_3O_4Li \cdot 2H_2O$: N, 32.56. Found: N, 32.63, 32.42.

Sodium Nitrocyanoamide.—The sodium salt of nitrocyanoamide was prepared by a variation of the method of McKay, *et al.*¹ To a solution of 0.8 g. (0.02 mole) of sodium hydroxide, kept at 0° by external cooling, in 10 ml. of ethanol was added 2.94 g. (0.02 mole) of N-methyl-N-nitroso-N'-nitroguanidine over a 5-minute period. The reaction mixture was concentrated and the solid residue recrystallized from absolute ethanol to yield 2 g. (91.7%) of sodium nitrocyanoamide. The white, crystalline salt softened with decomposition at 202°. It gave a light-green Franchimont test with diethylaniline.

Anal. Calcd. for CN_3O_2Na : N, 38.53. Found: N, 38.21, 38.27.

Strontium Nitrocyanoamide.—To a solution of 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile was added 10 ml. of 1 N hydrochloric acid. There was an immediate precipitate of silver chloride. After 15 minutes of shaking, the mixture was filtered and the filtrate immediately poured over 0.78 g. (0.005 mole) of strontium carbonate. Effervescence began at once and continued until no solid remained. The resulting liquid was concentrated overnight to yield 1.56 g. of a cream-colored solid. This quantity represented a 120% yield based on a non-hydrated strontium nitrocyanoamide or a 99.4% yield assuming a trihydrate. When this material was dissolved in a minimum amount of methanol and petroleum ether added to the point of cloudiness, recrystallization occurred after overnight standing. The purified salt, $Sr(N(NO_2)CN)_2 \cdot 3H_2O$, melted at 77–79°, resolidified, and did not remelt below 250°. A sample submitted for analysis exploded while undergoing composition incidental to determination of carbon and hydrogen, scattering the material on the walls of the combus-

tion tube. This occurrence may well explain the low carbon value, particularly if the solid on the walls was strontium carbonate. Strontium nitrocyanoamide gave a dark-green Franchimont test with diethylaniline.

Anal. Calcd. for $C_2N_6O_4Sr \cdot 3H_2O$: C, 7.66; H, 1.91; N, 26.78. Found: C, 5.01; H, 2.01; N, 26.46.

Tin(II) Nitrocyanoamide.—To 1.13 g. (0.005 mole) of stannous chloride in 10 ml. of acetonitrile was added 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile. The reaction mixture was permitted to stand overnight then filtered. Vacuum-evaporation of the filtrate yielded 1.3 g. (89.6% of the expected yield) of a light brown salt. This material could be successively recrystallized from either water or acetonitrile without undue loss and analyzed for the pentahydrate. It gave a green Franchimont test with diethylaniline. The purified sample melted at 151° dec.

Anal. Calcd. for $C_2N_6O_4Sn \cdot 5H_2O$: N, 22.06. Found (recrystd. from water): N, 22.09, 22.23. Found (recrystd. from acetonitrile): N, 22.25, 22.31.

Zinc Nitrocyanoamide.—To a solution of 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile was added an excess of a saturated zinc chloride solution. The reaction mixture was filtered after aging for 20 minutes, the precipitate washed with acetone, and the filtrate evaporated to yield a viscous liquid which gave crystals upon trituration in the presence of ether. Excess zinc chloride was removed from the zinc nitrocyanoamide by washing repeatedly with ether. Recrystallization from acetone-ether gave 2.34 g. (98.7%) of white hygroscopic solid which showed no apparent change nor inclination to melt up to 250°. It gave a light-green Franchimont test with diethylaniline.

Anal. Calcd. for $C_2N_6O_4Zn$: N, 35.38. Found: N, 35.37, 35.17.

Nitrocyanoamide.—To a solution of 1.94 g. (0.01 mole) of silver nitrocyanoamide in 10 ml. of acetonitrile was added enough anhydrous hydrogen chloride to cause complete precipitation of silver chloride. After removal of this precipitate the filtrate was evaporated *in vacuo* to give a white, crystalline material, the amount of which was about 12% more than was expected on the basis of the formula, $HN(NO_2)CN$. The 1.04-g. yield was quantitative on the basis of this formula when calculated to contain a mole of water of crystallization. It melted sharply at 137–138° and gave a light-green Franchimont test with diethylaniline. The free acid decomposed slowly but was identified by its well known potassium salt. The elemental analysis was in much better agreement with the constitution of the hydrated form than with the non-hydrated.

Anal. Calcd. for $CHN_3O_2 \cdot H_2O$: C, 11.43; H, 2.86; N, 40.00. Found: C, 12.38, 12.37; H, 2.90, 2.96; N, 40.03, 40.10.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, UNIVERSITY OF MICHIGAN, MEDICAL SCHOOL]

Dissociation of Copper Pyridoxylidenevaline¹

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The chelate cupric pyridoxylidenevaline is exceedingly stable in water, more stable than copper valine₂. Excesses of the order of 1000 to 1 of valine can, however, displace the Schiff base from the Cu to permit evaluation of the stability constant. As the *pH* is lowered to *pH* 4.5, the reaction proceeds more slowly, showing first-order reversible kinetics. The valine anion is clearly a reactant. Part of the pyridoxylidenevaline formed then breaks down, this reaction being the slower one at higher *pH* and the more rapid one at lower *pH*. Release of pyridoxal preceding the release of copper occurs slowly if at all.

In its coenzyme function pyridoxal-5-phosphate undoubtedly forms Schiff bases with the amino acids.^{2–5} Metal chelation of the Schiff base⁴ may

(1) Supported in part by a Grant (C-2645) from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service.

(2) E. Koch and W. Werle, *Biochem. Z.*, **319**, 305 (1949).

or may not be necessary for the enzymatic catalysis. We have been interested in determining

(3) J. Baddiley, *Nature*, **170**, 711 (1952).

(4) D. E. Metzler, M. Ikawa and E. E. Snell, *THIS JOURNAL*, **76**, 648 (1954).

(5) W. T. Jenkins and I. W. Sizer, *ibid.*, **79**, 2655 (1957).