[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

THE NITRATION OF 5-AMINOTETRAZOLE[1]

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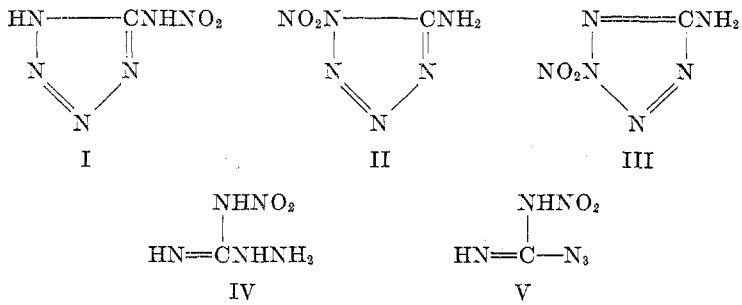
The similarity between 5-aminotetrazole and guanidine in certain structural features suggested that nitraminotetrazole might be prepared from 5-aminotetrazole much as nitroguanidine can be prepared from guanidine. 5-Aminotetrazole has generally been looked upon as an acidic substance since it was first described by Thiele (1). Although the amino group can be acylated (2) and under suitable conditions diazotized (1), its salts with mineral acids are extensively hydrolyzed in aqueous solution.

5-Aminotetrazole nitrate (3) can be prepared by crystallization of 5-aminotetrazole from warm, moderately concentrated nitric acid. Presumably the amino group is involved in salt formation, although participation of the ring nitrogens cannot be excluded. Dehydration of the nitrate with sulfuric acid at room temperature led to the formation of a nitraminotetrazole. Analogy with the guanidine series suggested that 5-nitroaminotetrazole (I) would be formed but structures such as 1-nitro-5-aminotetrazole (II) or 2-nitro-5-aminotetrazole (III) could not be excluded.



Lieber, *et al.* (4) have recently described a compound prepared by the interaction of N-nitro-N′-aminoguanidine (IV) and nitrous acid followed by cyclization of the resulting azide (V) to which they have assigned the structure of 5-nitraminotetrazole (I). Assignment of structure was based on the reduction of the nitro compound to 5-tetrazolylhydrazine which Thiele had prepared by reduction of diazotized 5-aminotetrazole (5) and by decomposition of 5-azotetrazole (6).

The nitraminotetrazole prepared from 5-aminotetrazole differed in certain respects from the compound prepared from nitroaminoguanidine. The former crystallized as a hydrated dioxanate which lost its solvent of crystallization in three or four days at room temperature or in 8–10 hours at 60–70°; drying at

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higher temperatures may be dangerous. Furthermore, the compound was not sensitive to shock even when struck very sharply with a hammer on an anvil. The product from nitroaminoguanidine was said to crystallize as an anhydrous solid which was sensitive to shock (4b).

In order to resolve these differences the preparation of 5-nitraminotetrazole according to Lieber, *et al.* (4b) was repeated. The product so prepared also crystallized as a hydrated dioxanate and failed to exhibit sensitivity to shock. The previously reported shock-sensitivity may have been due to a trace of the azide as a contaminant. In other respects, including ultraviolet absorption spectrum and potentiometric titration, the nitraminotetrazoles prepared by both methods were identical. The ultraviolet absorption spectrum showed a peak at 277–278 mμ for solvated and anhydrous nitraminotetrazoles prepared by both methods.

On potentiometric titration 5-nitraminotetrazole behaves as a dibasic acid. The first dissociation has been described as that of a completely dissociated strong acid (4a) while the second dissociation constant is about 9×10^{-7}. Al-

TABLE I

*p*H OF AQUEOUS SOLUTIONS OF DIFFERENT CONCENTRATIONS OF NITRAMINOTETRAZOLE

MOLARITY $\times 10^3$	*p*H CALC'D	*p*H OBSERVED	APPARENT $K_{a_1} \times 10^2$ FROM OBSERVED *p*H
7.98	2.10	2.23	1.66
8.33	2.08	2.22	1.59
59	1.23	1.45	5.38
99.3	1.00	1.28	5.89
150	0.82	1.12	7.77

though the results of potentiometric titrations of solvated and anhydrous products prepared by both methods were identical, we cannot subscribe to the conclusion that the first dissociation is that of a completely dissociated strong acid. In Table I are given observed values for the *p*H of aqueous solutions of nitraminotetrazole at several concentrations together with *p*H values calculated on the assumption of complete dissociation. Apparent "dissociation constants" calculated from the observed *p*H of the solutions are also included in the Table. The data, although not adequate for determination of the first dissociation constant, do not support the contention that nitraminotetrazole is completely dissociated in dilute aqueous solutions. Its behavior is more comparable to that of a moderately strong dibasic acid such as oxalic acid. Our values, 8.9 and 9.1×10^{-7} for the two preparations, for the second dissociation constant are in good agreement with the value observed by Lieber, *et al.* (4a).

EXPERIMENTAL[2,3]

5-Aminotetrazole. (All operations should be done in a good hood.) A large scale adaptation of the preparation of 5-aminotetrazole (7) is described. Powdered dicyandiamide (328 g.) and 528 g. of powdered sodium azide were suspended in 800 ml. of water in a 5 l.-resin flask.

[2] Analyses were done by the Micro-Tech Laboratories, Skokie, Illinois.

[3] Temperatures for melting points are corrected.

The top of the flask was secured and fitted with an efficient reflux condenser, a stirrer, and a dropping-funnel. The flask was warmed to 50° in a water-bath after which 680 ml. of concentrated hydrochloric acid was added with stirring through the dropping-funnel at such a rate that the hydrazoic acid liberated refluxed very slowly. Addition of the acid required about an hour during which period the water-bath was allowed to warm to 65–70° where it was maintained for six hours. The stirrer was stopped and crystallization of the product began soon after addition of the hydrochloric acid was complete. The reaction mixture was allowed to stand at room temperature overnight, then thoroughly chilled in an ice-bath before the product was filtered by suction and washed with ice-water. The crude product was recrystallized from 1500 ml. of boiling water from which it separated as the monohydrate. After drying at 110° anhydrous 5-aminotetrazole was obtained, yield 610 g., m.p. 206° with decomposition in a capillary (1).

5-Aminotetrazole nitrate. The salt was prepared by crystallization of 10 g. of anhydrous 5-aminotetrazole from a warm mixture of 16 g. of concentrated nitric acid and 15 ml. of water. Prolonged heating of the solution causes decomposition of the aminotetrazole. The crude product, still wet with nitric acid, was recrystallized from water, yield 15 g. (97%), m.p. 178–179° with decomposition in a capillary; previously (3) m.p. 174–175° had been reported.

Anal. Calc'd for $CH_4N_6O_3$: C, 8.11; H, 2.72; N, 56.78.
Found: C, 8.48; H, 2.91; N, 56.82.

5-Nitraminotetrazole from 5-aminotetrazole nitrate. Finely divided 5-aminotetrazole nitrate (14.8 g., 0.1 mole) was added in small portions with stirring and cooling to 20 ml. of concentrated sulfuric acid. The milky mixture was allowed to stand at room temperature until it became homogeneous. The cold sulfuric acid solution was diluted with 250 ml. of ice and water after which slightly less than the amount of barium carbonate required for complete neutralization of the sulfuric acid was added. The mixture was digested on a steam-bath until carbon dioxide evolution ceased. Barium sulfate was separated by centrifugation and was washed twice by resuspension in hot water. The aqueous solutions were combined and evaporated to about 100 ml. under reduced pressure on a water-bath. The concentrate was shaken with five 100-ml. portions of ether. After evaporating the combined ethereal extracts almost to dryness in a current of air, the residue was treated with 250 ml. of benzene which caused the product to separate as colorless plates. Recrystallization by dissolving in a small volume of 1,4-dioxane and adding a large excess of benzene gave 10.7 g. (54%) of solvated 5-nitraminotetrazole which decomposed with a reddish flash at about 135° on the melting point block. In a capillary the product decomposed with gas evolution at 160–170°.

The aqueous concentrate was evaporated to about 10 ml. and extracted with three 50-ml. portions of ether. The ethereal extracts were treated as just described to give 0.8 g. of solvated product of the same decomposition characteristics. The total yield of solvated product was 11.5 g. (58%).

Although several samples of the solvated product had been dried successfully at 100°, one sample of about 0.15 g. exploded with shattering force in the oven at 100°. Subsequently drying temperatures of 60–70° were used without untoward occurrences. Solvent of crystallization was also lost slowly on standing with exposure to the atmosphere at room temperature. The presence of water in the solvated product was demonstrated qualitatively by the evolution of acetylene when calcium carbide was added to a solution of the material in dry ether. The gas evolved gave a colorless precipitate when passed into alcoholic silver nitrate solution. Anhydrous 5-nitraminotetrazole did not cause gas evolution under these conditions. Water was also estimated quantitatively with the Karl Fischer reagent.

Anal. Calc'd for $2CH_2N_6O_2 \cdot C_4H_8O_2 \cdot 2H_2O$: C, 18.8; H, 4.2; N, 43.7; H_2O, 9.4.
Found: C, 19.4, 19.5; H, 4.2, 4.3; N, 43.1, 43.3; H_2O, 10.3.

Anal. Hydrated dioxanate dried at 70° for 24 hours. Calc'd for $2CH_2N_6O_2 \cdot C_4H_8O_2 \cdot 2H_2O$: $C_4H_8O_2 \cdot 2H_2O$, 32.3.
Found: 29.6. When air-dried at room temperature for six days the weight loss was 30.5%.

Anal. Anyhdrous 5-nitraminotetrazole. Calc'd for $CH_2N_6O_2$: C, 9.2; H, 1.6, N, 64.6. Found: C, 9.6, 9.6; H, 1.7, 1.6; N, 64.7, 64.5.

5-Nitraminotetrazole from N-nitro-N'-aminoguanidine. A quantity of 5-nitraminotetrazole was prepared from nitroaminoguanidine (8) following the procedure of Lieber, *et al.* (4b). The product was isolated as described by these authors and was found to be solvated.

Anal. Hydrated dioxanate dried at 70° for 24 hours. Calc'd for $2CH_2N_6O_2 \cdot C_4H_8O_2 \cdot 2H_2O$: $C_4H_8O_2 \cdot 2H_2O$, 32.3. Found: 29.1.

The yield of 5-nitraminotetrazole was improved substantially by the following modified procedure. To a cold solution of 9.4 g. of sodium nitrite and 13.7 g. of N-nitro-N'-aminoguanidine in 50 ml. of water there was added with cooling (below 15°) and stirring a cold mixture of 11.8 ml. of concentrated hydrochloric acid and 50 ml. of water. The mixture was allowed to come to room temperature and was filtered and evaporated to dryness in a current of air. The residue was extracted with three 100-ml. portions of ether. Evaporation of

TABLE II

SALTS OF 5-NITRAMINOTETRAZOLE WITH ORGANIC BASES

AMINE	M.P.,[a] °C.	M.P.,[b] °C.	FORMULA	N[a]	
				Calc'd	Found
Pyridine[c]	131–132	131–132	$C_6H_7N_7O$	46.2	46.7 46.7
N-Diethylaniline[d]	124–125	124–125	$C_{11}H_{17}N_7O$	35.1	35.5 35.7
2-Aminopyridine[e]	181–182	181–182	$C_6H_8N_8O$	50.0	49.9 50.2
Ethylenediamine[f]	239	239	$C_3H_{10}N_8O$	58.9	58.9 59.0

[a] Salts of 5-nitraminotetrazole prepared from 5-aminotetrazole. All compounds decompose in the capillary at the melting point. Temperatures corrected. [b] Salts of 5-nitraminotetrazole prepared from N-nitro-N'-aminoguanidine. Corrected temperature; compounds decompose in the capillary on melting. [c] Recrystallized from acetone. [d] Recrystallized from ethyl acetate; m.p. 109° previously reported (4d). [e] Recrystallized from 1:1 isopropyl alcohol-ethanol. [f] Recrystallized from aqueous isopropyl alcohol.

the ether left a residue of crude nitroguanyl azide that was taken up in 100 ml. of 95% ethanol and treated with an aqueous-alcoholic solution of sodium acetate until precipitation of the sodium salt of 5-nitraminotetrazole was complete. The sodium salt was filtered and air-dried. Yield 13 g. (75%); explodes at 210–220° on the melting point block.

A solution of 8.7 g. of sodium nitraminotetrazole in 30 ml. of water was treated with 25 ml. of 18% hydrochloric acid. The solution was extracted with five 100-ml. portions of ether from which 8.0 g. of solvated 5-nitraminotetrazole was isolated by concentration and precipitation with benzene. Concentration of the aqueous solution to 10 ml. and extraction with three 100-ml. portions of ether, followed by evaporation of the ether and precipitation with benzene gave 2 g. of the product. The combined fractions were recrystallized from a 1,4-dioxane-benzene mixture as before to give 9.5 g. of solvated product (86% from the sodium salt) showing the decomposition behavior described before.

Salts of 5-nitraminotetrazole. A solution of solvated 5-nitraminotetrazole in ether was treated with an ethereal solution of the appropriate amine. The salt precipitated immediately and was filtered and recrystallized from the solvent indicated in Table II. Salts were pre-

pared from 5-nitraminotetrazole prepared by both methods. The amines used, physical constants, and analytical data are given in Table II.

Ultraviolet absorption spectra of 5-nitraminotetrazole prepared by both methods were observed in aqueous solutions at molarities of 10^{-4} to 10^{-5} using a Beckman Model DU Spectrophotometer. Both anhydrous and solvated materials were examined. The absorption curves for all were identical; a single maximum was noted at 277–278 mμ as previously reported (4c).

Potentiometric titrations were done with approximately 0.005–0.008 *molar* aqueous solutions of solvated and anhydrous preparations of 5-nitraminotetrazole from both sources using a Beckman Model G *p*H Meter. All titrations were done at 25° ± 0.02° in an initial volume of 200 ml. and using 0.1043 *N* potassium hydroxide. From the titration curves the apparent Ka_2 for the anhydrous compounds was determined as 8.9×10^{-7} and 9.1×10^{-7} for products prepared from 5-aminotetrazole and nitroaminoguanidine, respectively. In addition the *p*H of small volumes of approximately 0.05, 0.1, and 0.15 *molar* solutions of anhydrous 5-nitraminotetrazole was determined with the Beckman *p*H meter. The data are recorded in Table I together with the *p*H calculated in each instance assuming complete dissociation of the first hydrogen and the "dissociation constant" calculated from the hydrogen ion concentration corresponding to the observed *p*H values. Data for two approximately 0.008 *molar* solutions, the initial points of the titrations curves, are also included in Table I.

Further studies on the nitration of aminotetrazole derivatives are in progress.

SUMMARY

The formation of a nitraminotetrazole by nitration of 5-aminotetrazole has been observed. The product is a dibasic acid whose first dissociation appears to be that of a moderately strong acid. The nitraminotetrazole so formed is identical with the product prepared from N-nitro-N′-aminoguanidine to which the structure of a 5-nitraminotetrazole has been assigned. The two products have been compared and they exhibit identical absorption spectra and potentiometric titration curves and form identical salts with a number of amines.

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