1.5 g. (0.0115 mole) of nitroguanyl azide in 15 ml. of water was heated to 60° on the steam-bath, cooled in an ice-bath and then left at room temperature until the solvent evaporated. The residual solid was stirred with 5 ml. of water and filtered, giving 1.21 g. (62.3%) of potassium 5-nitroaminotetrazole.

Reaction of Nitroguanyl Azide with Amines. A. Aniline.—A solution of 4.8 g. (0.05 mole) of freshly distilled aniline in 10 ml. of ethanol was added to a solution of 6.5 g. (0.05 mole) of nitroguanyl azide in 50 ml. of ethanol. The mixture turned yellow, then red-orange, and after three hours began to deposit small plates. After standing overnight, filtration gave 4.81 g. of solid product. Spontaneous evaporation of the filtrate gave another 4.83 g. of solid, 2.66 g. of which was soluble in water and was, after isolation, combined with the first crop of crystals.

The water insoluble residue, 2.0 g., was crystallized from aqueous ethanol and then from absolute ethanol, giving fine white needles, melting at 152–155°. This compound was identified as N-phenyl-N′-nitroguanidine by analysis and by comparison with an authentic specimen prepared by the method of McKay and Wright[10]; yield 20%.

The water soluble product phenylammonium 5-nitroaminotetrazole, 7.47 g. (67%), was recrystallized from absolute ethanol, giving large lustrous plates which decompose without melting at about 160°. This substance soluble in water and hot ethanol, insoluble in the common organic solvents, gives a weakly acid reaction in water solution, liberates aniline when treated with dilute sodium hydroxide and liberates 5-nitroaminotetrazole when treated with dilute sulfuric acid. It also results from the addition of aniline to an absolute ether solution of 5-nitroaminotetrazole.

Anal. Calcd. for $C_7H_9N_7O_2$: C, 37.67; H, 4.06; N, 43.93. Found: C, 37.88; H, 4.28; N, 44.20.

B. **β-Naphthylamine.**—Application of the procedure described in A, using 2.86 g. (0.02 mole) of β-naphthylamine and 2.6 g. (0.02 mole) of nitroguanyl azide, gave a 75% yield of crude β-naphthylammonium 5-nitroaminotetrazole. This salt is rather insoluble in the common solvents, including water, but can be recrystallized from an acetone–water mixture (one drop of water to one ml. of acetone), giving thin white plates which decompose without melting at 175–177°.

Anal. Calcd. for $C_{11}H_{11}N_7O_2$: C, 48.35; H, 4.06; N, 35.88. Found: C, 48.28; H, 4.20; N, 35.70.

C. ***n*-Butylamine.**—A solution of 1.46 g. (0.02 mole) of *n*-butylamine in 10 ml. of ethanol was added to a solution of 2.6 g. (0.02 mole) of nitroguanyl azide in 20 ml. of ethanol. An immediate temperature rise was noted. Spontaneous evaporation of the solution gave a mixture of crystals and oil which was washed with acetone. Recovery of a second crop of crystals from the acetone gave a total of 2.3 g. (79%) of *n*-butylammonium 5-nitroaminotetrazole. Recrystallization from hot 3:1 benzene–ethanol gave lustrous colorless plates decomposing at 161–163°. This salt is very soluble in water and alcohol and rather insoluble in the other common solvents.

Anal. Calcd. for $C_5H_{13}N_7O_2$: C, 29.55; H, 6.45; N, 48.25. Found: C, 29.60; H, 6.35; N, 48.55.

D. **Diethylamine.**—A solution of 1.46 g. of diethylamine in 10 ml. of ethanol was added to a solution of 2.6 g. of nitroguanyl azide in 20 ml. of ethanol. An immediate temperature rise was noted. Spontaneous evaporation of the solution gave 1.0 g. of crystals, after washing with ether, and an oil. The oil treated with an additional 1.46 g. of diethylamine in ethanol, gave another 4.0 g. of crystalline product. The total yield of di-(diethylammonium)-5-nitroaminotetrazole was about 90%. Recrystallization from warm 3:1 benzene–ethanol gave white needles melting at 105° with decomposition. This double salt is soluble in water and ethanol but not soluble in the common solvents. The salt was also synthesized in good yield by adding diethylamine to an absolute ether solution of 5-nitroaminotetrazole.

Anal. Calcd. for $C_9H_{24}N_8O_2$: C, 39.11; H, 8.75; N, 40.55. Found: C, 39.10; H, 8.84; N, 40.60.

Acknowledgment.—The support rendered to E. L. and E. S. by Research Contract N-123S-61517, Task Order 1, with the U. S. Naval Ordnance Test Station, Inyokern, China Lake, California, is gratefully acknowledged.

CHICAGO, ILLINOIS RECEIVED JULY 31, 1950

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[10] A. F. McKay and G. F Wright, THIS JOURNAL, **69**, 3028 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

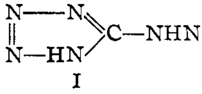
The Ultraviolet Absorption Spectra of 5-Nitroaminotetrazole and its Salts

BY EUGENE LIEBER, EDWARD SHERMAN[1] AND SEYMOUR H. PATINKIN

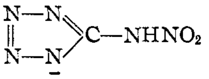
The ultraviolet absorption spectra for 5-nitroaminotetrazole and four of its salts have been studied in water solution. The free acid and its mono- and di-salts all have the same peak at 277 mμ. The removal of the first proton from the nitramide side chain of 5-nitroaminotetrazole yields an absorbing species similar in structure to the doubly charged anion. It is postulated that these species absorb at the same frequency. A zwitterion structure is proposed for nitroaminoguanidine and related substances.

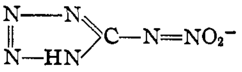
Introduction

In a previous communication[2] the preparation and properties of 5-nitroaminotetrazole (I) were described. I is an acidic substance combining


I

in a single compound the acidic properties of the tetrazole ring and the nitramide group. Well-defined crystalline mono- and di-acid salts of inorganic and organic bases are readily formed either by direct reaction with I or by isomerization of nitroguanyl azide with the desired base.[2] The interesting problem of determining the structure of the mono-acid salt arises, since the anion may have either the structure II or III.


II


III

It was suggested[2] that the mono-acid salts of I are in the *aci-nitro* form (III) on the basis of the comparative greater acidity of I with respect to tetrazoles which lacked the nitramine group. Evidence for either II or III was sought by a comparative ultraviolet absorption spectra study of I and its salts with other nitramides of the type of nitramide[3] and nitroaminoguanidine.

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[1] Quaker Oats Company, Chicago, Illinois.

[2] Lieber, Sherman, Henry and Cohen, THIS JOURNAL, **73**, 2327 (1951).

[3] R. N. Jones and G. D. Thorn, *Can. J. Research*, **B**, **27**, 830 (1949).

Results

The spectral data obtained in water solution are summarized in Table I. All of the derivatives of 5-nitroaminotetrazole (I), including the free acid, have a peak at 277 mμ with molecular extinction coefficients of 9000 to 15,000. Only the spectrum of the anilinium salt shows an additional peak (Table I) at 228 mμ, with an extinction coefficient of 11,800. This absorption peak can be assigned to the anilinium ion by comparison with the spectrum of aniline hydrochloride. The types of ultraviolet absorption curves obtained in this study are illustrated by that for 5-nitroaminotetrazole (Fig. 1) and its mono-potassium salt (Fig. 2).

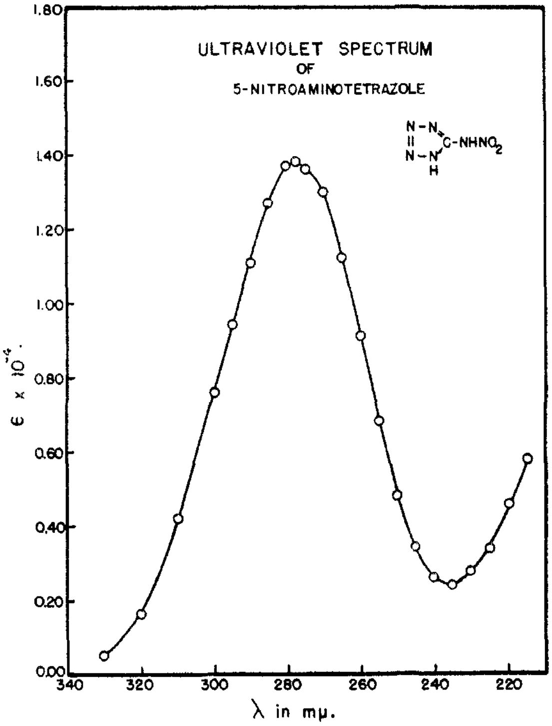
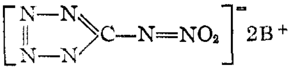


Fig. 1.—Ultraviolet absorption spectrum for 5-nitroaminotetrazole.

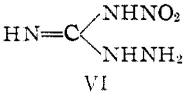
Discussion

The diammonium (IV) and di-(diethylammonium)-5-nitroaminotetrazole (V) are di-acid salts and hence must exist in the form



IV, B = NH_4^+
V, B = $(C_2H_5)_2NH_2^+$

The anions of IV and V are extended conjugated systems. The nitramine group in conjugation with the tetrazole ring would be expected to cause a bathochromic shift with respect to related compounds like nitroguanidine and nitroamino-guanidine (VI) which also contain the nitramine group. This is borne out by the spectral evidence. This



$$HN{=}C\begin{matrix}\diagup NHNO_2\\ \diagdown NHNH_2\end{matrix}$$

VI

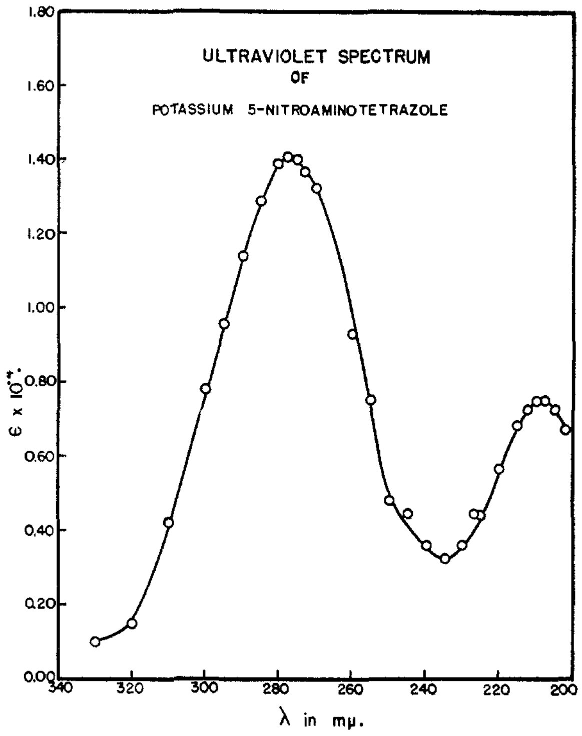


Fig. 2.—Ultraviolet absorption spectrum for potassium 5-nitroaminotetrazole.

may be seen from Table I. Table I further shows that all derivatives of 5-nitroaminotetrazole, including the free acid (I) have a peak at 277 mμ. The acidic dissociation constants for the first and second proton have recently been determined,[4] the first constant is strong and the second of the order of 8×10^{-7}. Calculation shows that the degree of ionization of the second proton of 5-nitroaminotetrazole is about 25% at 1×10^{-5} molar and about 10% at 1×10^{4} molar. Since the free

Table I

Spectral Data[a]

Compound	mμ	ε	mμ	ε
5-Nitroaminotetrazole	277	13,800		
Potassium 5-nitroamino-tetrazole	277	14,100		
Anilinium 5-nitroamino-tetrazole	277	12,800	228	11,800
n-Butylammonium 5-nitro-aminotetrazole	277	12,100		
Diammonium 5-nitroamino-tetrazole	277	9,100		
Di-(diethylammonium)-5-nitroaminotetrazole	277	9,100[b]	277	15,200[b]
Nitroaminoguanidine	267	14,100	214	5,200
Nitroguanidine[c]	265	14,100		
Nitramide[d]	225	5,900		
Anilinium hydrochloride	228	11,800		

[a] All spectral data were obtained in water solutions. [b] First value for ε at concentration of 0.971×10^{-4} and second value for ε at concentration of 0.971×10^{-5}. [c] The spectral data in buffered solutions of *p*H 3 and 10 show the same absorption maxima and extinction coefficient. [d] Taken from the data of Jones and Thorn.[3]

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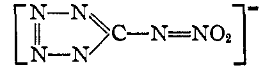
(4) E. Lieber, S. H. Patinkin and H. H. Tao, This Journal, **73**, 1792 (1951).

acid (I) together with its mono- and di-basic salts have the same peak at 277 mμ, it is reasonable to assume that both the singly charged anion (III) and the doubly charged anion (VII)

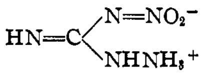


VII

absorb at the same frequency, possibly with a difference in extinction coefficients. For this to be so, it is necessary to conclude that the initial proton removed is from the nitramine group in the singly charged anion (III). For the hydrogen to be removed initially from the ring, yielding the singly charged anion (II) would result in a large hypsochromic shift and a corresponding decrease in extinction coefficient. Accordingly, another peak should have been resolvable. This was not found to be the case.

It will be noted (Table I) that di-(diethylammonium)-5-nitroaminotetrazole (V) deviates by a large amount from Beer's law in contrast to the other compounds which follow Beer's law to approximately 10%. This may indicate incomplete dissociation.

The absorption frequency at the major peak of nitroaminoguanidine (VI) in comparison with nitramide,[3] NH_2NO_2, is found shifted by a very large amount toward the visible region. Nitramide has an absorption maximum at 225 mμ and a molecular extinction coefficient of 5900, whereas VI has its major peak at 267 mμ with a molecular extinction coefficient of 14,200. These data may be readily explained by considering that in neutral aqueous solution, a "*zwitterion*" species VIII is present, the large increase in conjugation



$$HN{=}C\begin{matrix}\diagup N{=}NO_2^- \\ \diagdown NHNH_3^+\end{matrix}$$

VIII

accounting for the large shift in frequency and an increase in extinction of better than 2.5. These arguments are strengthened by the identical ultraviolet spectra data for nitroguanidine in acid, neutral and basic media (Table I). In 5-nitroaminotetrazole (I) the shift of 10 mμ to the visible is then due to the addition of another double bond to extend the already conjugated system. Work along these lines is being continued in order to further substantiate the "zwitterion" structure for nitroaminoguanidine and related nitroammonocarbonic acids.

Experimental

Measurements.—All measurements were made with a Beckman ultraviolet quartz spectrophotometer Model D-U, using 0.999 and 0.997 cm. quartz cells. All compounds were run in concentrations from 1×10^{-4} *M* to 1×10^{-5} *M*.

Materials.—The preparation and purity of 5-nitroaminotetrazole and its salts have been described in a separate communication.[2] Nitroaminoguanidine has also been previously described.[3] Aniline hydrochloride was prepared by precipitation of an ether solution of redistilled aniline and dry hydrogen chloride and recrystallization. (*Anal.* Calcd. for C_6H_8NCl: Cl, 27.36; N, 10.81. Found: Cl, 27.39; N, 10.80.)

Acknowledgment.—The support of the U. S. Naval Ordnance Test Station, Inyokern, China Lake, California, under Research Contract N-123S-61517 is gratefully acknowledged.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Hydrocarbon Synthesis Catalyst Studies. Use of Deuterochloric Acid

BY H. I. WECK, S. MEYERSON AND H. S. SEELIG

Iron catalysts that have been used in hydrocarbon synthesis studies liberate hydrogen and hydrocarbons when dissolved in hydrochloric acid. By the use of deuterochloric acid instead of hydrochloric acid, it has been proved that these hydrocarbons are derived from iron carbide and the acid and are not adsorbed synthesis products that were liberated when the catalyst dissolved. From an examination of the methanes formed it has been concluded that stable iron alkyls do not exist on the catalyst. No exchange was observed between the hydrogen in a sample of *n*-pentane absorbed on metallic iron and the deuterium in the acid used to dissolve the iron.

Introduction

Promoted iron catalysts[1] have been employed frequently for the synthesis of hydrocarbons from carbon monoxide and hydrogen. As the starting material, iron oxides are generally used and these are reduced, usually with hydrogen, before an active catalyst is obtained. In some instances the reduced metal is further treated with carbon monoxide to yield the carbide,[2] but this is not necessary. During the synthesis, changes take place in the composition of the catalyst; the metallic phase tends to disappear and oxides and carbides of iron are formed.[3] In addition carbon and wax are deposited on the catalyst.

To follow the complex changes of the catalyst during the synthesis reaction, a chemical method of analysis was devised. The hydrocarbons liberated when the catalyst is dissolved in hydrochloric acid were assumed to have come from iron carbide (Fe_2C) and the quantity of this material was calculated accordingly. The purpose of the experiments to be described was to determine by the use of deuteriochloric acid whether these liberated hydrocarbons were adsorbed on the catalyst, were present as iron alkyls, or came from iron carbide.

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[1] F. Fischer and H. Tropsch, *Brennstoff Chem.*, **4**, 276 (1923).

[2] H. Pichler, Report to Kaiser Wilhelm Institute for Kohlenforschung in Mülheim-Ruhr, Sept. 10, 1940; T. O. M. Reel 101; British Admiralty Report PG-21574-NID; M. Leva, Translation of German Documents on the Development of Iron Catalysts for Fischer-Tropsch Synthesis, Part I, Office of Synthetic Liquid Fuels Report, Pittsburgh, 1947.

[3] Anderson, Hofer, Cohn and Seligman, THIS JOURNAL, **73**, 944 (1951).