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I hereby recommend that the thesis prepared under my supervision by Peter V. Paulus

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THE ACTION OF SODIUM METHYLATE ON NITRO AND NITROSO DERIVATIVES OF AMMONO CARBONIC ACIDS

A dissertation submitted to the

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by

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INTRODUCTION

This research was originally undertaken to ascertain whether or not the action of sodium methylate on certain aliphatic nitro compounds in methyl alcohol solution would be analogous to the action of aqueous sodium hydroxide on these same compounds as investigated by Fry and Treon (1). They postulated a mechanism for the reactions which accurately predicted as well as quantitatively accounted for the results obtained.

It was found that the reactions with sodium methylate, studied in the present work, did not give the expected results which would be analogous to those of Fry and Treon, but were somewhat analogous to those studied in part by Davis and his coworkers (2). The latter postulated a mechanism which differs from that given by Fry and Treon, although, as will be shown in this thesis, it does not predict the results as well.

It is to be noted at the outset that the main difference between the present work and the work of previous investigators is that the latter carried out their reactions in water, or in acidic, or aqueous alkali media, whereas the present reactions were conducted in the presence of sodium methylate in methyl alcohol and pyridine solutions. Consequently, the conditions imposed minimized the occurrence of hydrolysis and other side reactions.

In view of the foregoing, the present study of the action of sodium methylate on (I) nitrourea, (II) mononitrobiuret, (III) dinitrobiuret, (IV) nitroguanidine and (V) nitrosoguanidine will offer: first, a critical evaluation of the mechanisms of the reactions postulated by previous investigators; second, new reaction mechanisms; and third, experimental procedure and data quantitatively determined in support of the postulated reaction mechanisms. Accordingly, each of the above sections (I thru V) will present the historical, theoretical, and experimental aspects.

I NITROUREA

Nitrourea---Historical

The historical treatment of this as well as the other sections will consider only such data as are directly relevant to the reactions and mechanisms involved.

Cardier(3) decomposed nitrourea with sodium hypobromite and obtained nitrogen.

Thiele and Lachman(4) reported that they obtained some nitroamide (NH_2NO_2) by the action of hypochlorous acid on nitrourea, but did not present any analytical data.

Thiele and Lachman(5) observed that nitrourea formed neutral alkali salts, and decomposed in the presence of warm alkalies with the formation of a gas. They(4) also noted that nitrourea decomposed upon melting or evaporation, and that a concentrated aqueous solution decomposed above 60° C. They separated the potassium salt of nitrourea by adding alcoholic potash to a solution of nitrourea.

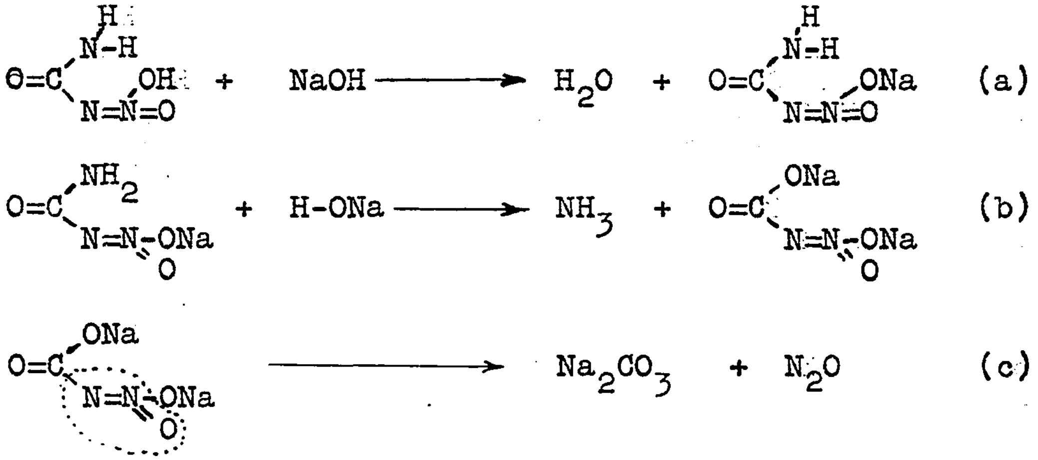
Willstätter and Pfannensteil(7) observed qualitatively that aqueous sodium hydroxide with nitrourea evolved nitrous oxide in the cold, and ammonia upon warming.

Davis and Blanchard(8) heated aqueous nitrourea in a sealed tube and obtained cyanic acid, nitrous oxide, and water. Upon heating nitrourea to 170° C. in vacuo, they found that it decomposed to give a sublimate and a residue. The gases consisted of water, nitrous oxide, cyanic acid, carbon dioxide, and ammonia, while the solids formed were urea, biuret, ammonium cyanurate, and ammelide. From these data they qualitatively deduced that nitrourea also decomposed in another manner to yield ammonia and nitrocyanic acid.

Fry and Treon(1) treated nitrourea with aqueous sodium hydroxide and quantitatively obtained nitrous oxide, ammonia, sodium carbonate, and water.

Nitrourea---Theoretical

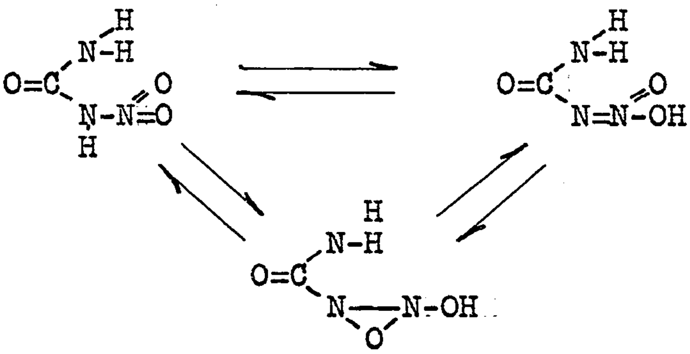
Fry and Treon postulated the following mechanism for the reaction between sodium hydroxide and nitrourea in aqueous solution:



A summary of equations (a) (b) and (c) gives the following completed equation, the products of which were quantitatively obtained:

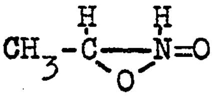
(A) $NH_2\text{-}CO\text{-}NH\text{-}NO_2 + 2\,NaOH \longrightarrow N_2O + NH_3 + Na_2CO_3 + H_2O$

In equation (a) the aci-form of the nitro compound is used. In equation (c) the formula for nitrous oxide is postulated as being N≡N=O. The enolization of aliphatic nitro compounds to give the aci-form has been definitely proven. Many chemical reactions and physico-chemical measurements of aliphatic nitro compounds have been carried out which give unequivocal support to the aci formation. A historical summary of these proofs was outlined by Palinchak (21). It is conceivable that nitrourea may exist in the following tautomeric forms:



This scheme does not consider the enolization of the carbonyl group.

There is some question as to the existence of the $-\mathrm{N}\underset{\mathrm{O}}{\text{—}}\mathrm{N}-$ grouping in a compound. For example, considering the $-\mathrm{C}\underset{\mathrm{O}}{\text{—}}\mathrm{N}-$ grouping as an analogy, Hantzsch's (22) formula for nitroethane,

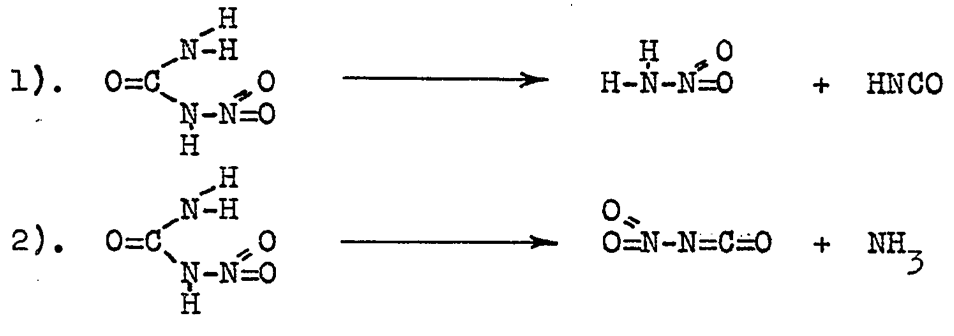


$CH_3-\overset{H}{C}\underset{O}{\text{—}}\overset{H}{N}=O$

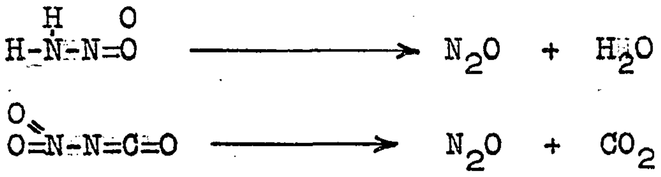
found no support in the spectro-chemical study of Auwers and Harres (23).

In their studies on the decomposition of nitrourea and similar compounds, Davis and Blanchard[(8)] proposed that these compounds undergo "dearrangement". The dearrangement products are then supposed to decompose or hydrolyze, depending on the conditions, to give other products. They defined the urea dearrangements thus: "Many reactions in the urea series consist in the direct combinations or un-combination of electrically neutral molecules, without metathesis, in a predictable manner. The urea dearrangement may be defined as the breaking down of a urea derivative in such a manner that the hydrogen atom, previously attached to one of the nitrogen atoms, goes off in combination with the other nitrogen atom and the atoms or groups originally attached to it, deserting the rest of the molecule. It gives rise to ammonia or a substituted ammonia and to cyanic acid or a substituted cyanic acid. If each nitrogen atom of an unsymmetrical urea derivative carries an hydrogen atom, two modes of dearrangement are possible and occur simultaneously".

These investigators proposed the following concomitant dearrangements of nitrourea:



The nitroamide and the nitrocyanic acid in equations 1) and 2) respectively are then pictured as decomposing spontaneously as follows:

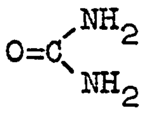


$$H-\overset{H}{N}-\overset{O}{N}=O \longrightarrow N_2O + H_2O$$

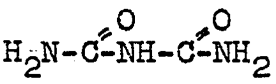
$$O=\overset{O}{N}-N=C=O \longrightarrow N_2O + CO_2$$

This means that nitrourea would decompose to give nitrous oxide, cyanic acid, carbon dioxide, ammonia, and water, the amounts of each depending on the extent of equations 1) and 2).

Furthermore, Davis and Blanchard found that nitrourea heated to 170° C. in vacuo decomposes to give, besides the products already noted, urea, biuret, ammonium cyanurate, and ammelide:

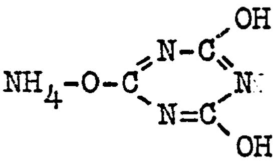


urea



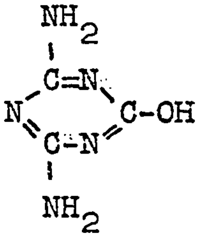
$$H_2N-\overset{O}{C}-NH-\overset{O}{C}-NH_2$$

biuret



ammonium

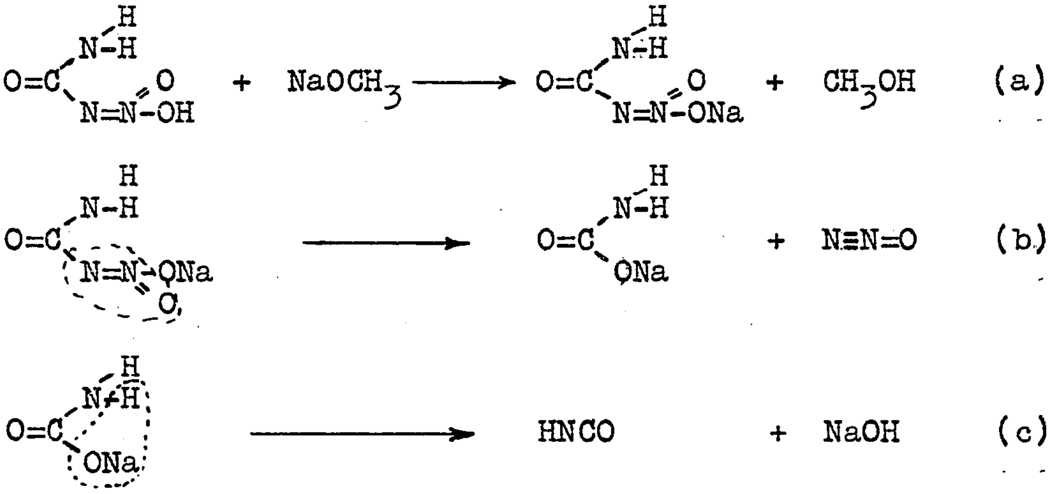
cyanurate



ammelide

It is obvious that the urea is formed from the reaction between ammonia and cyanic acid, while the biuret results from the urea. Ammonium cyanurate would result from the action of ammonia on cyanuric acid, the latter of which is the trimer of cyanic acid. Ammelide would then be formed by the action of ammonia on cyanuric acid with subsequent dehydration.

In the present research nitrourea was reacted with sodium methylate in methyl alcohol solution. Nitrous oxide was quantitatively evolved, while sodium cyanate was found in a yield approximately ninety-five percent of the theoretical. A small amount of ammonia and sodium carbonate were also found. The mechanism of Davis and Blanchard would hold well in this case. However, for reasons that will become obvious later, the following mechanism is submitted to explain this reaction:



$$HNCO \quad + \quad NaOCH_3 \longrightarrow NaNCO \quad + \quad CH_3OH \qquad (d)$$

The summation of equations (a) (b) (c) and (d) gives the following equation for the reaction:

$$NH_2\text{-}CO\text{-}NH\text{-}NO_2 + 2\ NaOCH_3 \rightarrow NaNCO + N_2O + NaOH + 2\ CH_3OH$$

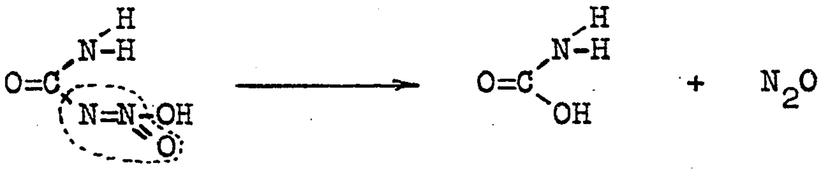
The small amount of ammonia and sodium carbonate that are also present may be explained by the action of sodium hydroxide on sodium cyanate as follows:

$$NaNCO \quad + \quad NaOH \quad + \quad H_2O \longrightarrow Na_2CO_3 \quad + \quad NH_3$$

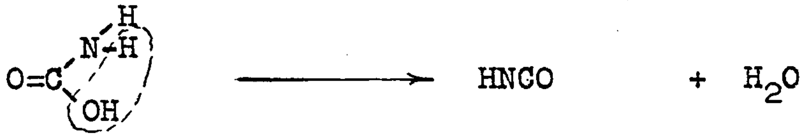
This mechanism accounts for and also predicts the formation of cyanic acid and nitrous oxide. It accounts for the products obtained by Davis and Blanchard as well as those obtained by Fry and Treon.

The likely occurrence of equation (c) in this mechanism, that is, the decomposition of sodium carbamate into sodium cyanate and water, is verified by Franklin (24). He states that when sodium carbamate is heated it loses water and passes over into sodium cyanate.

Using this mechanism to explain the reactions of Davis and Blanchard, the following equations are obtained:



(a)



(b)

The summation of equations (a) and (b) gives:

$$NH_2\text{-}CO\text{-}NH\text{-}NO_2 \longrightarrow N_2O + HNCO + H_2O$$

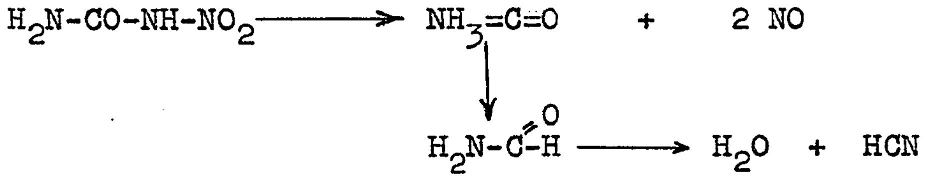
The ammonia and carbon dioxide observed by these investigators are then formed from the hydrolysis of the cyanic acid:

$$HNCO + \cancel{2}\ HOH \longrightarrow NH_3 + CO_2 + \cancel{H_2O}$$

Franklin (24) states that cyanic acid reacts readily with water to form carbon dioxide and ammonia.

The presence of urea, biuret, ammonium cyanurate, and ammelide, found by Davis and Blanchard when they heated dry nitrourea in vacuo, is readily explained by the ammonation and polymerization of cyanic acid (noted above).

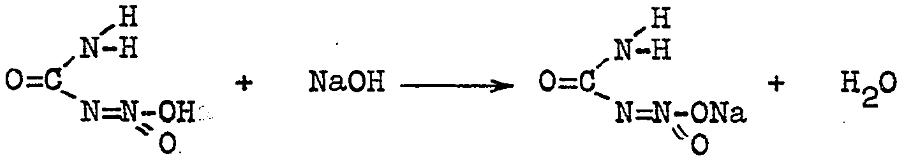
Davis and Blanchard proposed their mechanism to explain the decomposition of nitrourea after the products of the reaction are determined. As will be seen later, they do this for all the reactions under consideration, and they do not arrive at one general reaction mechanism which would predict exclusively the products formed in all the cases studied. The dearrangement mechanism, for example, will predict more compounds than are actually formed. In the case of nitrourea the following dearrangement mechanism is possible:



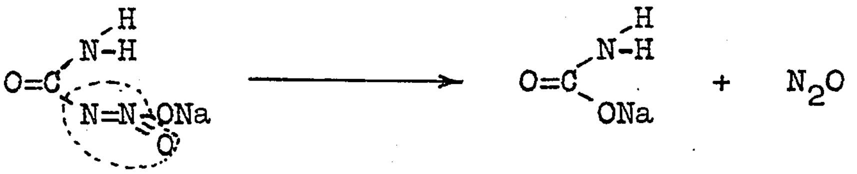
$$\begin{tikzcd} H_2N\text{-}CO\text{-}NH\text{-}NO_2 \arrow[r] & NH_3{=}C{=}O \arrow[d] & + \; 2\,NO \\ & H_2N\text{-}\overset{O}{C}\text{-}H \arrow[r] & H_2O + HCN \end{tikzcd}$$

The products predicted by this scheme are not formed in the decomposition of nitrourea. The new mechanism proposed in this thesis obviates this difficulty of predicting more compounds than are actually formed.

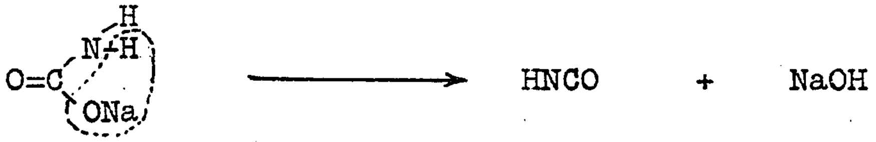
The new mechanism also gives a different interpretation to the reactions of Fry and Treon. Their reactions of nitrourea and sodium hydroxide are thus explained by the following scheme:



(a)



(b)



(c)

$$HNCO + 2\ NaOH \longrightarrow Na_2CO_3 + NH_3 \qquad (d)$$

The summation of equations (a) (b) (c) and (d) gives the completed equation:

$$H_2N\text{-}CO\text{-}NH\text{-}NO_2 + 2\ NaOH \longrightarrow N_2O + NH_3 + Na_2CO_3 + H_2O$$

In other words, these investigators carried the reaction to its ultimate completion, and obtained practically one hundred percent yield of the products noted. According to the above scheme, the main products of the reaction would be nitrous oxide and sodium cyanate if the alkaline hydrolysis (equation d) were prevented. As will be shown in the experimental part of this study, nitrous oxide and sodium cyanate are the main products when the reaction is carried out in a medium that greatly restricts the occurrence of hydrolysis.

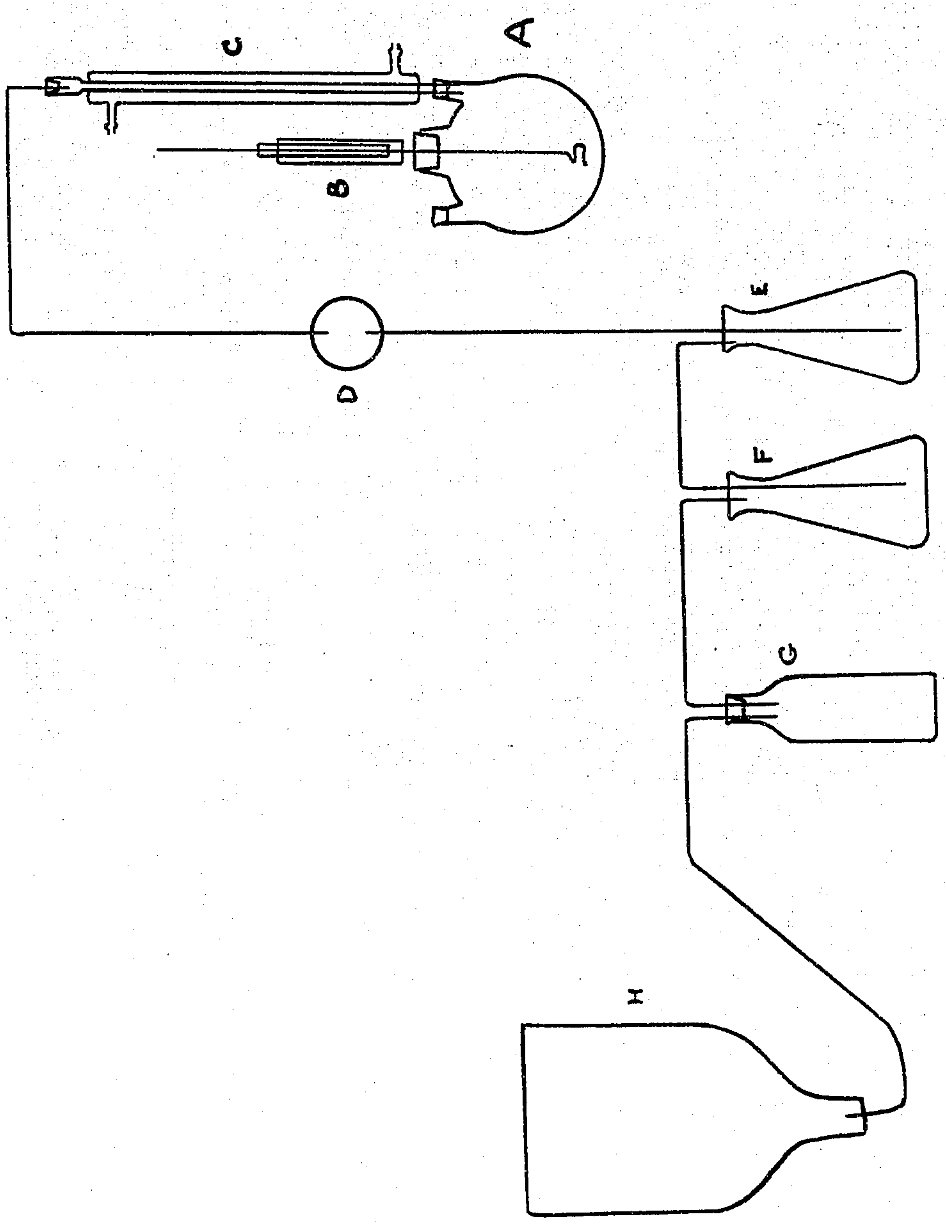
Nitrourea---Experimental

The nitrourea used in these experiments was prepared from urea according to the method of Davis and Blanchard (8). After purification it melted sharply at 158° C. Merck's absolute methyl alcohol was used and the sodium methylate was made by adding metallic sodium thereto.

A sketch of the apparatus used is given on page 13. A three-neck, one-liter flask (A) is attached to a motor-driven, mercury sealed stirrer (B), and a water condenser (C). Glass tubing leads from the condenser to a trap (D), and from there to a 500 ml. erlenmeyer flask (E), which is connected to a similar flask (F). The latter is connected by glass tubing to a 250 ml. safety flask (G), and in turn to the mouth of an inverted 8-liter bottle (H). Flasks (E) and (F) each contained dilute hydrochloric acid to absorb any ammonia that might be evolved. The carboy (H) was filled with a saturated aqueous solution of sodium chloride. This carboy received any volatile gases not absorbed in flasks (E) and (F). The solution was saturated to minimize the absorption of these gases.

The sodium methylate was prepared in the reaction flask (A) by dissolving a weighed amount of sodium in an excess of methyl alcohol. When the solution had cooled, a weighed amount of nitrourea was added, and the solution was heated, with stirring, on a water bath until the evolution of gas had ceased. The time required for the reaction was about two and one-half hours.

When the contents of the reaction flask had cooled to room temperature, the white precipitate which was present was filtered, washed with methyl alcohol, and dried first in the air and then over calcium chloride. The washings were added to the filtrate. A sample of the solid residue effervesced markedly when it was acidified. At this stage of the


A
B
C
D
E
F
G
H

experimental work the presence of cyanate was not expected, but sodium carbonate was. A quantitative analysis for carbon dioxide was made according to the method of Foulk(28). The following results were obtained:

1).	Weight of solid residue taken for analysis	0.5018gm.
	Weight ascarite bulb (tared) before analysis	0.3555
	Weight ascarite bulb after analysis	0.6712
	Weight CO_2 obtained from sample	0.3157
	Percent CO_2 apparently in sample	63.0%
2).	Weight of solid residue taken for analysis	0.5060gm.
	Weight ascarite bulb before analysis	0.6712
	Weight ascarite bulb after analysis	0.9904
	Weight CO_2 obtained from sample	0.3192
	Percent CO_2 apparently in sample	63.1%

It was thus evident that the solid residue had a higher percentage of carbon dioxide than is theoretically possible in pure sodium carbonate.

A weighed amount of the reaction residue was then dissolved in a little water, an excess of concentrated sulfuric acid was added dropwise and with care, and the solution was then evaporated to dryness in a platinum crucible. The weight of the residue, which would likely be sodium sulfate, would thus give some evidence as to the molecular weight of the compound under consideration. This, of course, assumes that the compound is quite pure. The following results were obtained:

1). Weight of sample taken------------------------ 0.1549g.
Weight of crucible---------------------------- 24.9583
Weight of crucible plus ignition residue------ 25.1275
Weight of residue----------------------------- 0.1692

2). Weight of sample taken------------------------ 0.1515g.
Weight of crucible---------------------------- 24.0247
Weight of crucible plus ignition residue------ 24.1900
Weight of residue----------------------------- 0.1653

The residue was found to be practically pure sodium sulfate by conversion to barium sulfate and a determination of the stoichiometrical relationship. Assuming that the unknown was a compound containing one atom of sodium per molecule, the following relationships would hold:

1). $$\frac{0.1549}{0.1692} = \frac{\text{molecular weight x 2}}{142.05}$$

$142.05 = Na_2SO_4$

Molecular Weight = 65.02

2). $$\frac{0.1515}{0.1653} = \frac{\text{molecular weight x 2}}{142.05}$$

Molecular Weight = 65.09

The molecular weight of the reaction product residue, 65.05, is the molecular weight of sodium cyanate. The reaction residue also gave the positive cobalt-pyridine test for cyanate.

The solid was then analyzed quantitatively for cyanate by the direct argentimetric method of Ripan-Tilici (30), which requires a fluorescent indicator to determine the end-point. The end-point that they describe appears when the solution takes on a pink color while the titration flask is being agitated. However, the analysis of some known samples of potassium cyanate indicated that a more accurate end-point is obtained when the precipitate takes on a pink color. This may occur before the color is visible in the solution when shaking the flask, and a warning of its occurrence is given by the rapid settling of the precipitate near the end-point. The analyses of the unknown samples were then made using the colored precipitate of a known sample for comparison. A few drops of a dilute solution of barium nitrate were added to the solution before titrating to remove any carbonate present, but further tests showed this to be unnecessary when very small amounts of carbonate were present. The following results were obtained:

Run 1

1). Weight solid residue taken for analysis---- 0.5106 g.
Milliliters 1.082 N $AgNO_3$ required--------- 6.85
Percent NaNCO thus found in sample--------- 94.5

2). Weight solid residue taken for analysis----- 0.5090 g.
Milliliters 1.082 N $AgNO_3$ required---------- 6.80
Percent NaNCO thus found in sample---------- 94.0

3). Weight solid residue taken for analysis---- 0.4989 g.
Milliliters 1.082 N $AgNO_3$ required--------- 6.80
Percent NaNCO thus found in sample--------- 95.7

Average Percent NaNCO = 94.73

Run 2

1). Weight solid residue taken for analysis---- 0.5000 g.
Milliliters 0.972 N $AgNO_3$ required--------- 7.57
Percent NaNCO thus found in sample--------- 95.6

2). Weight solid residue taken for analysis---- 0.5260 g.
Milliliters 0.972 N $AgNO_3$ required--------- 7.95
Percent NaNCO thus found in sample--------- 95.6

Average Percent NaNCO = 95.6

The contents of the absorption bottles (E) and (F) were tested for ammonia by means of Nessler's reagent(31). The first bottle, (E), gave a positive test, while the second bottle (F) gave a negative test. Aliquot parts of bottle (E) were then taken for analysis, and a quantitative determination was made for ammonia as follows: The solution was made strongly alkaline, and was then distilled into a known volume of standard acid until the volume of the solution in the distillation flask was slightly more than the volume of alkali added. The solution containing the distillate was then titrated with standard base, and the effective volume of the acid, and the equivalent amount of ammonia in the aliquot, was thus determined. The following results were obtained:

<u>Run 1</u>-----10 ml. aliquots were taken for analysis

1). Effective volume 0.1636 N HCl----------------- 0.49 ml.
Weight NH_3 equivalent to 0.49 ml.0.1636 N HCl- 0.001362 g.
Weight NH_3 in 500 ml.solution----------------- 0.068 g.

2). Effective volume 0.1636 N HCl----------------- 0.49 ml.
Weight NH_3 equivalent to 0.49 ml.0.1636 N HCl- 0.001362 g.
Weight NH_3 in 500 ml.solution----------------- 0.068 g.

<u>Run 2</u>-----25 ml. aliquots taken for analysis

1). Effective volume 0.1932 N HCl----------------- 0.79 ml.
Weight NH_3 equivalent to 0.79 ml.0.1932 N HCl- 0.00262 g.
Weight NH_3 in 400 ml.solution----------------- 0.0418 g.

2). Effective volume 0.1932 N HCl----------------- 0.79 ml.
Weight NH_3 equivalent to 0.79 ml.0.1932 N HCl- 0.00262 g.
Weight NH_3 in 400 ml.solution----------------- 0.0418 g.

As already noted, the amount of ammonia present is equivalent, mole for mole, to the amount of sodium carbonate present in the residue, since each is formed by the alkaline hydrolysis of cyanic acid.

The gas which was evolved ignited a glowing splint and supported combustion. It was readily absorbed by alcohol. This indicated that it was nitrous oxide.

The tabulated results of the action of sodium methylate on nitrourea in methyl alcohol solution are recorded in the following tables. These results are based first upon the interaction of sodium methylate and nitrourea yielding nitrous oxide and sodium cyanate

(A). $H_2N\text{-}CO\text{-}NH\text{-}NO_2 + 2\ NaOCH_3 \longrightarrow N_2O + NaNCO + NaOH + 2\ CH_3OH$,

and second upon the concurrent reaction, taking place to a limited extent, of sodium cyanate with sodium hydroxide yielding ammonia and sodium carbonate

(B). $NaNCO + NaOH + H_2O \longrightarrow Na_2CO_3 + NH_3$.

TABLE I

Yields of Nitrous Oxide and Sodium Cyanate

Based Upon Equation (A)

(A). $H_2N\text{-}CO\text{-}NH\text{-}NO_2 + 2\ NaOCH_3 \longrightarrow N_2O + NaNCO + NaOH + 2\ CH_3OH$

	A	B	C	D
Run	Nitrourea g.	Sodium g.	N_2O found liters S.T.P.	N_2O theory liters S.T.P.
I	21.0	17.25	4.45	4.48
II	21.0	17.25	4.40	4.48

	E	F	G	H
Run	N_2O % theory	NaNCO found g.	NaNCO theory g.	NaNCO % theory
I	99.5	11.98	13.00	92.2
II	99.3	12.10	13.00	93.1

The data of Table I conclusively show~~s~~ that, in terms of the yields of nitrous oxide, equation (A) proceeds quantitatively to completion, but the yield of sodium cyanate is about eight percent below the theoretical. This discrepancy is explained by the secondary reaction of sodium cyanate with sodium hydroxide yielding sodium carbonate and ammonia in conformity with equation (B). The following table II embodies data quantitatively confirming the occurrence of the reaction according to equation (B).

TABLE II

Correlation of Yields of Ammonia (Equation B) with Decreased Yield of Sodium Cyanate (Equation A)

(A). $H_2N\text{-}CO\text{-}NH\text{-}NO_2 + 2\ NaOCH_3 \rightarrow N_2O + NaNCO + NaOH + 2\ CH_3OH$

(B). $NaNCO + NaOH + H_2O \longrightarrow NH_3 + Na_2CO_3$

	A	B	C	D	E	F
Run.	NH_3 found (Eq. B) moles	NaNCO NH_3 g. (Eq. B)	NaNCO found g.	NaNCO total (B+C) g.	NaNCO theory g. (Eq.A)	Total NaNCO % theory
I	0.004	0.260	11.98	12.240	13.00	94.2
II	0.0025	0.163	12.10	12.273	13.00	94.4

The data in the above Table II ~~shows~~ show that the yield (column B) of sodium cyanate equivalent to the yield of ammonia plus the decreased yield of sodium cyanate found equals the total yield of sodium cyanate determined (column D). This total yield of sodium cyanate is practically equal to the total theoretical yield of sodium cyanate based upon equation (A).

The nitrourea is shown to react with sodium methylate in methyl alcohol solution in quantitative conformity to the proposed reaction (A).

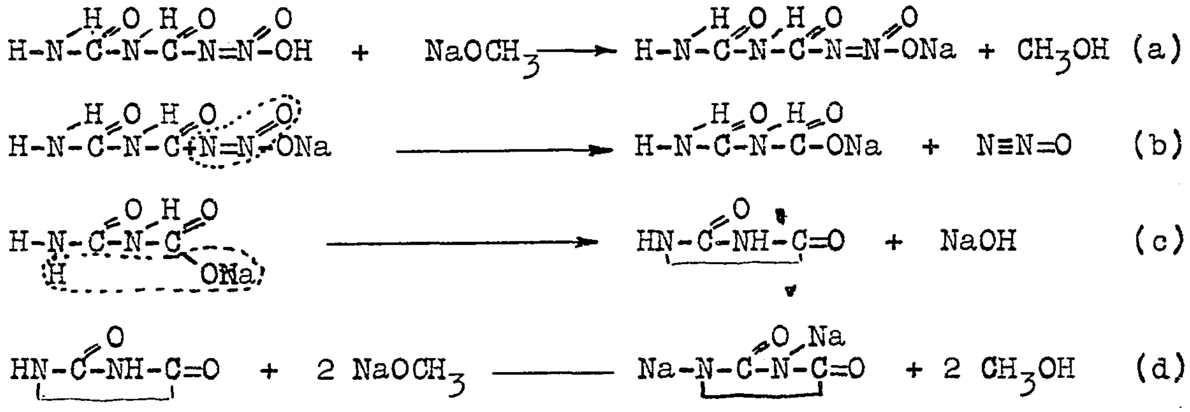
II MONONITROBIURET

Mononitrobiuret---Historical

Davis and Blanchard (20) heated an aqueous solution of mononitrobiuret, and obtained nitrous oxide, urea, dicyanic acid, and cyanuric acid. They report that upon drying the liquid residue they obtained a solid residue the weight of which "varied between 44.8% and 47.2% of the nitrobiuret which was taken. About 80% of the residue consisted of urea; about 20% of cyanuric acid. No other substance was found". They gave no other quantitative data relative to this reaction.

Mononitrobiuret---Theoretical

If the proposed mechanism is applied to the action of sodium methylate on nitrobiuret, the products predicted by the following scheme would be expected:

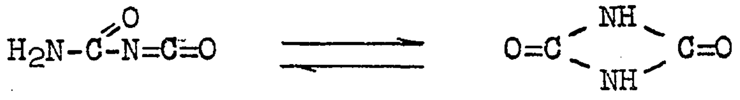


The summation of equations (a) (b) (c) and (d) gives the complete equation:

(C) $H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 + 3\ NaOCH_3 \longrightarrow N_2O + (NaNCO)_2 + NaOH + 3\ CH_3OH$

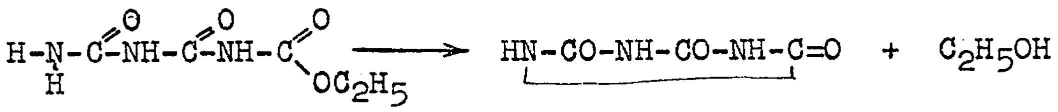
The principal products, therefore, would be nitrous oxide, and the sodium salt of dicyanic acid.

Dicyanic acid may exist in two tautomeric forms, viz.:



According to the mechanism above, the cyclic form is the one that is first formed. Dicyanic acid or its salts have never been isolated in the free state, although dicyanic acid is supposed to exist in water solutions of cyanic acid (25). Since the cyclic form is composed of a four-membered ring, it would be expected to be unstable according to the principles of the Baeyer strain theory. It would, consequently, break down readily (if not spontaneously) to cyanic acid, and accordingly sodium cyanate would be the reaction product in equation (c).

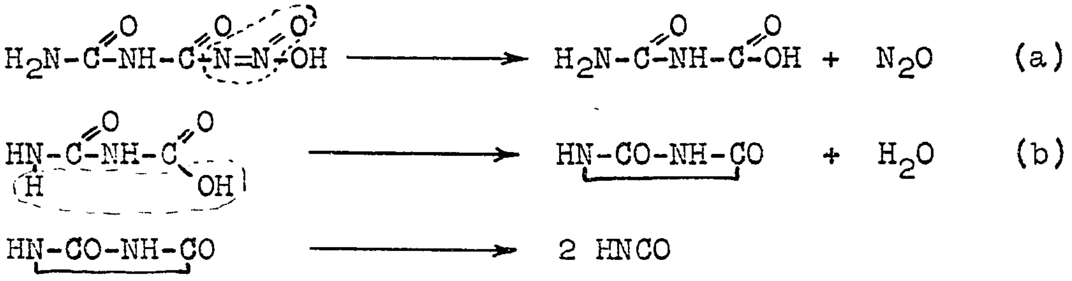
In the above scheme, the intermediate equation (c) represents the decomposition of the sodium salt of allophanic acid (carboxyurea). The acid itself is so unstable that it also is unknown in the free state, so it would be expected that the sodium salt soln. would readily decompose on heating. The likely occurrence of this decomposition is supposted by Davic, Greider, and Kidwell (26), who found that carbethoxy biuret, when dissolved in dilute alkali and then acidified, gave only cyanuric acid. The solution then gives a test for ethyl alcohol. This is shown as follows:



$$H-\underset{H}{N}-\overset{O}{C}-NH-\overset{O}{C}-NH-\overset{O}{C}-OC_2H_5 \longrightarrow \underline{HN-CO-NH-CO-NH-C{=}O} + C_2H_5OH$$

As is shown in the experimental part of this discussion, the reaction between sodium methylate and mononitrobiuret in pyridine solution did give nitrous oxide and sodium cyanate in a yield exceeding ninety percent of the theoretical. Some ammonia and sodium carbonate were also formed, and these again probably result from the action of sodium hydroxide on cyanic acid as noted in equation (B) in the discussion above on nitrourea. It was found that no decomposition occurred when mononitrobiuret was treated with sodium methylate in absolute methyl alcohol solution, but the sodium salt of the nitrobiuret was isolated.

Using the above mechanism to predict the products that would be formed if an aqueous solution of mononitrobiuret were heated, the following scheme would be postulated:



$$H_2N-\overset{O}{C}-NH-\overset{O}{C}-N{=}\overset{O}{N}-OH \longrightarrow H_2N-\overset{O}{C}-NH-\overset{O}{C}-OH + N_2O \qquad (a)$$

$$\underset{H}{HN}-\overset{O}{C}-NH-\overset{O}{C}-OH \longrightarrow \underline{HN-CO-NH-CO} + H_2O \qquad (b)$$

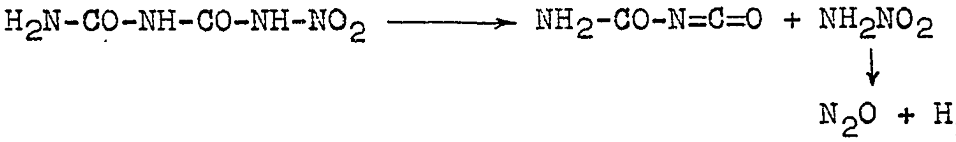
$$\underline{HN-CO-NH-CO} \longrightarrow 2\ HNCO$$

The summation of equations (a) (b) and (c) gives the completed equation:

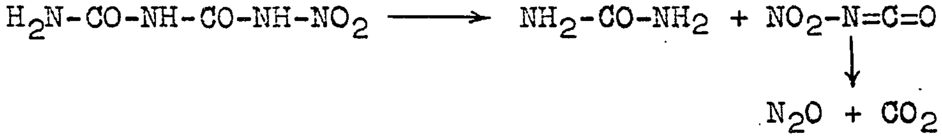
$$H_2N-CO-NH-CO-NH-NO_2 \longrightarrow 2\ HNCO + N_2O + H_2O$$

The primary products would, therefore, be cyanic acid and nitrous oxide. Since cyanic acid hydrolyzes to give carbon dioxide and ammonia these products would also be expected. Furthermore, since ammonia reacts with cyanic acid to give urea(27,35), some of the latter compound would also be expected.

Davis and Blanchard(20) performed the decomposition of mononitrobiuret by heating an aqueous solution of this compound. They obtained nitrous oxide and carbon dioxide from the boiling solution, and upon evaporating the solution to dryness they found urea and cyanuric acid in the residue. They gave the following mechanism for the reaction:



$$H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 \longrightarrow NH_2\text{-}CO\text{-}N{=}C{=}O + \underset{\displaystyle N_2O + H_2O}{\underset{\downarrow}{NH_2NO_2}} \qquad (1)$$



$$H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 \longrightarrow NH_2\text{-}CO\text{-}NH_2 + \underset{\displaystyle N_2O + CO_2}{\underset{\downarrow}{NO_2\text{-}N{=}C{=}O}} \qquad (2)$$

According to these investigators, the dearrangements (1) and (2) occur simultaneously to give, in the first instance, dicyanic acid and nitroamide, and in the second instance urea and nitrocyanic acid. The nitroamide is then supposed to decompose into nitrous oxide and water, while the nitrocyanic acid is supposed to decompose into carbon dioxide and nitrous oxide. The carbon dioxide formed should be equivalent, mole for mole, to the urea formed, but these investigators gave no quantitative account of the gases.

The solid residue which remained after evaporation of the solution contained eighty percent urea and twenty percent cyanuric acid, and no other substance was found. The presence of dicyanic acid in the solution was proved by the formation of disubstituted biurets as follows:

$$R_2NH \quad + \quad NH_2\text{-}CO\text{-}N{=}C{=}O \longrightarrow NH_2\text{-}CO\text{-}NH\text{-}CO\text{-}NR_2$$

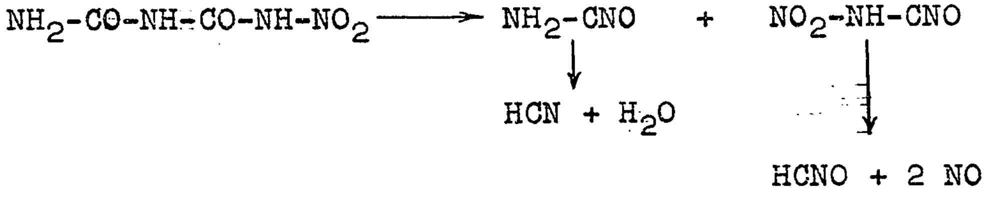
Thus they prepared ω,ω-dimethyl; ω,ω-diethyl; ω,ω-di-n-propyl, and ω,ω-di-n-butyl biurets.

It is important to note that in the present work no urea was found when mononitrobiuret was reacted with sodium methylate in pyridine solution, but a little carbonate and ammonia were found. It is thus evident that the carbon dioxide evolved when an aqueous solution of the nitrobiuret was heated resulted from the hydrolysis of the cyanic acid and not from the hypothetical nitrocyanic acid.

The dearrangement mechanism of Davis and Blanchard is only *a posteriori* useful, since it is derived to explain reactions *after* the products are definitely determined. Different mechanisms are thus postulated for different compounds. For example, the dearrangement reaction which gives dicyanic acid and nitroamide, (1) above, is analogous to the dearrangement mechanism postulated for the decomposition of nitrourea, but a new dearrangement reaction is postulated for the formation of urea from mononitrobiuret. As far as prediction is concerned, that is the *a priori* usefulness of the dearrangement mechanism, it would be possible to postulate other dearrangements also. For example, the following dearrangement is possible:

$$NH_2\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 \longrightarrow HNCO + NH_2\text{-}CO\text{-}NH\text{-}NO_2$$

This would give cyanic acid and nitrourea, the latter decomposing as noted previously. Another possible dearrangement would be



$$\begin{array}{ccccc} NH_2\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 & \longrightarrow & NH_2\text{-}CNO & + & NO_2\text{-}NH\text{-}CNO \\ & & \downarrow & & \downarrow \\ & & HCN + H_2O & & HCNO + 2\ NO \end{array}$$

which would give, as the ultimate products, hydrocyanic acid, cyanic acid, and nitric oxide. In short, the mechanism would predict more compounds than are actually formed.

The new mechanism proposed in this thesis does not predict any more or fewer compounds than are formed in the reactions. Another shortcoming of Davis' work is that he fails to take side reactions fully into consideration. For example, in the mononitrobiuret reaction, instead of considering the formation of urea as a consequence of the action of ammonia (from the hydrolysis of some cyanic acid) on cyanic acid, he proposes a new mode of dearrangement.

Mononitrobiuret---Experimental

The nitrobiuret used in this experiment was made according to the method of Thiele and Uhlfelder (36). It was purified by recrystallizing from ethyl alcohol, and a sample melted with decomposition at 165° C. The sodium methylate, prepared by the Mathieson Alkali Works, was 95.4% pure. The pyridine was obtained from Coleman and Bell manufacturing

Chemists.

The apparatus was identical with that used in the nitrourea experiments above. For the first run 5.93 grams of the nitrobiuret were mixed with 7.3 grams of sodium methylate and 250 ml. of methyl alcohol, and this mixture was refluxed for several hours. No gas was evolved, and the solid which settled in the reaction flask was the sodium salt of mononitrobiuret. This was filtered and dried, and 6.2 grams of it as the initial reactant were placed in 250 ml. pyridine with 4.3 grams of sodium methylate. This mixture was heated to 140° C. in an oil bath, and the evolution of gas occurred slowly over a period of eighteen hours heating. In the second run the nitrobiuret was placed in pyridine with sodium methylate and heated in an oil bath. At 110° C. a rapid evolution of gas commenced, and the reaction was complete in one hour.

After the reaction flask had cooled to room temperature the contents were filtered, and the solid residue was washed with pyridine and dried first in the air and then over calcium chloride. A test with silver nitrate showed that considerable alkali was present, and this was removed by washing with absolute methyl alcohol. The solid then gave reactions characteristic of cyanate, that is it gave a whitish precipitate with silver nitrate, effervesced vigorously when acidified, and gave Werner's (29) test with cobalt and pyridine.

The following data represent~~s~~ the quantitative estimation of cyanate according to the method of Ripan-Tilici (30) using the modifications outlined in the nitrourea experiment above:

Run 1

Amount solid residue taken for analysis	0.2517 g.
Milliliters 1.000 N $AgNO_3$ required	3.49
Amount NaNCO 3.49 ml. 1.000 N $AgNO_3$	0.2273
Total amount NaNCO in residue	4.23 g.

Run 2

Amount solid residue taken for analysis	0.3151 g.
Milliliters 1.000 N $AgNO_3$ required	4.43
Amount NaNCO 4.43 ml. 1.000 N $AgNO_3$	0.2880
Total amount NaNCO in residue	4.27 g.

The absorption bottle (E) showed the presence of ammonia upon the addition of Nessler's reagent. This ammonia was quantitatively estimated by making an aliquot portion of the acid solution strongly alkaline, and steam distilling until 500 ml. of distillate had come over. The ammonia in the distillate was absorbed by a four percent boric acid solution (method by Winkler(39)), and the boric acid solution was titrated with standard acid. The following results were obtained:

Run 1

Volume of absorption acid taken for analysis----- 50 ml.
Milliliters 0.4875 N HCl required to titrate NH_3- 0.70
Amount NH_3 0.70 ml. 0.4875 N HCl------------ 0.0058 g.
Total NH_3 found in absorption bottle------------- 0.029 g.
NaNCO 0.029 g. NH_3-------------------------- 0.111 g.

Run 2

Volume of absorption acid taken for analysis----- 50 ml.
Milliliters 0.4875 N HCl required for titration-- 0.70
Amount NH_3 0.70 ml. 0.4875 N HCl------------ 0.0058 g.
Total NH_3 found in absorption bottle------------- 0.029 g.
NaNCO 0.029 g. NH_3-------------------------- 0.111 g.

The tabulated results of the action of sodium methylate on mononitrobiuret in pyridine solution are shown in the following tables III and IV. They are based first upon the interaction of sodium methylate and mononitrobiuret yielding nitrous oxide and sodium cyanate (equation C), and second upon the secondary reaction, taking place to a limited extent, of sodium cyanate with sodium hydroxide (equation D) yielding sodium carbonate and ammonia. In Run 1, the amount of nitrobiuret as given is the equivalent of the amount of the sodium nitrobiuret used as the initial reactant.

TABLE III

The Action of Sodium Methylate on Mononitrobiuret

Data Based on Equation (C)

(C). $H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 + 3\ NaOCH_3 \longrightarrow$

$N_2O + 2\ NaNCO + 3\ CH_3OH + NaOH$

	A	B	C	D
Run	Nitrobiuret g.	Sodium Methylate g.	N_2O found liters S.T.P. (Equation C)	N_2O theory liters S.T.P. (Equation C)
1	5.53	5.95	0.72	0.80
2	5.53	6.00	0.80	0.80

	E	F	G	H
Run	N_2O % theory (Equation C)	NaNCO found g.	NaNCO theory g. (Equation C)	NaNCO % theory (Equation C)
1	90%	4.23	4.68	90.4%
2	100%	4.27	4.68	91.2%

Since the yield of sodium cyanate is 90% of the theoretical according to equation (C), the presence of ammonia indicates that some cyanate is hydrolyzed. The following table IV correlates the amount of cyanate hydrolyzed in terms of the amount of ammonia found.

TABLE IV

Data Based on Equation (D)

(D). $NaNCO + NaOH + H_2O \longrightarrow Na_2CO_3 + NH_3$

	A	B	C	D	E	F
Run	NH_3 found g.	NaNCO NH_3 g.	NaNCO found	NaNCO total (B+C)	NaNCO theory g.	Total NaNCO % theory
1	0.029	0.111	4.23	4.341	4.68	92.8
2	0.029	0.111	4.27	4.381	4.68	93.6

The data in the above tables show~~s~~ that the yields of sodium cyanate and nitrous oxide exceed ninety percent of the theoretical yields of these compounds based upon the occurrence of the predicted reaction represented by equation (C).

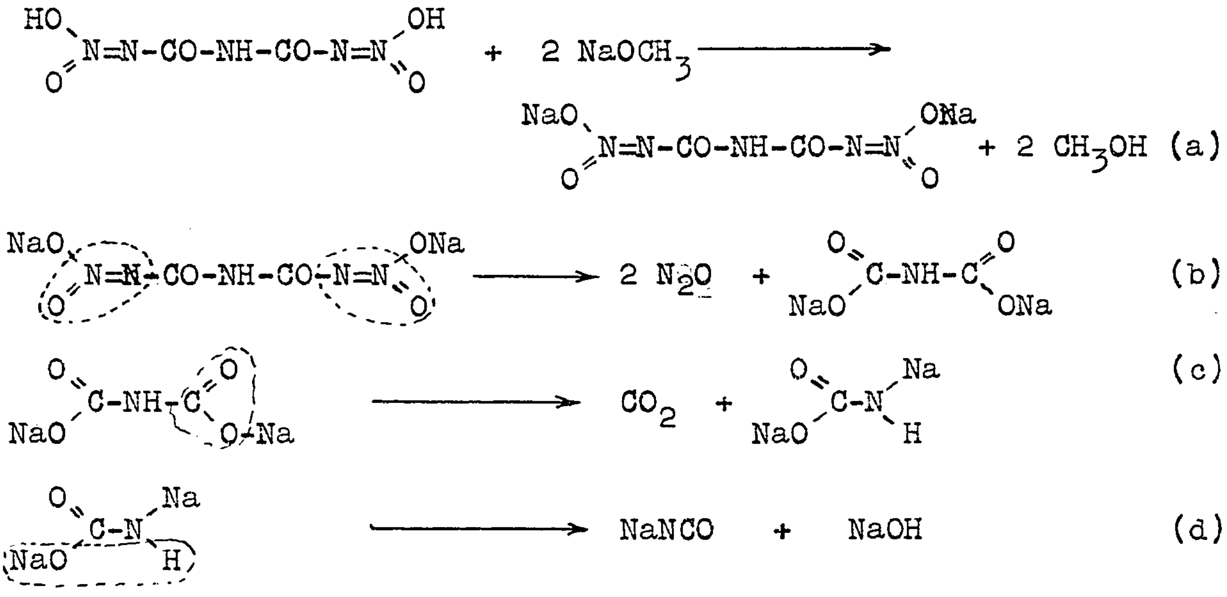
III DINITROBIURET

Dinitrobiuret---Historical

Thiele and Uhlfelder (36) heated an aqueous solution of dinitrobiuret and obtained nitrous oxide, carbon dioxide, and ammonia. They apparently did not make a quantitative study of this reaction, but they did report that no residue remained. The potassium salt was isolated from methyl alcohol.

Dinitrobiuret---Theoretical

According to the mechanism proposed in this thesis, the following equations would represent the reaction of dinitrobiuret with sodium methylate in pyridine solution:



$$CO_2 + NaOH \longrightarrow NaHCO_3 \qquad (e)$$

The summation of equations (a) (b) (c) (d) and (e) gives the completed equation:

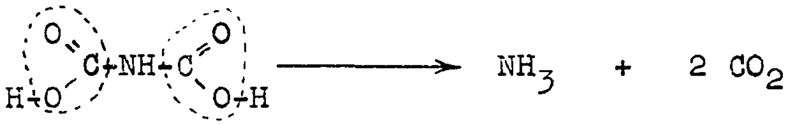
$$\text{(E).}\ NO_2\text{-}NH\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 + 2\,NaOCH_3 \longrightarrow 2\,N_2O + NaNCO + 2\,CH_3OH + NaHCO_3$$

As will be shown by experimental data, the reaction between sodium methylate and dinitrobiuret in pyridine solution did give these products in quantitative yields conforming to the summation equation (E).

Evidence for the occurrence of the reactions noted in equations (c) and (d) is given by Nef(37), who found that when the diethyl ester of carboxycarbamic acid is heated in an alcoholic solution of potassium hydroxide it decomposes to give potassium cyanate and ethyl alcohol. Hydrolysis of this ester apparently occurs first to give the alcohol and the potassium salt of the acid, while the latter then decomposes in the manner indicated by equations (c) and (d) to give the cyanate.

According to this mechanism, an aqueous solution of dinitrobiuret might be expected to give, upon heating, nitrous oxide, cyanic acid, and carbon dioxide, and water. The cyanic acid would decompose to give ammonia and carbon dioxide, while, as a side reaction, some ammonia would react with cyanic acid to give urea.

There is, however, the possibility that the acid whose sodium salt is represented in equation (c) above would decompose spontaneously to give ammonia and carbon dioxide, thus:

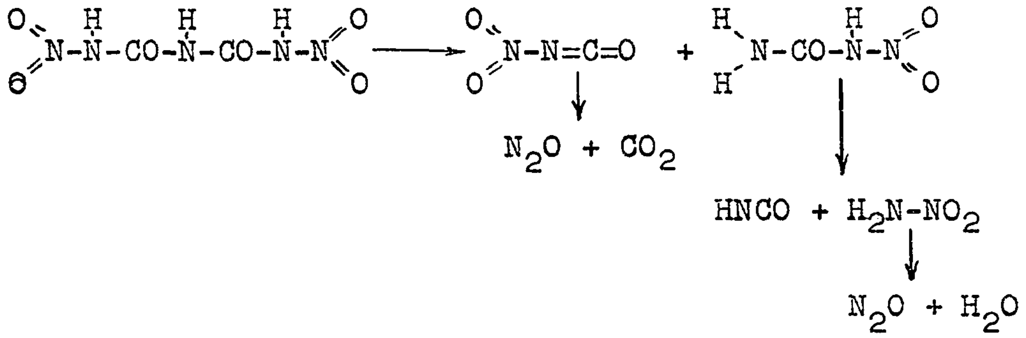


$$H\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}H \longrightarrow NH_3 + 2\,CO_2$$

In this case no cyanic acid or urea would be formed.

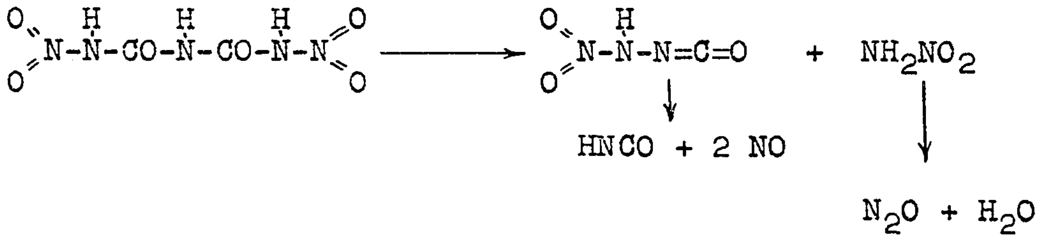
Since Thiele reported that no residue remained when he heated an aqueous solution of dinitrobiuret, this latter decomposition apparently occurs in aqueous solution. The carboxycarbamic acid (imidodicarboxylic acid) is not known in the free state or in the form of its salts, although some esters and ester salts are known. The potassium, sodium, and silver salts of the diethyl esters have been prepared.

Davis did not study the "dearrangement" of dinitrobiuret. If his mechanism is used to predict the probably products, the following might be postulated:



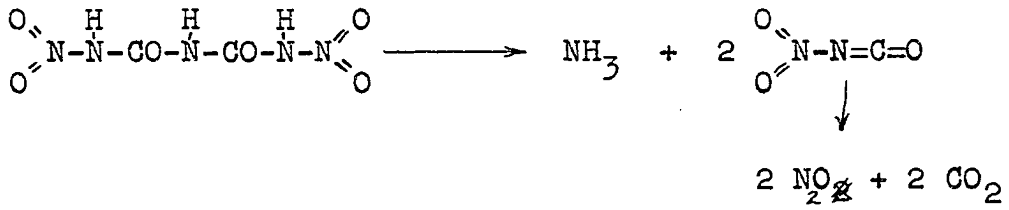
From this mode of dearrangement, nitrous oxide, carbon dioxide, and cyanic acid would be expected. These are the products obtained by the action of sodium methylate on dinitrobiuret in pyridine solution.

Another mode of dearrangement is conceivable:



This mode of dearrangement would predict the formation of cyanic acid, nitrous oxide, and nitric oxide. It is evident that this predicts more products than are obtained.

The first mode of dearrangement would both predict and explain the results obtained in the present work. It is not likely that the results obtained by Thiele would be predicted by the dearrangement mechanism, because the migration of two hydrogens from two different nitrogens to the same nitrogen is not stated in the rule for dearrangement. However, the results obtained by Thiele could be explained by a dearrangement as just outlined even if they could not be predicted. The following scheme would explain the results:



$$O_2N-\overset{H}{N}-CO-\overset{H}{N}-CO-\overset{H}{N}-NO_2 \longrightarrow NH_3 + 2\ O_2N-N=C=O$$
$$\downarrow$$
$$2\ NO_2 + 2\ CO_2$$

The advantage of the mechanism proposed, in the present work, leading to equation (E), over that of Davis, is thus made evident. In other words, prediction is more in conformity with both the proposed mechanism and the products formed.

Dinitrobiuret---Experimental

The dinitrobiuret used in this experiment was made according to the method of Thiele and Uhlfelder (36), namely, first the formation of mononitrobiuret, and second its nitration yielding dinitrobiuret.

The apparatus was modified for this experiment because of the very little amount of materials available for use. Instead of the one-liter, three-neck flask (A) shown in the apparatus on page (13), a 200 ml. round-bottom flask was used. No stirrer was used, occasional stirring being effected by swirling the flask in the oil bath. The absorption bottles contained a four percent solution of boric acid, and dilute sodium hydroxide respectively. The former was intended as an absorption medium for ammonia, while the latter was intended to absorb any carbon dioxide that might excape from the reaction misture. Instead of the eight liter bottle (H), a one-liter graduated cylinder was used.

After charging the reaction flask, it was heated on an oil bath, and at 100° C. a constant evolution of gas was evident, increasing rapidly at 120° C. The reaction was completed within two hours.

After cooling the reaction mixture, the precipitate was filtered, washed with pyridine, and dried first in the air and then over calcium chloride. The residue was of a light gray color. An aqueous solution of the solid effervesced vigorously when acidified, and gave a light tan precipitate when treated with silver nitrate. This was indicative of a mixture of sodium cyanate and sodium carbonate. Werner's test showed the presence of cyanate.

It is interesting to note that about 0.004 grams of dinitrobiuret sublimed and crystallized in the lower end of the condenser in the first run.

The absorption bottles contained no ammonia or carbon dioxide.

The cyanate was quantitatively determined by the argentimetric method of Ripan-Tilici (30), the same procedure being followed as in the case of the analysis for cyanate in the nitrourea experiment above. Before adding the silver nitrate, however, the carbonate was precipitated as barium carbonate by adding dropwise a saturated solution of barium nitrate, filtered, and washed. Silver nitrate was then added until the end-point was observed. The following data was obtained:

Run 1

1).	Weight of solid taken for analysis-----------	0.1241 g.
	Milliliters of 1.007 N $AgNO_3$ required--------	0.47
	Weight NaNCO 0.47 ml. 1.007 N $AgNO_3$------	0.0312 g.
	Weight NaNCO in total amount of residue------	0.720 g.
2).	Weight of solid taken for analysis-----------	0.1830 g.
	Milliliters of 1.007 N $AgNO_3$ required--------	0.71
	Weight NaNCO 0.71 ml. 1.007 N $AgNO_3$------	0.0465 g.
	Weight NaNCO in total amount of residue------	0.731 g.

Average weight of NaNCO found in solid residue: 0.725 g.

Run 2

1). Weight of solid taken for analysis---------- 0.690 g.

Milliliters of 1.007 N $AgNO_3$ required------- 8.00

Weight NaNCO 8.00 ml. 1.007 N $AgNO_3$----- 0.532 g.

Weight NaNCO in total amount of residue----- 1.88 g.

2). Weight of solid taken for analysis---------- 0.321 g.

Milliliters of 1.007 N $AgNO_3$ required------- 3.80

Weight NaNCO 3.80 ml. 1.007 N $AgNO_3$----- 0.2485

Weight NaNCO in total amount of residue----- 1.93 g.

Average weight of NaNCO found in solid residue: 1.90 g.

The volume of nitrous oxide that was evolved, corrected to standard conditions, amounted to 0.525 liters and 1.39 liters respectively.

The following table V contains the experimental data relating to the interaction of dinitrobiuret and sodium methylate in pyridine solution:

TABLE V

Data Based Upon Equation (E)

(E). $NO_2\text{-NH-CO-NH-CO-NH-}NO_2 + 2\ NaOCH_3 \longrightarrow 2\ N_2O + NaNCO + NaHCO_3 + 2\ CH_3OH$

	A	B	C	D	E	F	G	H
Run	Dinitro-biuret g.	$NaOCH_3$ g.	NaNCO found g.	NaNCO theory g.	NaNCO % theory	N_2O found liters S.T.P.	N_2O theory liters S.T.P.	N_2O % theory
1	2.3	2.0	0.725	0.773	93.8	0.525	0.533	98.5
2	6.0	3.5	1.90	2.01	94.5	1.39	1.39	100.0

The percent theory yields of sodium cyanate and nitrous oxide establish the occurrence of the interaction of dinitrobiuret with sodium methylate conforming with the proposed equation (E).

IV NITROGUANIDINE

Nitroguanidine---Historical

Cardier (3) reacted nitroguanidine with sodium hypobromite and split off two atoms of nitrogen from the nitro compound.

The following investigators reported that nitroguanidine melted with decomposition giving off ammonia:

Jousselein (9)	at 220°
Pellizzari (10)	at 225°
Franchimont (11)	at 222°
Thiele (12)	at 230°

Jousselein (13) noticed that a concentrated solution of potassium hydroxide, sodium hydroxide, or barium hydroxide with nitroguanidine immediately evolved ammonia.

Pellizzari (10) found that when nitroguanidine was heated in an alkaline solution it decomposed into nitrous oxide, ammonia, and carbon dioxide. His quantitative results were not constant.

Franchimont (11) observed that nitroguanidine dissolved readily in aqueous ammonia, and that this solution evolved nitrous oxide at ordinary temperatures. He reported that nitroguanidine dissolved in aqueous potassium hydroxide or barium hydroxide evolving nitrous oxide, that in the latter solution there appeared a precipitate of barium carbonate, and that the liquid smelled strongly of ammonia. He proposed that the nitroguanidine hydrolyzed to give urea and nitroamide;

the urea then hydrolyzed to carbon dioxide and ammonia, while the nitroamide decomposed to give nitrous oxide and water.

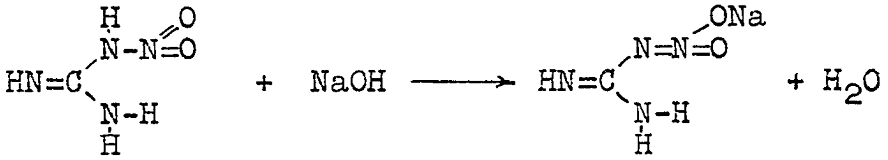
Thiele (14) warmed an alkaline solution of nitroguanidine and discovered that there was a lively evolution of nitrous oxide and ammonia and that the liquid residue contained carbonate.

Davis and Abrams (15) stated that the reactions of nitroguanidine in aqueous solution supported the view that decomposition occurred to give nitrous oxide, cyanamide, ammonia, and water. They observed that when nitroguanidine is decomposed by heat it yields cyanamide and ammonia as such, and some other products which would result from the decomposition, polymerization, and interaction of the postulated dearrangement products. When they heated a solution of nitroguanidine in concentrated sulfuric acid for a long time, nitrous oxide, ammonia and carbon dioxide were formed (16). They state that the ammonia and carbon dioxide were produced quantitatively, while nitrogen was present with the nitrous oxide.

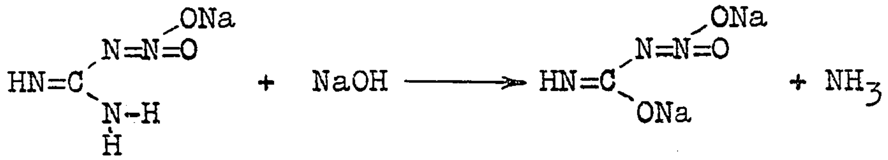
Fry and Treon (1) heated nitroguanidine with an aqueous solution of sodium hydroxide, and obtained a quantitative yield of nitrous oxide, ammonia, and sodium carbonate.

Nitroguanidine---Theoretical

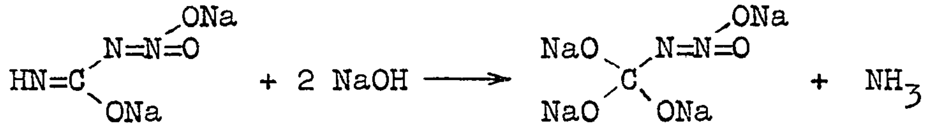
Fry and Treon (1) proposed the following mechanism for the reaction between sodium hydroxide and nitroguanidine:



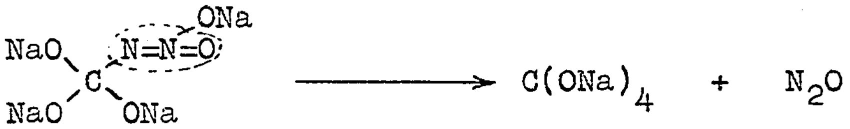
$$HN{=}C(NH{-}NO{=}O)NH_2 + NaOH \longrightarrow HN{=}C(N{=}N(ONa){=}O)NH_2 + H_2O \quad (a)$$



$$HN{=}C(N{=}N(ONa){=}O)NH_2 + NaOH \longrightarrow HN{=}C(N{=}N(ONa){=}O)ONa + NH_3 \quad (b)$$



$$HN{=}C(N{=}N(ONa){=}O)ONa + 2\ NaOH \longrightarrow (NaO)_2C(ONa)(N{=}N(ONa){=}O) + NH_3 \quad (c)$$



$$(NaO)_2C(ONa)(N{=}N(ONa){=}O) \longrightarrow C(ONa)_4 + N_2O \quad (d)$$

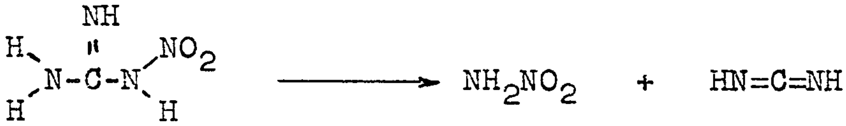
$$C(ONa)_4 + H_2O \longrightarrow Na_2CO_3 + 2\ NaOH \quad (e)$$

A summary of equations (a) (b) (c) (d) and (e) gives the completed equation:

$$HN{=}C(NH_2)NH{-}NO_2 + 2\ NaOH \longrightarrow Na_2CO_3 + 2\ NH_3 + N_2O$$

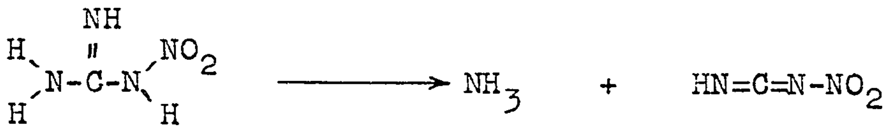
Davis and Abrams (15) heated nitroguanidine in the dry state, in aqueous solution, and in concentrated sulfuric acid solution. They say that nitroguanidine would be expected to dearrange in two modes, as follows:

1).



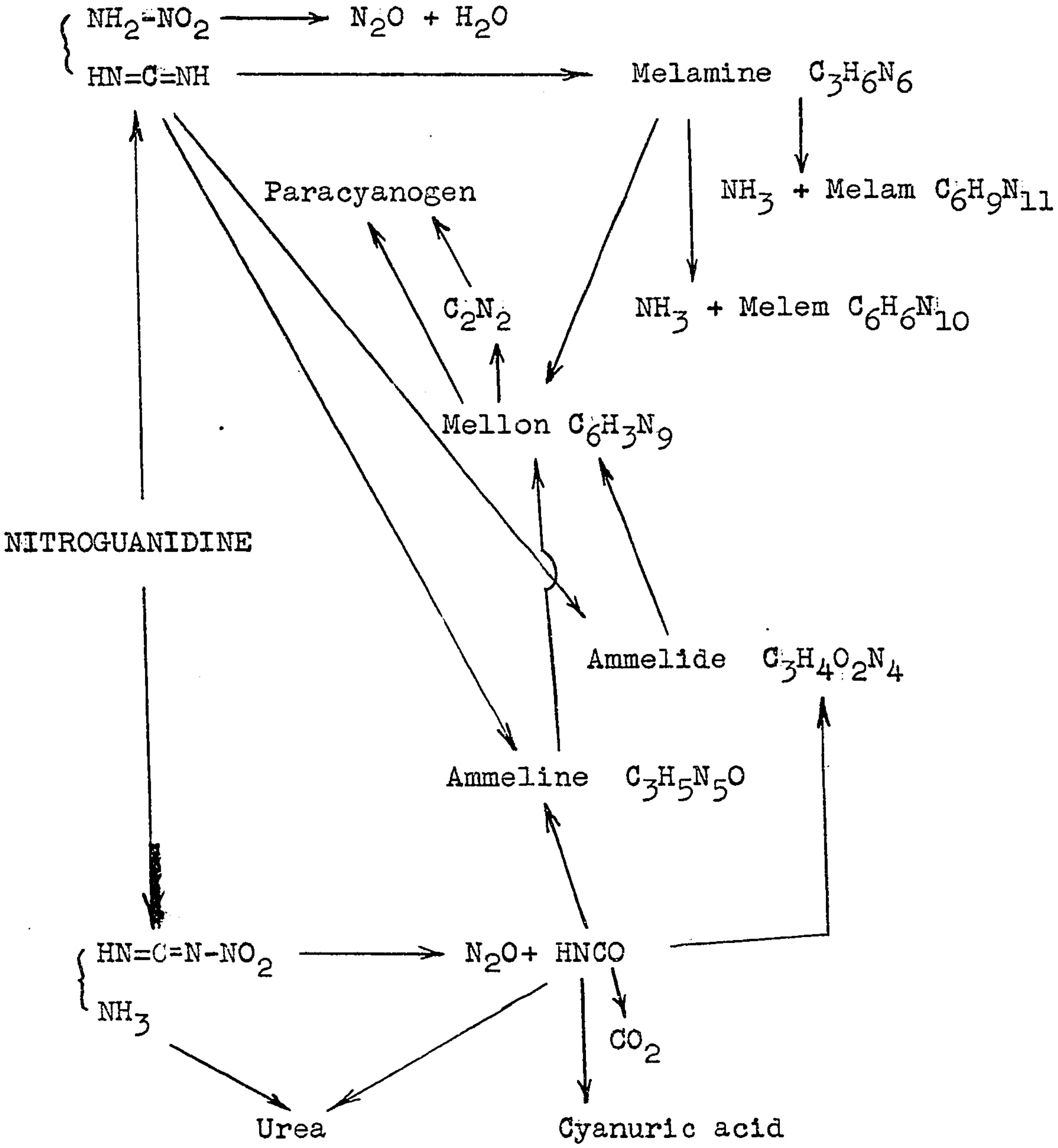
$$H_2N{-}C({=}NH){-}NH{-}NO_2 \longrightarrow NH_2NO_2 + HN{=}C{=}NH$$

2).

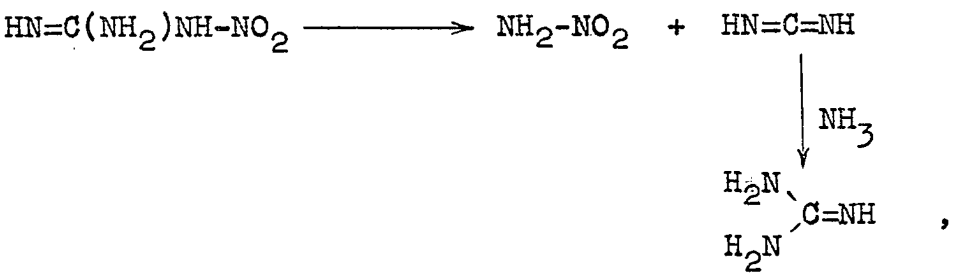


$$H_2N{-}C({=}NH){-}NH{-}NO_2 \longrightarrow NH_3 + HN{=}C{=}N{-}NO_2$$

According to these investigators, when nitroguanidine is decomposed by heat, cyanamide and ammonia are produced as such, and the other products are "precisely those which would result from the decomposition, polymerization, and interaction of the expected dearrangement products". They found that when the gases from the decomposition were passed through water and through potassium hydroxide solution, the water was found to contain carbon dioxide. They inferred that the carbon dioxide resulted from the interaction of cyanic acid (from the nitrocyanamide in 2) above) and water vapor. The alkaline solution was found to contain prussic acid and cyanic acid, and they state that these substances "may very well have been produced as such by the decomposition, or may equally well have been produced by the interaction of cyanogen, from the decomposition, with the alkali in the solution". They isolated, from the solid residue, cyanuric acid, melamine, melam, melem, ammeline, mellon, and paracyanogen. In the sublimate they found urea, cyanamide, and melamine. Thay gave the following scheme to represent the formation of all these products:

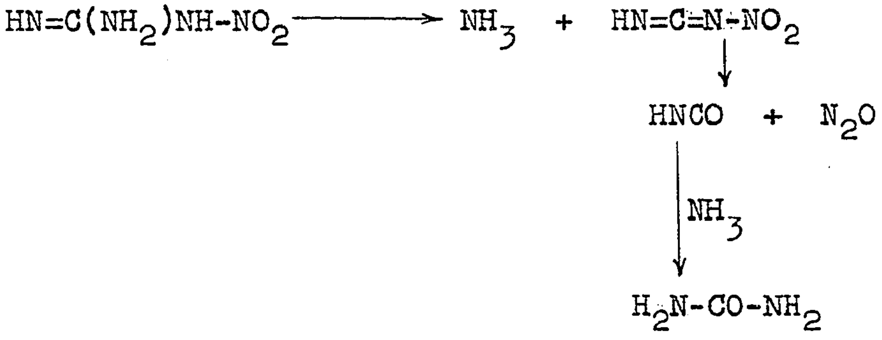

NH_2-NO_2
$N_2O + H_2O$
$HN=C=NH$
Melamine $C_3H_6N_6$
NH_3 + Melam $C_6H_9N_{11}$
Paracyanogen
C_2N_2
NH_3 + Melem $C_6H_6N_{10}$
Mellon $C_6H_3N_9$
NITROGUANIDINE
Ammelide $C_3H_4O_2N_4$
Ammeline $C_3H_5N_5O$
$HN=C=N-NO_2$
NH_3
N_2O+ HNCO
CO_2
Urea
Cyanuric acid

When they heated an aqueous ammoniacal solution of nitroguanidine, Davis and Abrams obtained guanidine and urea. They do not give any quantitative results for this reaction, but state that guanidine results from the action of ammonia on cyanamide,



$$\begin{tikzcd} \mathrm{HN{=}C(NH_2)NH{-}NO_2} \arrow[r] & \mathrm{NH_2{-}NO_2} + \mathrm{HN{=}C{=}NH} \arrow[d, "\mathrm{NH_3}"] \\ & \mathrm{(H_2N)_2C{=}NH} \quad , \end{tikzcd}$$

while the urea results from the action of ammonia on cyanic acid,

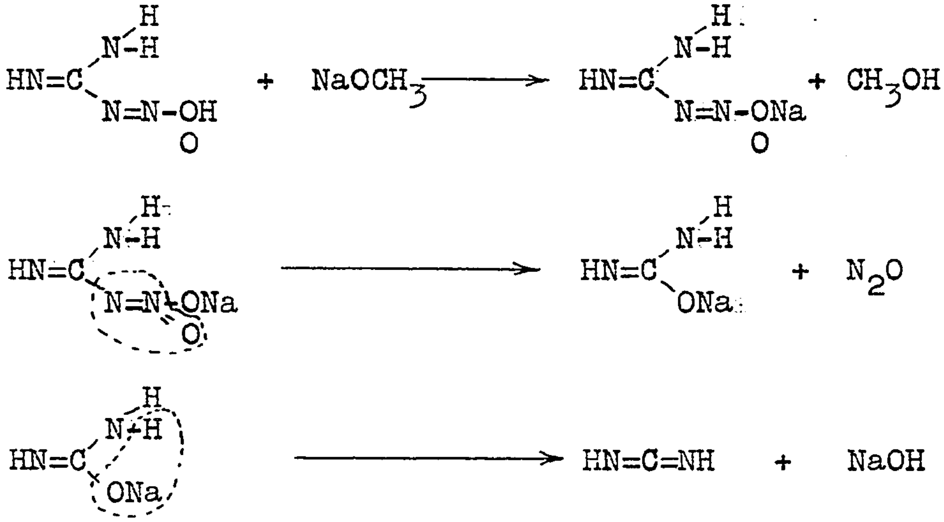


$$\begin{tikzcd} \mathrm{HN{=}C(NH_2)NH{-}NO_2} \arrow[r] & \mathrm{NH_3} + \mathrm{HN{=}C{=}N{-}NO_2} \arrow[d] \\ & \mathrm{HNCO} + \mathrm{N_2O} \arrow[d, "\mathrm{NH_3}"] \\ & \mathrm{H_2N{-}CO{-}NH_2} \end{tikzcd}$$

They prepared guanidine carbonate in a yield of about ninety percent by digesting nitroguanidine at 65° with an excess of ammonium carbonate in aqueous solution. Small amounts of urea and melamine were also found.

According to these investigators, when nitroguanidine is refluxed for some time in water solution, the liquid becomes distinctly ammoniacal, and they isolated guanidine in the form of guanidine picrate from such a solution. When they heated a solution of nitroguanidine in concentrated sulfuric acid, nitrous oxide wis evolved, and carbon dioxide and ammonia are produced quantitatively. These was some evidence of cyanamide in a sulfuric acid solution of nitroguanidine.

In the present research nitroguanidine was reacted with sodium methylate in pyridine solution, yielding nitrous oxide and sodium cyanamide quantitatively. The reaction mechanism, following those postulated for the action of sodium methylate on nitrourea and nitrobiuret, is as follows:



$$HN{=}C\begin{matrix}\overset{H}{N}\text{-}H\\ N{=}\underset{O}{N}\text{-}OH\end{matrix} + NaOCH_3 \longrightarrow HN{=}C\begin{matrix}\overset{H}{N}\text{-}H\\ N{=}\underset{O}{N}\text{-}ONa\end{matrix} + CH_3OH \quad (a)$$

$$HN{=}C\begin{matrix}\overset{H}{N}\text{-}H\\ N{=}\underset{O}{N}\text{-}ONa\end{matrix} \longrightarrow HN{=}C\begin{matrix}\overset{H}{N}\text{-}H\\ ONa\end{matrix} + N_2O \quad (b)$$

$$HN{=}C\begin{matrix}\overset{H}{N}\text{-}H\\ ONa\end{matrix} \longrightarrow HN{=}C{=}NH + NaOH \quad (c)$$

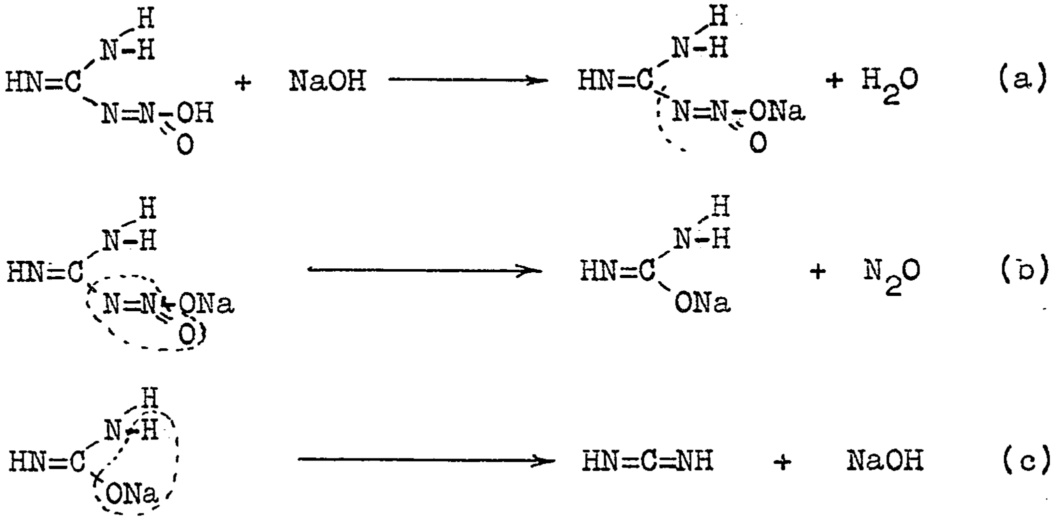
$$HN{=}C{=}NH + 2\ NaOCH_3 \longrightarrow NaN{=}C{=}NNa + 2\ CH_3OH \quad (d)$$

The summation of equations (a) (b) (c) and (d) gives the completed equation:

$$(f).\ HN{=}C(NH)NH\text{-}NO_2 + 3\ NaOCH_3 \longrightarrow Na_2NCN + N_2O + NaOH + 3\ CH_3OH$$

<u>No ammonia was evolved in this reaction.</u>

Using this mechanism the results of Fry and Treon may be explained by the following alternative scheme to represent the action of aqueous sodium hydroxide upon nitroguanidine. It differs primarily from the scheme presented by Fry and Treon in that it calls for the intermediate formation of cyanamide.



$$\mathrm{HN{=}C(NH_2)N{=}N(\rightarrow O)OH + NaOH \longrightarrow HN{=}C(NH_2)N{=}N(\rightarrow O)ONa + H_2O} \qquad (a)$$

$$\mathrm{HN{=}C(NH_2)N{=}N(\rightarrow O)ONa \longrightarrow HN{=}C(NH_2)ONa + N_2O} \qquad (b)$$

$$\mathrm{HN{=}C(NH_2)ONa \longrightarrow HN{=}C{=}NH + NaOH} \qquad (c)$$

$$\mathrm{HN{=}C{=}NH + 4\ NaOH \longrightarrow 2\ NH_3 + C(ONa)_4} \qquad (d)$$

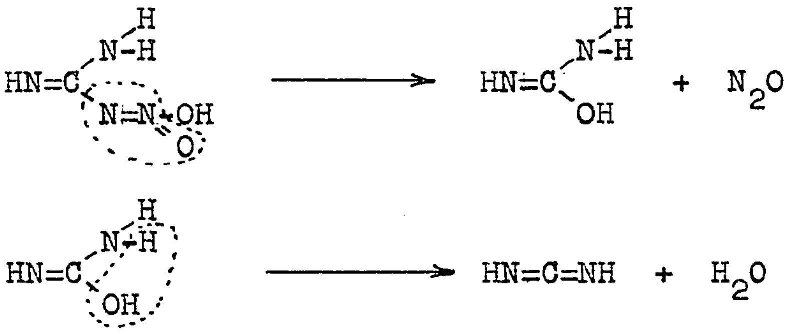
$$\mathrm{C(ONa)_4 + H_2O \longrightarrow Na_2CO_3 + 2\ NaOH} \qquad (e)$$

The summation of equations (a) (b) (c) (d) and (e) gives the completed equation:

$$\mathrm{NH{=}C(NH_2)NH{-}NO_2 + 2\ NaOH \longrightarrow 2\ NH_3 + N_2O + Na_2CO_3}$$

This equation is identical with that given by Fry and Treon.

The dearrangement mechanism proposed by Davis and Abrams for nitroguanidine, if correct, should predict the products obtained by the decomposition of nitroguanidine irrespective of the medium used. Consequently, if we accept their mechanism, we should expect to obtain cyanic acid and ammonia when the decomposition takes place in pyridine solution. However, neither cyanic acid nor ammonia was found when nitroguanidine was reacted with sodium methylate in pyridine solution in the present study, but cyanamide was obtained in quantitative yield. This indicates that the production of cyanamide occurred quantitatively in the work of Davis and Abrams in accordance with the following scheme:


(a)

(b)

The summation of equations (a) and (b) gives the completed equation:

$$H_2N-C(NH)NH-NO_2 \longrightarrow N_2O + HN{=}C{=}NH + H_2O$$

The cyanic acid which they obtained would result from the hydrolysis of cyanamide, as follows:

$$H_2N-C{\equiv}N + HOH \longrightarrow NH_3 + HOCN$$

Therefore, it is not a main product of the decomposition of nitroguanidine, but results from a side reaction. The various other products that Davis and Abrams found, such as cyanuric acid, urea, melamine, etc. would result, as previously noted, from the interaction and polymerization of the first-formed products.

Davis and Abrams observed, when a sulfuric acid solution of nitroguanidine was heated, that the nitrous oxide came off first and fairly rapidly while the carbon dioxide was evolved later and more slowly. This observation was used by them to support their contention that the nitroguanidine dearranged in two modes to yield two or more substances. One of these substances, they contend, is attacked by warm sulfuric acid more readily to yield nitrous oxide, and the other less readily to yield carbon dioxide. The mechanism proposed in the present work shows that the evolution of nitrous oxide would come first and rather rapidly, whereas the carbon dioxide and ammonia, being formed by the rather slow hydrolysis of cyanamide, would come later and less readily. It is significant to note that if cyanic acid were formed from nitrocyanamide in this solution, as Davis and Abrams contend, the evolution of carbon dioxide should come earlier and be more rapid. This should be so because nitrocyanamide as well as cyanic acid would be extremely unstable.

In order to support further their hypothesis that nitrocyanamide is a dearrangement product of nitroguanidine, Davis and Abrams heated aqueous solutions of nitroguanidine in the presence of amines. They obtained substituted nitroguanidines, and proposed the following reaction:

$$HNCN\text{-}NO_2 \quad + \quad R\text{-}NH_2 \longrightarrow R\text{-}NH\text{-}C(NH)\text{-}NH\text{-}NO_2$$

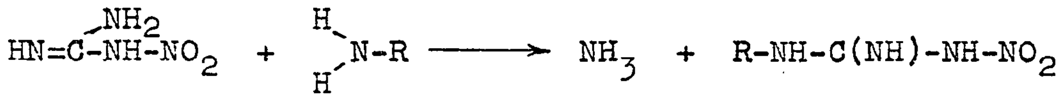
However, it is not necessary to assume the formation of nitrocyanamide as a requisite for the formation of the substituted nitroguanidines. Franklin (32), for example, gives the following reactions:

$$NCNHR \quad + \quad NH_3 \longrightarrow R\text{-}NH_2 \quad + \quad NCNH_2$$
$$NCNR_2 \quad + \quad NH_3 \longrightarrow R_2\text{-}NH \quad + \quad NCNH_2$$
$$RNCNR \quad + \quad NH_3 \longrightarrow 2\ R\text{-}NH_2 \quad + \quad HNCNH$$

The reverse of the ammonolyses shown here yields esters of cyanamide with the elimination of ammonia. Franklin (33) also gives the equation,

$$C_6H_5\text{-}N{=}C(NH\text{-}C_6H_5)_2 \quad + \quad 3\ NH_3 \longrightarrow HN{=}C(NH_2)_2 + 3\ C_6H_5NH_2,$$

the reverse of which represents the formation of an ester of guanidine by the action of an amine on guanidine with the elimination of ammonia. Consequently, the formation of the substituted nitroguanidines, as observed by Davis and Abrams, may well have resulted as follows:



$$HN{=}\overset{NH_2}{C}\text{-}NH\text{-}NO_2 \quad + \quad \begin{matrix}H\\ \\H\end{matrix}\!\!>\!N\text{-}R \longrightarrow NH_3 \quad + \quad R\text{-}NH\text{-}C(NH)\text{-}NH\text{-}NO_2$$

This would eliminate the necessity of assuming the intermediate formation of nitrocyanamide.

Thus the various other products besides cyanamide and nitrous oxide that Davis and Abrams obtained may well have been formed in side reactions. This view is supported by the present work in which only cyanamide and nitrous oxide were obtained and no side reactions occurred.

Nitroguanidine---Experimental

The nitroguanidine used in these experiments (Eastman product) had a melting point of 246-247° C. The apparatus was identical with that used in the experiments with nitrourea.

In each of the runs the reaction mixture (non-homogeneous) contained 20 grams (0.192 moles) of nitroguanidine, 23 grams (0.426 moles), a slight excess, of sodium methylate, and 300 ml. of pyridine. This mixture was heated on a water bath until the evolution of gas had ceased, about four hours' heating being required. When the contents of the reaction flask had cooled to room temperature, the pink precipitate was filtered, washed with pyridine, and dried first in the air and then over calcium chloride.

In this reaction, as in all the reactions in this work in which pyridine was the solvent, the solid residue weighed much more than it would if only the theoretical amount of the expected product (in this case sodium cyanamide) were present. Some material was present which was difficult to separate entirely from the main product. The pink color indicated a possibly pyridine complex, and in fact the solid retained, even when dry, the odor of pyridine. Methyl alcohol seemed to dissolve most of it, but this was not quantitative because it dissolved some sodium cyanamide also.

A little of the solid was dissolved in water, in which solvent it was readily soluble, and ammoniacal silver nitrate was added. A bright yellow precipitate, indicative of silver cyanamide precipitated. This precipitate was soluble in dilute nitric acid.

Werner's(29) test showed no indication of the presence of cyanate.

The sodium cyanamide was quantitatively determined by the argentimetric method of L. A. Pinck(34). A weighed amount of the solid reaction residue was dissolved in water and diluted to a volume of 250 ml. Aliquot parts of this solution were then taken for analysis. The following results were obtained:

<u>Run 1</u>

0.4451 grams of solid were dissolved in water, made up to 250 ml. solution, and 50 ml. aliquots were taken for analysis.

<u>Ml. of 0.147 N KCNS used:</u>

1). 9.40 ml.
2). 9.30 ml.
3). 9.30 ml.
Average--9.33 ml.

Amount Na_2NCN 9.33 ml. of 0.147 N KCNS: 0.059 g.

Amount Na_2NCN in 23.95 g. solid residue: 16.34 g.

Run 2

0.4662 grams of solid residue were dissolved in water, made up to 250 ml. solution, and 50 ml. aliquots were taken for analysis.

Ml. of 0.147 N KCNS used:

1). 10.1 ml.
2). 10.1 ml.
3). 10.0 ml.
Average- 10.07 ml.

Amount Na_2NCN 10.07 ml. of 0.147 N KCNS: 0.0632 g.
Amount Na_2NCN in 23.8 g. solid residue: 15.91 g.

The following table VI contains the experimental data relating to the interaction of nitroguanidine and sodium methylate in pyridine solution.

TABLE VI

Data Based on Equation (F)

$$\text{(F). } H_2N\text{-}C(NH)\text{-}NH\text{-}NO_2 + 2\ NaOCH_3 \longrightarrow Na_2NCN + N_2O + 2\ CH_3OH + H_2O$$

	A	B	C	D
Run	Nitro-guanidine moles	$NaOCH_3$ moles	Na_2NCN found moles	Na_2NCN theory moles
1	0.192	0.426	0.190	0.192
2	0.192	0.426	0.185	0.192

	E	F	G	H
Run	Na_2NCN % theory	N_2O found liters S.T.P.	N_2O theory liters S.T.P.	N_2O % theory
1	98.9	4.15	4.3	96.5
2	96.35	4.2	4.3	97.6

The percent theory yields of sodium cyanamide (column E) and nitrous oxide (column H) establish the occurrence of the interaction of nitroguanidine and sodium methylate conforming with the proposed equation (F).

V. NITROSOGUANIDINE

Nitrosoguanidine---Historical

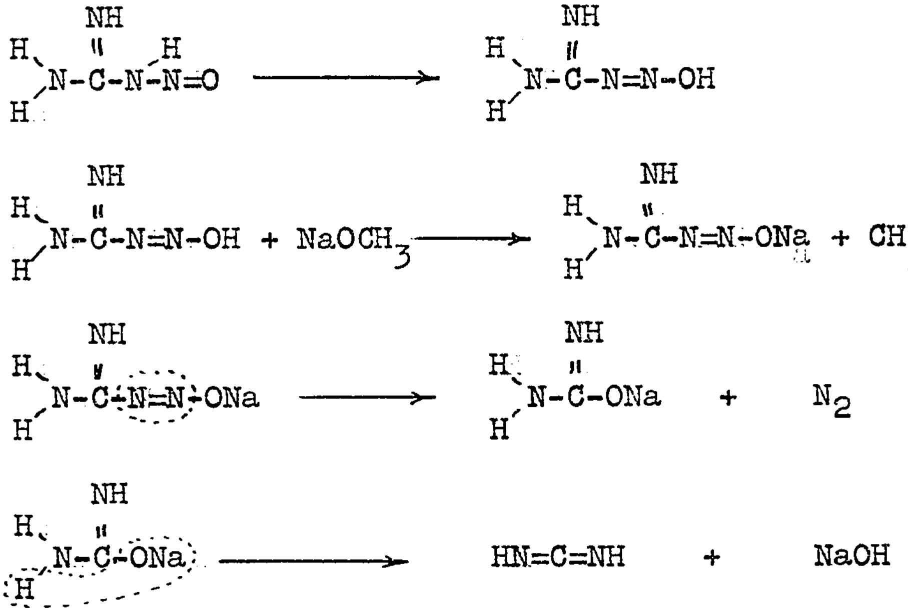
Thiele(38) heated an aqueous solution of nitrosoguanidine, and obtained cyanamide, nitrogen, and water. He gave no quantitative data, but stated that the reaction proceeded "nearly all" in this manner.

Davis and Abrams(15) state that nitrosoguanidine explodes when heated alone or when treated with strong sulfuric acid, and that an aqueous hydrochloric acid solution yields nitrous acid. They report that nitrosoguanidine dissolves in cold concentrated hydrochloric acid to form a yellow solution which gives off red oxides of nitrogen when it is warmed. They gave no quantitative data for these reactions.

Sabetta, Himmelford, and Smith(19) report that acidic aqueous solutions of nitrosoguanidine decompose when heated to give guanidine and nitrous acid. They recovered the nitrous acid quantitatively, and isolated the nitrate and picrate of guanidine from these solutions. When they heated alkaline solutions of nitrosoguanidine, these investigators detected carbon dioxide, ammonia, cyanamide, and nitrogen. They reported that cyanamide and nitrogen are formed when nitrosoguanidine is heated in neutral solution. No quantitative data are presented for these reactions.

Nitrosoguanidine---Theoretical

If the proposed mechanism is applied to the action of sodium methylate on nitrosoguanidine, the products predicted by the following scheme would be expected:



$$H_2N-\overset{\displaystyle NH}{\overset{\|}{C}}-NH-N=O \longrightarrow H_2N-\overset{\displaystyle NH}{\overset{\|}{C}}-N=N-OH \qquad (a)$$

$$H_2N-\overset{\displaystyle NH}{\overset{\|}{C}}-N=N-OH + NaOCH_3 \longrightarrow H_2N-\overset{\displaystyle NH}{\overset{\|}{C}}-N=N-ONa + CH_3OH \qquad (b)$$

$$H_2N-\overset{\displaystyle NH}{\overset{\|}{C}}-N=N-ONa \longrightarrow H_2N-\overset{\displaystyle NH}{\overset{\|}{C}}-ONa + N_2 \qquad (c)$$

$$H_2N-\overset{\displaystyle NH}{\overset{\|}{C}}-ONa \longrightarrow HN=C=NH + NaOH \qquad (d)$$

$$HN=C=NH + 2\ NaOCH_3 \longrightarrow Na_2NCN + 2\ CH_3OH \qquad (e)$$

The summary of equationf (a) (b) (c) (d) and (e) gives the completed equation:

(G). $H_2N-C(NH)NH-NO + 3\ NaOCH_3 \longrightarrow Na_2NCN + N_2 + NaOH + 3\ CH_3OH$

As will be shown by experimental data these predicted products, sodium cyanamide and nitrogen, were obtained in almost quantitative yield, some side reactions, represented by the equations below, occurring to a small extent:

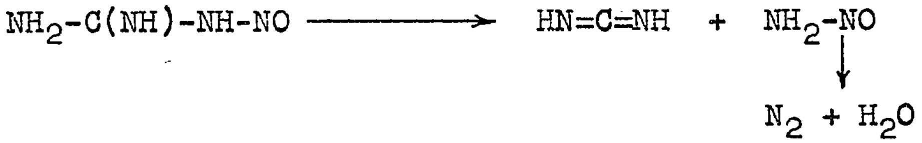
(H). $H_2N-C(NH)NH-NO + NaOH \longrightarrow H_2N-C(NH)-NH_2 + NaNO_2$

(I). $HN=C=NH + 4\ H_2O \longrightarrow 2\ NH_3 + H_2CO_3$

The water represented in equation (H) is derived from the equilibrium:

$$HOCH_3 + NaOH \longrightarrow NaOCH_3 + H_2O$$

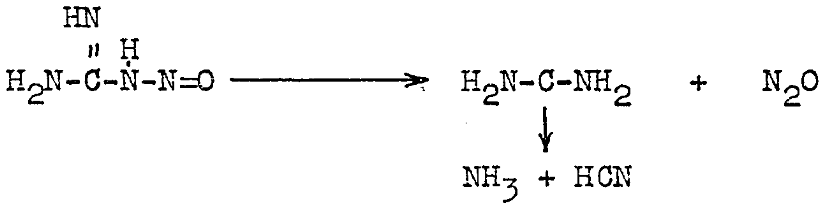
Davis and Abrams(15) present the following dearrangement of nitrosoguanidine to explain Thiele's findings that an aqueous solution of this compound decomposes, when heated, to give cyanamide and nitrogen:



$$NH_2\text{-}C(NH)\text{-}NH\text{-}NO \longrightarrow HN{=}C{=}NH + \underset{\displaystyle N_2 + H_2O}{\underset{\downarrow}{NH_2\text{-}NO}}$$

They state that "the probably presence of nitrosoamide in an aqueous solution of nitrosoguanidine is indicated by the fact that the solution yields nitrous acid under the hydrating action of hydrochloric acid". However, the nitrous acid may readily be derived from the hydrolysis of nitrosoguanidine, and in fact Sabetta, Himmelfarb and Smith(19) obtained nitrous acid quantitatively in this manner. If the nitrous acid were derived from nitrosoamide, then Sabetta and his coworkers should not have obtained nitrous acid quantitatively because the nitrosoamide would decompose preferentially to give nitrogen and water. Consequently, the presence of nitrous acid is in no way indicative of the formation of nitrosoamide.

Furthermore, another mode of dearrangement is conceivable:



$$H_2N\text{-}\overset{\displaystyle HN}{\overset{\|}{C}}\text{-}\overset{H}{\dot{N}}\text{-}N{=}O \longrightarrow \underset{\displaystyle NH_3 + HCN}{\underset{\downarrow}{H_2N\text{-}C\text{-}NH_2}} + N_2O$$

However, neither nitrous oxide nor hydrocyanic acid has been detected in any of the decomposition reactions of nitrosoguanidine.

Nitrosoguanidine---Experimental

The nitrosoguanidine used in this experiment was prepared according to the method of Sabetta, Himmelfarb, and Smith(19), namely by the reduction of nitroguanidine. Eastman's nitroguanidine was the starting material. A sample of the purified nitrosoguanidine exploded when heated to 165° C.

The apparatus and procedure were essentially identical to those used in the nitrourea experiments noted above.

The reaction flask was charged with a mixture of nitroseguanidine, sodium methylate, and 250 ml. of pyridine. The mixture was refluxed on an oil bath for eight hours, at which time the evolution of gas had ceased. The flask was then allowed to cool to room temperature, and the pink solid which had settled was filtered, washed with pyridine, and dried first in the air and then over calcium chloride.

An aqueous solution of a sample of the solid residue gave the characteristic yellow precipitate of silver cyanamide upon the addition of ammoniacal silver nitrate. A quantitative estimation of sodium cyanamide was conducted according to the argentimetric method of Pinck(34). Preliminary tests showed that sodium cyanamide is slightly soluble in ammonia; consequently, the silver nitrate used as precipitant must be made just sufficiently ammoniacal to dissolve the silver oxide.

In Run 1, the analysis was made on the solid reaction residue which had been isolated. In Run 2, however, the total solid was made up to a liter aqueous solution, and aliquot parts were taken for analysis. The analytical data for the estimation of sodium cyanamide are as follows:

Run 1

Amount of solid residue taken for analysis------ 0.1229 g.
Average ml. of 0.147 N KCNS required------------ 12.05
Total amount of Na_2NCN thus found--------------- 6.00 g.

Run 2

10 ml. aliquots were taken for analysis
Average ml. of 0.147 N KCNS required------------ 9.5
Total amount of Na_2NCN thus found--------------- 6.15 g.

Some sodium cyanamide was found to have remained in the pyridine mother liquor, and analyses of the filtrates in these runs gave the following results:

Run 1

50 ml. aliquots taken for analyses
Average ml. 0.147 N KCNS required--------------- 3.64
Total amount of Na_2NCN thus found--------------- 0.142 g.

Run 2

50 ml. aliquots taken for analyses

Average ml. of 0.147 N KCNS required---------- 0.216

Total amount of Na_2NCN thus found------------- 0.008 g.

Thus a total of 6.142 g. of sodium cyanamide was found in Run 1, while a total of 6.158 was found in Run 2.

The absorption bottle (D) was found to contain ammonia after each of the runs, formed by the hydrolysis of cyanamide according to the equation:

$$HN{=}C{=}NH \quad + \quad 4\ H_2O \longrightarrow \quad 2\ NH_3 \quad + \quad H_2CO_3$$

For the quantitative estimation of ammonia 50 ml. of the acid solution from the absorption bottle was placed in a Kjeldahl flask and made strongly alkaline by the addition of 25 ml. of a saturated solution of sodium hydroxide. It was then steam distilled until 500 ml. of distillate had passed over into 50 ml. of a four percent boric acid solution. The contents of the receiving flask were then titrated with standard hydrochloric acid using brom-cresol green as indicator. This is a modification of the Kjeldahl-Winkler (39) method of determining nitrogen. The following results were obtained:

Run 1

Average ml. of 0.4875 N HCl required-------------- 1.1

Weight of NH_3 equivalent to 1.1 ml. 0.4875 N HCl-- 0.009g.

Total weight of NH_3 in absorption bottle---------- 0.045g.

Run 2

Average ml. of 0.4875 N HCl required------------- 1.1

Weight on NH_3 equivalent to 1.1 ml. 0.4875 N HCl- 0.009g.

Total weight of NH_3 in absorption bottle--------- 0.045g.

In each case, therefore, the weight of sodium cyanamide that was lost through hydrolysis amounted to 0.224 g.

When a little of the solid reaction residue was dissolved in water, acidified, and treated with potassium iodide and chloroform free iodine was liberated. This was shown by the purple color which appeared in the chloroform. This indicated the presence of a nitrite which could have resulted from the hydrolysis of nitrosoguanidine according to the equation:

$$H_2N\text{-}C(NH)\text{-}NH\text{-}NO + NaOH \qquad H_2N\text{-}C(NH)\text{-}NH_2 + NaNO_2$$

In order to further check the occurrence of this reaction a solution of ammonium picrate was added to an aqueous solution of the solid reaction residue. In a few hours some crystals had formed which were filtered and dried. They showed a melting point of 328° C. which is approximately the melting point of guanidine picrate, 333° C. The presence of guanidine was thus established. This is the method of Vozarick(40) as modified by Smith, Sabetta, and Steinbach(41).

The sodium nitrite present was quantitatively determined according to the method of Pandalai and Rao(42), the following modifications being made: instead of 10 ml. of 5 N H_2SO_4, 20 ml. were added, and chloroform was used instead of starch indicator. The following results were obtained:

Run 1

Amount of solid taken for analysis------------ 0.1726 g.

Milliliters of 0.002 N $Na_2S_2O_3$ required------- 21.5
24.3
23.5

Average ml. of 0.002 N $Na_2S_2O_3$ required------- 23.1

Total amount of $NaNO_2$ thus found-------------- 0.178 g.

Run 2

Volume of solution taken for analysis--------- 50 ml.

Milliliters of $Na_2S_2O_3$ required--------------- 9.05
8.95

Average ml. of $Na_2S_2O_3$------------------------ 9.00

Total amount of $NaNO_2$ found------------------- 0.025 g.

These data shows that in Run 1, 0.227 grams of nitrosoguanidine were hydrolyzed to give quanidine and sodium nitrite according to equation (H) given in the theoretical discussion, and in Run 2, 0.0318 grams of nitrosoguanidine were thus hydrolyzed.

The tabulated results of the action of sodium methylate on nitrosoguanidine in pyridine solution are shown in the following table. They are based, first upon the interaction of sodium methylate and nitrosoguanidine yielding sodium cyanamide and nitrogen (equation G), and second upon the concurrent reactions (equations H and I), taking place to a limited extent, namely, the hydrolysis of cyanamide and nitrosoguanidine respectively:

(G). $H_2N\text{-}C(NH)\text{-}NH\text{-}NO + 3\ NaOCH_3 \longrightarrow Na_2NCN + N_2 + NaOH + 3\ CH_3OH$

(H). $H_2N\text{-}C(NH)\text{-}NH\text{-}NO + NaOH \longrightarrow H_2N\text{-}C(NH)\text{-}NH_2 + NaNO_2$

(I). $HN{=}C{=}NH + 4\ H_2O \longrightarrow 2\ NH_3 + H_2CO_3$

TABLE VII

Yields of Nitrogen and Sodium Cyanamide

Based upon Equation G

(G). $H_2N\text{-}C(NH)NH\text{-}NO + 3\ NaOCH_3 \longrightarrow Na_2NCN + N_2 + NaOH + 3\ CH_3OH$

	A	B	C	D
Run	Nitrosoguanidine g.	Sodium Methylate g.	N_2 found liters S.T.P.	N_2 theory liters S.T.P. (equation G)
1	7.25	8.8	1.68	1.83
2	7.21	15.0	1.80	1.80

	E	F	G	H
Run	N_2 % theory (equation G)	Na_2NCN found g.	Na_2NCN theory g. (equation G)	Na_2NCN % theory (equation G)
1	93.1	6.142	7.08	86.7
2	100.0	6.158	7.05	87.3

The data of table VII shows that, in terms of the yields of nitrogen, equation (G) proceeds nearly quantitatively in Run 1, and conclusively quantitatively in Run 2. The yields of sodium cyanamide, however, are about thirteen percent below the theoretical. This discrepancy is partly explained by the concomitant hydrolysis reactions represented by equations (H) and (I).

The following table VIII embodies data quantitatively confirming the occurrence of the reactions represented by equations (H) and (I). Column E represents the sodium cyanamide that should theoretically be formed from the actual amount of nitrosoguanidine that reacted according to equation (G). It is the amount of sodium cyanamide theoretically available according to equation (G) minus the amount of sodium cyanamide unavailable due to the hydrolysis of nitrosoguanidine according to equation (H). Column F represents the sodium cyanamide found as such plus that equivalent to the ammonia found.

TABLE VIII

Correlation of Yields of Ammonia (Equation H) and Nitrite (Equation I) with Decreased Yield of Sodium Cyanamide

(H). $H_2N\text{-}C(NH)\text{-}NH\text{-}NO + NaOH \longrightarrow H_2N\text{-}C(NH)\text{-}NH_2 + NaNO_2$

(I). $HN{=}C{=}NH + 4\ H_2O \longrightarrow 2\ NH_3 + H_2CO_3$

	A	B	C	D
Run	NH_3 found g. (equation I)	Na_2NCN NH_3 (equation I) found g.	$NaNO_2$ found g.	Nitroso-guanidine $NaNO_2$ found g.
1	0.045	0.228	0.178	0.227
2	0.045	0.228	0.025	0.032 0.037

	E	F	G
Run	Na_2NCN theory g. corrected	Na_2NCN found g. corrected	Na_2NCN theory (equation G)
1	6.86	6.37	93.0
2	7.01	6.386	91.3

The data in the above table VIII show~~s~~ that when the amount of sodium cyanamide equivalent to the ammonia formed (column B) is added to the amount of sodium cyanamide found (column F, table VII), the total yield of sodium cyanamide is obtained. Furthermore, the number of moles of nitrosoguanidine available for reaction according to equation (G) is lowered to the extent shown by the number of moles of sodium nitrite formed according to equation (H). Consequently, the theoretical amount of sodium cyanamide is lowered. Thus it is shown that the total amount of sodium cyanamide found exceeds ninety percent of the theoretical amount based upon equation (G).

SUMMARY AND CONCLUSIONS

The hydrolyses of I nitrourea, II mononitrobiuret, III dinitrobiuret, IV nitroguanidine, and V nitrosoguanidine have been studied by numerous investigators, and various reaction mechanisms have been proposed for the changes taking place. With the exception of the acid hydrolysis of nitrosoguanidine, however, no quantitative data is recorded in the literature to prove that the reactions proceed according to any of the specifically proposed equations.

The study of the action of concentrated aqueous solutions of sodium hydroxide, performed in this laboratory, upon nitrourea and nitroguanidine afforded data conforming with equations derived from proposed mechanism schemes. Therefore, the present investigation was undertaken to determine quantitatively the nature and the extent of occurrence of the action of sodium methylate upon the several above-named (I through V) aliphatic nitro amides and amidines in non-aqueous media.

Reaction mechanism schemes were proposed leading to the derivation of equations for reactions which have been quantitatively verified. The results are summarized as follows:

I. Nitrourea reacted in conformity with the equation:

(A). $H_2N\text{-}CO\text{-}NH\text{-}NO_2 + 2\ NaOCH_3 \longrightarrow NaNCO + N_2O + NaOH + 2\ CH_3OH$

This reaction was accompanied by the hydrolysis of of sodium cyanate to a limited but quantitatively determined extent according to the equation:

(B). $NaNCO + NaOH + H_2O \longrightarrow Na_2CO_3 + NH_3$

II. Mononitrobiuret reacted in conformity with the equation:

(C). $H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 + 3\ NaOCH_3 \longrightarrow 2\ NaNCO + N_2O + NaOH + 3\ CH_3OH$

This reaction also was accompanied by the hydrolysis to a limited but quantitatively determined extent according to the equation:

(D). $NaNCO + NaOH + H_2O \longrightarrow Na_2CO_3 + NH_3$

III. Dinitrobiuret reacted in conformity with the equation:

(E). $O_2N\text{-}NH\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 + 2\ NaOCH_3 \longrightarrow NaNCO + 2\ N_2O + NaHCO_3 + 2\ CH_3OH$

No other concomitant reactions were found to occur.

IV. Nitroguanidine reacted in conformity with the equation:

(F). $H_2N\text{-}C(NH)\text{-}NH\text{-}NO_2 + 3\ NaOCH_3 \longrightarrow Na_2NCN + N_2O + NaOH + 3\ CH_3OH$

Here also no other concomitant reactions were found to occur.

V. Nitrosoguanidine reacted in conformity with the equation:

(G). $H_2N\text{-}C(NH\text{-}NH\text{-}NO + 3\ NaOCH_3 \longrightarrow Na_2NCN + N_2 + NaOH + 3\ CH_3OH$

This reaction was accompanied by the hydrolysis of sodium cyanamide as well as of nitrosoguanidine to a limited but quantitatively determined extent according to the equations:

(H). $Na_2NCN + 3\ H_2O \longrightarrow 2\ NH_3 + Na_2CO_3$

(I). $H_2N\text{-}C(NH)\text{-}NH\text{-}NO + NaOH \longrightarrow H_2N\text{-}C(NH)\text{-}NH_2 + NaNO_2$

ADDENDUM

A Modified Method for the Preparation of Biuret

Since the nitrobiuret~~s~~ used in these experiments were made by nitrating biuret, a satisfactory method for perparing this compound was sought. A modification of the method recorded by Schiff(43) was found to be more satisfactory than any of the other methods recorded in the literature for the preparation of biuret from urea. If the procedure given by Schiff is followed closely, very little biuret is obtained, and the main product is cyanuric acid. A description of the modified method follows:

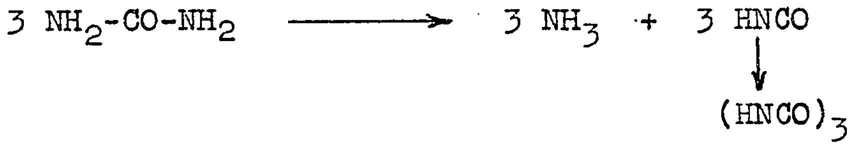
Eight hundred grams of powdered urea ~~are~~ placed in a two-liter erlenmeyer flask. A stream of dry hydrogen chloride gas is introduced which reacts with the urea, and the heat of reaction causes the product to melt. Soon the flask contains only a clear liquid which is slowly heated until a temperature of 120° C. is reached. The introduction of HCl is then stopped, the flame is removed, and the solution continues to rise in temperature. At about 135° C. the evolution of a gas is apparent, and the temperature continues rising until it reaches 170-180° C. The contents are then allowed to cool to 100° C., when a liter of water is added alowly and with stirring.

The reactions occurring to this point may be represented by the equations:

$$H_2N\text{-}CO\text{-}NH_2 \quad + \quad HCl \longrightarrow H_2N\text{-}CO\text{-}NH_2.HCl$$

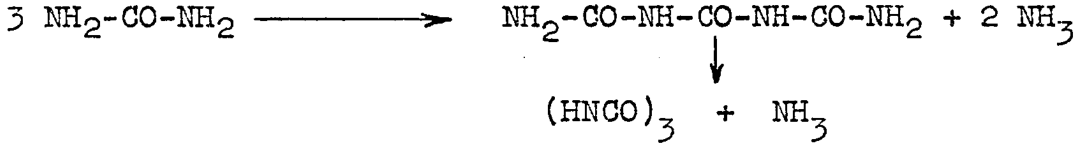
$$H_2N\text{-}CO\text{-}NH_2.HCl + H_2N\text{-}CO\text{-}NH_2 \longrightarrow H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH_2 + NH_4Cl$$

Cyanuric acid is also formed, probably either through the decomposition of urea,



$$3\ NH_2\text{-}CO\text{-}NH_2 \longrightarrow 3\ NH_3 + 3\ \underset{\displaystyle (HNCO)_3}{\underset{\downarrow}{HNCO}}$$

or through the deammination of triuret:



$$3\ NH_2\text{-}CO\text{-}NH_2 \longrightarrow NH_2\text{-}CO\text{-}NH\text{-}\underset{\displaystyle (HNCO)_3 + NH_3}{\underset{\downarrow}{CO}}\text{-}NH\text{-}CO\text{-}NH_2 + 2\ NH_3$$

The solution is then chilled in an ice bath, and a white solid settles out. This solid, a mixture of biuret and cyanuric acid weighing about 450 grams, is filtered, washed with a little water, and dried. The ammonium chloride and any excess urea remain in the filtrate.

The biuret is separated from the cyanuric acid by treating ~~aliquot~~ portions (about 40-50 g.) of the mixture with 600 ml. boiling 95% alcohol (the cyanuric acid is practically insoluble in boiling alcohol). The hot alcoholic solution is filtered, and the filtrate is chilled in an ice bath effecting the re-crystallization of biuret. The biuret is filtered and dried. The alcoholic mother liquor is then used to separate more biuret from the original solid mixture, and this process is continued until all the solid has been thus treated. 175 grams of biuret, which has a melting point of 196° C., is recovered in this manner. Some biuret may be recovered from the residue (from the filtration of the hot alcohol) by again treating it as above, and some may be recovered from the alcoholic mother liquor by evaporating the liquor to one-third its volume and then cooling.

This method gave far better yields of biuret than the other recorded methods.

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